Characterization, prediction, and remediation of salt-affected soils in the High Valley of Cochabamba - Bolivia

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Dissertation originale présentée en vue de l’obtention du grade de doctorat en sciences agronomiques et ingénierie biologique

Promoteur : Gilles Colinet
Année civile: 2024

Abstract

In a broad sense, soil salinity relates to high levels of soluble salts in the soil solution phase and soil sodicity refers to an excess of sodium in the exchangeable complex, while alkalinity indicates the dominance of alkaline salts and high pH. Salt-affected soils are mainly caused by natural conditions and/or anthropogenic activities and negatively affect plant growth and soil-water properties. The High Valley of Cochabamba - Bolivia is characterized by low soil and crop productivity, and land degradation primarily due to salinization processes, which in turn, are driven by semiarid conditions, population increase, deforestation, and inadequate agricultural practices. Some studies have been conducted primarily focused on mapping and characterizing salt-affected soils in this region, but there are still gaps in soil information, prediction tools, and amelioration techniques for their proper management. Therefore, this study aimed to contribute to the sustainable management and rehabilitation of salt-affected soils in the High Valley through baseline soil information, salinity/sodicity prediction models, and insights into amendment-based remediation techniques.

Regarding the characterization and classification of soil samples and profiles, the saline-sodic and saline classes dominate among the salt-affected soil samples, and most salt-affected soil profiles' horizons showed high levels of salinity and sodicity. The alternative classification approach can overcome the confusion caused by the – USSL – saline-sodic soil class by considering the nature of soluble ions; in this context, some differences between the two methods, for salinity and sodicity distributions were observed. The spatial interpolation was unsatisfactory due to insufficient spatial correlation. Incorporating additional soil profiles and samples might improve the representativeness of the soil information, spatial prediction, and classification system.

Concerning the performance evaluation of machine learning models to predict soil salinity/sodicity variables, random forests (RF) and support vector machines (SVM) regressions outperformed the partial least squares algorithm in estimating soil ESP and EC_e, as well as for predicting salt-affected soil classes. Multivariate regressions predicting soil ESP as a function of EC, SAR, and pH showed relatively good performance, somewhat similar to simple regression predicting ESP from SAR. The models to predict soil ESP and EC from remote sensing-based and geomorphometric features showed relatively low performance. Overall, these models might contribute to the monitoring and management of salt-affected soils in the High Valley; however, validations with additional samples and predictor variables are essential to improve their accuracy.

According to the first soil-column experiment assessing the effectiveness of individual mineral and organic amendments with leaching in remediating saline-sodic soils, gypsum was more effective than sulphur, while cattle/chicken manure was better than biochar and peat in lowering soil ESP, and any organic or mineral amendment was as efficient as water alone in decreasing soil EC_e. The superiority of gypsum was mainly due to its Ca^{2+} content which displaces exchangeable Na^+, while that of manure was probably due to its contribution of organic matter and divalent cations, which also improve soil-water properties. The second soil-column experiment evaluating the combined effect of manures and gypsum showed that either cattle or chicken manure together with gypsum at any dose was more effective than gypsum alone in reducing the soil ESP to below 5%; furthermore, except for water alone, all treatments were effective in lowering the soil EC_e to below 1.6 dS m^{-1}, and any combination was effective in decreasing soil pH to below 8.7. Thus, the effectiveness of manure combined with gypsum was mainly due to their synergistic effect on adsorbed Na^+ displacement and soil structure improvement. The addition of manure might enhance and hasten the effect of gypsum with leaching in ameliorating saline-sodic/sodic soils. Further validation of the most effective amendment-based remediation techniques through field experiments is recommended, and alternative approaches such as biosaline agriculture and phytoremediation should also be explored.

In sum, the proper management and rehabilitation of salt-affected soils in the High Valley of Cochabamba relies on adequate characterization, correct classification, accurate estimation, and effective amelioration of these soils; consequently, this study contributes to these goals by providing: (1) comprehensive baseline soil information, (2) tailored prediction and classification tools, and (3) insights into amendment-based remediation techniques, all of which are subject to further refinement.

Résumé

La salinité et la sodicité du sol sont essentiellement liées à une quantité élevée de sels dans la solution du sol pour la première et à un excès de sodium sur le complexe échangeable pour la deuxième. L'alcalinité correspond à une dominance de sels alcalins et à un pH élevé. Les sols sont affectés par la salinisation soit en relation avec des conditions naturelles défavorables ou suite aux activités anthropiques. La salinité a un impact négatif sur la croissance des plantes et la qualité de l'eau. La Haute Vallée de Cochabamba en Bolivie se caractérise par une faible productivité des agrosystèmes et une dégradation des sols, principalement suite à des processus de salinisation, eux-mêmes induits par des conditions climatiques semi-arides, l'augmentation de la population, la déforestation et des pratiques agricoles inadéquates. Les études précédentes menées sur cette zone étaient principalement axées sur la cartographie et la caractérisation des sols affectés par le sel, mais il reste encore des lacunes en matière de connaissance sur les caractéristiques des sols, d'outils de prédiction et de techniques de remédiation pour une gestion appropriée de ces sols. La bonne gestion et la réhabilitation des sols affectés par le sel reposent sur une classification rigoureuse, une estimation précise et une amélioration efficace de la salinité et de la sodicité. Par conséquent, cette recherche vise à contribuer à la gestion durable et à la réhabilitation des sols affectés par les sels dans la Haute Vallée de Cochabamba à travers l'acquisition d'informations de base sur les sols, la constitution de modèles de prédiction de la salinité/sodicité, et une évaluation de techniques de remédiation basées sur les amendements pour récupérer les sols salins/sodiques.

D'après la caractérisation et la classification des échantillons et des profils de sols, les classes salines-sodiques et salines étaient dominantes parmi les échantillons de sol affectés par le sel, et la plupart des horizons des profils affectés par le sel et présentaient des niveaux élevés de salinité et de sodicité. Une classification alternative peut pallier le manque de discrimination de la classe saline-sodique de la USSL en considérant les ratios d'ions solubles. Des différences entre les distributions spatiales de salinité/sodicité ont été trouvées suite à l'application des deux méthodes. L'interpolation spatiale n'était pas satisfaisante en raison de la faible portée de la corrélation spatiale. Des profils de sol et des échantillons supplémentaires pourraient améliorer la représentativité des informations sur les sols, la prédiction spatiale et le système de classification adapté.

En ce qui concerne l'évaluation des performances des modèles d'apprentissage automatique de prévision des variables exprimant la salinité/sodicité, les algorithmes par forêts aléatoires (RF) et des machines à vecteurs de support (SVM) régressions ont donné de meilleurs résultats que les techniques par moindres carrés partiels pour l'estimation de l'ESP et de l'ECe du sol, ainsi que pour la prévision des classes de sol affectées par la salinité. Les régressions multivariées pour prédire l'ESP du sol en fonction de EC, SAR et pH ont montré une performance

relativement bonne et quelque peu similaire au modèle simple pour estimer l'ESP à partir de SAR. Les modèles multivariés pour prédire l'ESP et l'EC du sol à partir de caractéristiques géomorphométriques et de télédétection, faciles d'accès ont montré une performance relativement faible. Ces modèles pourraient contribuer à une meilleure gestion des sols affectés par les sels dans la Haute Vallée. Cependant, ici encore, davantage d'échantillons et des variables supplémentaires sont nécessaires pour améliorer leurs précisions.

Une première expérience en colonnes de sol visant à évaluer l'efficacité d'amendements minéraux et organiques avec lixiviation pour la remédiation des sols salins-sodiques a montré que le gypse était plus efficace que le soufre d'une part, ainsi que le fumier de bovin/poulet par rapport au biochar et à la tourbe par ailleurs, sur la réduction de l'ESP du sol. Par ailleurs l'ajout d'amendements qu'il soient organiques ou minéraux était aussi efficace que la seule lixiviation pour la réduction de l'ECe du sol. La supériorité du gypse était principalement due à sa teneur en Ca^{2+} qui déplace le Na^{+} échangeable, tandis que celle des fumiers était probablement due à leur teneur en matière organique et en cations divalents qui améliorent également les propriétés des sols. La deuxième expérience en colonne de sol visant à évaluer l'effet combiné des fumiers et du gypse a montré que le fumier de bovins ou de poulets associé au gypse, quelle que soit la dose, était plus efficace que le gypse seul, pour réduire l'ESP du sol à moins de 5 %, que tous les traitements, à l'exception de l'eau seule, étaient efficaces pour abaisser l'ECe du sol à moins de 1,6 dS m^{-1} , et que toutes les combinaisons étaient efficaces pour abaisser pH du sol à moins de 8,7. Ainsi, l'efficacité du fumier combiné au gypse était principalement due à leur effet synergique sur le déplacement du Na^{+} adsorbé et la structure du sol. L'ajout de fumier pourrait renforcer et accélérer l'effet du gypse avec la lixiviation dans l'amélioration des sols salins-sodiques. Il est recommandé de poursuivre les techniques de remise en état à base d'amendements les plus efficaces par le biais d'expériences sur le terrain, et d'explorer d'autres approches telles que l'agriculture biosaline et la phytoremédiation.

Resumen

En términos generales, la salinidad del suelo se caracteriza por un elevado contenido de sales en la fase soluble, la sodicidad por un exceso de sodio en el complejo intercambiable del suelo, y la alcalinidad por la dominancia de sales alcalinas y pH elevado. Los suelos afectados por sales se generan por causas naturales y/o antropogénicas y afectan negativamente el crecimiento de las plantas y las propiedades suelo-agua. El Valle Alto de Cochabamba - Bolivia se caracteriza por la baja productividad de los cultivos y la degradación de suelos debido principalmente a procesos de salinización que, a su vez, se originan a partir de las condiciones semiáridas, aumento de la población, deforestación y prácticas agrícolas inadecuadas. Estudios previos se enfocaron principalmente en el mapeo y caracterización de suelos afectados por sales en esta región, no obstante, aún falta información actualizada sobre estos suelos, herramientas para predecir salinidad/sodicidad, y técnicas de remediación para mejorar el manejo de estos suelos. En ese contexto, el objetivo de este estudio fue contribuir al manejo sostenible y rehabilitación de suelos afectados por sales en el Valle Alto a través de la generación de una línea de base con información de suelos, la validación de modelos predictivos y evaluación del uso de enmiendas minerales/orgánicas para remediación de suelos salino/sódicos.

En cuanto a la caracterización y clasificación de las muestras y perfiles de suelo, los suelos salino-sódicos y salinos fueron predominantes entre las muestras de suelo, y la mayoría de los perfiles de suelo afectados por sales presentaron altos niveles de salinidad y sodicidad. El método alternativo de clasificación de suelos contribuye a resolver la confusión generada por la clase de suelo salino-sódico del sistema de clasificación del USSL, considerando la naturaleza de las sales solubles; en este contexto, se observaron algunas diferencias en las distribuciones de salinidad y sodicidad entre los dos métodos. La interpolación espacial fue limitada debido a una correlación espacial insuficiente. Se requieren perfiles y muestras de suelo adicionales para mejorar la representatividad de la información de suelos, la predicción espacial y el sistema de clasificación.

Respecto a la evaluación de los modelos de aprendizaje automático para predecir variables de salinidad/sodicidad de suelo, los algoritmos de *random forests* (RF) y *support vector machines* (SVM) obtuvieron mejor desempeño que aquel basado en *partial least squares* para estimar el porcentaje de sodio intercambiable (PSI) y la conductividad eléctrica (CE) del suelo, así como para predecir las clases de suelos afectados por sales. Las regresiones multivariables para predecir el PSI en función de las variables CE, relación de adsorción de sodio (RAS) y pH obtuvieron un rendimiento aceptable, y a la vez, similar al de la regresión univariada basada en la RAS. Los modelos para predecir el PSI y la CE del suelo a partir de variables – de fácil obtención – basadas en teledetección y geomorfometría, obtuvieron un desempeño regular. Los modelos obtenidos pueden contribuir al manejo sostenible

de los suelos afectados por sales en el Valle Alto; sin embargo, es esencial validarlos con muestras de suelo y variables predictoras adicionales para mejorar su precisión.

Según el experimento preliminar en columnas de suelo para evaluar la eficacia individual de las enmiendas minerales y orgánicas con lixiviación para la recuperación de suelos salino-sódicos, el yeso fue más eficaz que el azufre, así como el estiércol de vacuno o la gallinaza comparado con el biocarbón o la turba, para reducir el PSI del suelo, y cualquier enmienda orgánica o mineral fue tan eficaz como el solo lavado para reducir la CE_e del suelo. La superioridad del yeso se debió principalmente a su aporte de Ca^{2+} que desplaza al Na^+ intercambiable, mientras que la de los estiércoles se debió probablemente a su contribución de materia orgánica y cationes divalentes que, a su vez, mejoraron las propiedades suelo-agua. El segundo experimento en columnas de suelo para evaluar el efecto combinado de estiércoles con el yeso, demostró que tanto el estiércol de vacuno como la gallinaza junto con el yeso independientemente de la dosis fueron más eficaces que solo yeso para reducir el PSI por debajo del 5%, además todos los tratamientos excepto el solo lavado fueron efectivos para disminuir la CE_e por debajo de 1,6 dS m^{-1}, y cualquier combinación fue efectiva en reducir el pH por debajo de 8,7. La notable eficacia del estiércol combinado con yeso radicó principalmente en el efecto sinérgico entre ambos para el desplazamiento del Na^+ adsorbido y el mejoramiento de la estructura del suelo, lo cual sugiere que la adición de estiércol potencia y acelera el efecto del yeso con lavado para remediar suelos salino-sódicos/sódicos. Se recomienda validar las técnicas de remediación más efectivas a través de experimentos de campo, y considerar estrategias alternativas como la agricultura biosalina y la fitorremediación.

Acknowledgements

I would first like to express my deepest gratitude to my advisor, Prof. Gilles Colinet, for his invaluable guidance, patience, and support throughout my PhD studies.

I would also like to sincerely thank my PhD thesis committee members, Prof. Aurore Degré, Prof. Jean-Thomas Cornelis, and Prof. Omar Arzabe, for their insightful feedback and guidance.

My deepest thanks go to Prof. Edgar Gutierrez† for his kind support and words of encouragement during this challenging journey.

I would like to acknowledge the participants who contributed to the research program on salt-affected soils, namely Alexis Weber, Claire de Froidmont, Daniel Castellón, Ivan Quispe, Jose Luis Mamani, Natalia Zambrana, Rubén Saire, Rufino Santos, and Zacharie Cortvrint. Their contributions to soil management in the High Valley of Cochabamba, as well as to this study, were invaluable.

I also extend my sincere thanks to the staff at the 'Universidad Mayor de San Simón', specifically to Prof. Ramiro Iriarte, Prof. Alfredo Cáceres, Prof. Jorge Rojas, Ms Karen Ovando, Mr Javier Burgos, Ms Jacqueline Maldonado, Mr Daniel Vega, for their kind support throughout this process.

I am grateful to the Water-Soil-Plant Exchanges team at Gembloux Agro-Bio Tech (ULiege) and the Soil-Water Lab team at FCAyP (UMSS) for their invaluable assistance.

I would like to gratefully acknowledge the funding I received from the 'Académie de Recherche et d'Enseignement Supérieur' (ARES), which enabled me to accomplish this PhD program.

A special thank you goes to my fellow PhD colleagues, Alejandro, Daniela, Enjun, Felix, Gianni, Luisa, Mehtap, Ryosuke, Sonia, Victor, and Wissem, for their friendship and words of encouragement.

Last but certainly not least, I wish to thank family and friends for their unconditional affection, support, and belief in me: AlexandraE, Alfredo, Carla, Demis, Esther, Galia, Giovanna, Graciela, Hilda, Kasandra, Katia, Lucciana, Lourdes, María, Marie, Mercedes, Merceditas, Milagros, Nancy, Nelson, Noemí, Norman, Rosario, Rosarito, Sim, Soledad, Steffy, Victoria, Wendy, Yenny, and Zhyl†… I could not have done this without all of you. Special mention also goes to my pets, Beto†, Bianca, Chapita, Gabo, Kailo, Kiara, Moises, Pepe†, Perico, Pocho, Pocho†, and Rex†.

Dedicatory

To my father... Norman†

To my mother… Rosario

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List of acronyms

AAS	Atomic adsorption spectrophotometry
AIC	*Akaike* information criterion
ARES	“Académie de Recherche et d’Enseignement Supérieur”
CEC	Cation exchange capacity
CROSS	Cations ratio of soil structural stability
DA	Discriminant analysis
EC	Electrical conductivity
ECR	Exchangeable cation ratio
ESP	Exchangeable sodium percentage
ESR	Exchangeable sodium ratio
FCAyP	“Facultad de Ciencias Agrícolas y Pecuarias”
FAO	Food and Agriculture Organization
ML	Machine learning
OOB	Out of bag error
PCA	Principal component analysis
PLS	Partial least squares
RF	Random forests
RMSE	Root mean square error
RSE	Residual standard error
SAR	Sodium adsorption ratio
SI	Salinity index
SOM	Soil organic matter
SP	Soil profile
SVM	Support vector machines
TEC	Threshold electrolyte concentration
TOC	Total organic carbon
TSS	Total Soluble salts
UMSS	“Universidad Mayor de San Simón”
USDA	United States Department of Agriculture
USSL	US salinity lab
WRB	World Reference Base for Soil Resources

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Articles as a contributor (Bolivia)

Quispe Zenteno et al. (2020), Mamani Flores et al. (2020) and Zambrana Yañez et al. (2020).

Chapter 1

Introduction

1. General context

In general, salt-affected soils contain high levels of soluble salts as the major ions (sodium, potassium, calcium, magnesium, bicarbonate, chloride, carbonate, and sulphate) and/or significant amounts of sodium in the exchange complex, as well as in the soil solution, and basically include saline and/or sodic soils (Figure 1.1). Salinization is a major soil-degrading process in arid and semi-arid regions, originating from natural processes such as weathering, climate, and soil-water dynamics, as primary salinization and/or being induced by anthropogenic activities such as the inappropriate management of land and water resources, as secondary salinization. Salinity negatively affects root and plant growth through the osmotic effect caused by the high concentration of soluble salts. Because of excess adsorbed Na^+, sodicity causes adverse effects on soil properties, such as an increase in soil pH, loss of physical structure (clay dispersion, swelling, and plugging of soil pores), and the deterioration of soil–water relations (decrease in infiltration, hydraulic conductivity, water retention and drainage), leading to soil erosion, crusting, compaction, runoff, waterlogging, nutrient imbalances and specific ion toxicity on plants, thus causing a reduction of soil productivity and crop production, and decreased biodiversity (Qadir et al., 2001a; Qadir and Schubert, 2002; Levy and Shainberg, 2005; Qadir et al., 2007; Keren, 2005; Stavi et al., 2021; Andrade Foronda and Colinet, 2023; FAO, 2022).

Based on the data from 118 countries covering 73% of the global land area and the threshold values of $EC_e > 2$ dS m^{-1}, ESP > 15%, and pH > 8.2, the Global Map of Salt-Affected Soils (FAO, 2021) indicates that more than 4,4% (85% saline, 10% sodic and 5% saline-sodic) of topsoils (0-30 cm) and 8,7% (62% saline, 24% sodic and 14% saline-sodic) of subsoils (30-100 cm) of the total land area is salt-affected; from this mapping, maps of salt-affected top/subsoils in Bolivia are shown in Appendix 1.1. Salt-affected soils in Bolivia exceed 5% of its territory and marginalize a large surface of agricultural lands, so their assessment as resources and the evaluation of cost-effective amelioration strategies are indispensable (Hervé et al., 2002). FAO (2022) addressed numerous potential negative impacts of salinity and sodicity during the global symposium on salt-affected soils in 2021, through three main themes: (1) Assessment, mapping, and monitoring of salt-affected soils, (2) Integrated soil-water-crop solutions in rehabilitation and management of salt-affected areas and (3) Agenda for action to prevent and rehabilitate salt-affected soils, protect natural saline and sodic soils, and scale-up sustainable soil management practices; in this regard, our research agrees with these topics by contributing to the assessment, characterization and monitoring of salt-affected soils, as well as the evaluation of appropriate remediation techniques.

The High Valley of Cochabamba used to be one of the most highly agriculturally productive valleys of Bolivia. However, nowadays it is characterized by low soil/crop productivity and land degradation mainly due to salinization processes, which in turn are caused by the semi-arid conditions, increase in population, deforestation, and inadequate agricultural practices, among other factors. Salinity and sodicity in the High Valley negatively impact not only soil health and crop yields but farmers‘ income. In this context, this research aimed at contributing to the sustainable management and rehabilitation of soils affected by salinity/sodicity in the High Valley of Cochabamba to improve the soil quality for environmental health and crop productivity, thus the economic situation of farmers. Consequently, as a result of previously identified problems, research gaps and questions we formulated some research objectives: Generation of a database of soil information as a baseline for this study and context of the current status of soils in the study area, characterization and classification of salt-affected soil samples and profiles, comparison between two salt-affected soil classifications systems about their output categories which could impact on soil management, performance evaluation of machine learning-based models in predicting salinity, sodicity and salt-affected soil classes from soluble salt ions, accuracy assessment of models to predict sodicity and salinity variables from easily obtained predictors, selection of most accurate models and important variables which can be used to predict salt-affected soils in the study area, evaluation of the effectiveness of singly/combined mineral and organic amendments with leaching in ameliorating saline-sodic soil under controlled conditions, and identification of the most effective organic or mineral amendment(s) and/or their optimal combination(s) for improving soil salinity/sodicity.

The structure of this manuscript is as follows :

- The relevant concepts linked to salt-affected soils, as well as a general introduction to the specific situation of the study area (High Valley of Cochabamba) within the scope of the study, besides the research questions and gaps, objectives, and outline are presented next in this **chapter 1**.
- The characterization of soil profiles and samples in the study area, as well as issues linked to the classification criteria of salt-affected soils and their spatial distribution are presented in **Chapter 2**.
- **Chapter 3** is dedicated to the performance evaluation of models to predict soil salinity and sodicity from the measurement of soluble salt ions, and other easily obtained features, using conventional and machine learning-based techniques.
- In **Chapter 4**, results from experiments under controlled conditions to evaluate the effectiveness of singly/combined mineral and organic amendments with leaching in ameliorating saline-sodic soils, are commented on.
- Finally, a general discussion, future perspectives, and overall conclusion of the study are presented in **Chapter 5**.

2. Salt affected soils: Concepts and definitions

2.1. Salinity and saline soils

Saline soils are characterized by significant levels of soluble salts comprising the major ions, namely, sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), and sulphate (SO_4^{2-}). These soils mainly contain sulphates and chlorides of Ca^{2+} and Mg^{2+}, and small quantities of K^+, NH_4^+, HCO_3^-, CO_3^{-2}, and NO_3^- are also present. In contrast to sodic/alkali soils, saline soils are usually flocculated, well-structured, and as permeable as normal soils or even more, because of the presence of excess salts and low amounts of Na^+ ion on exchange sites; moreover, during the salinization process, the accumulated salts are mostly NaCl, Na_2SO_4, $CaCO_3$ and $MgCO_3$ with a dominance of Na^+ salts in the early stages and Ca^{2+} / Mg^{2+} salts accumulating gradually, thus developing saline soils and later white alkali soils (Choudhary and Kharche, 2015; Alemayehu and Haile, 2022).

Saline soils are often recognized visually by the presence of efflorescence as white crusts of salts on the soil surface formed through evaporation during a drought period. Soil salinity negatively impacts root/plant growth and crop yield through the osmotic effect caused by the high concentration of soluble salts (Figure 1.2). Salinity levels are usually expressed as soil electrical conductivity (EC) in DeciSiemen per meter (dS m^{-1}) as a standard unit measured either in saturated extract or in soil–water suspensions which measures the ability of soil-water to carry electrical current as an electrolytic process in the soil solution along with soluble ions. Salinity can also be expressed as the total soluble salts (TSS). Moreover, Abrol et al. (1980) observed that saline soils contain neutral soluble salts of Cl^- and SO_4^{2-} of Na^+, Ca^{2+}, and Mg^{2+}; and also, that - instead of EC_e – the nature of the soluble salts would be a more reliable indicator for differentiating saline from sodic/alkali soils.

The threshold electrolyte concentration (TEC) refers to the electro-osmotic effect of saline solutions in counteracting the repulsive forces caused by the hydration of adsorbed sodium ions; and tough, the salt concentration is useful in maintaining soil structural integrity, but it is harmful to plants when it exceeds a threshold related to their salt tolerance (Rengasamy, 2016). Appendix 1.2b shows the relationship between salinity and sodicity, as well as the diagonal line that distinguishes between flocculated and dispersed soils. Saline-sodic soils normally contain excessive amounts of soluble salts and exchangeable Na+ from the combined processes of salinization and sodication, however, Chhabra (2004) warns about the ambiguity of saline-sodic soils in terms of salinity or sodicity behaviour normally determined by their Na^+ and alkali salts to neutral salts ratios, besides soil pH, ESP and EC.

2.2. Sodicity and sodic soils

Sodic soils have an accumulation of excess Na^+ and variable amounts of free salts in soil solution and mainly occur under arid and semiarid climates. Sodication or alkalinization is a process which comprises the progressive leaching of soluble salts and the accumulation of adsorbed Na^+ on the soil particles at concentrations which adversely affect the structure of soils (Marchuck, 2013); also characterized by a pH generally higher than 8.5 (Gupta et al., 1984). Alkali soils contain soluble salts capable of causing alkaline hydrolysis, which are predominately CO_3^{2-} and HCO_3^- of Na^+, leading to an increase in SAR due to precipitation of soluble Ca^{2+} as $CaCO_3$, and when soils accumulate $CaCO_3$, there is a gradual increase in the proportion of Na^+ in solution and thereby the proportion of the Na^+ adsorbed on soil colloids also increases; then the addition of Na^+-containing salts as carbonates to the soil may result in a saturation of Na^+ in the soil exchange complex – known as sodication process - and as the salt concentration increases, Ca^{2+} and Mg^{2+} may precipitate as their respective carbonates; (Abrol et al., 1980; Choudhary and Kharche, 2015); additionally, when the plants extract the water from the soil, the salts remain and become concentrated, causing the calcium to precipitate as calcium carbonate, while much of the Na^+ remains in the soil-water (Alemayehu and Haile, 2022). Alkali soils from arid and semiarid lands contain free $CaCO_3$ with concentrations of soluble Na^+ and CO_3^{2-} + HCO_3^- as the dominant ions and very low Ca^{2+} and Mg^{2+}; moreover, soil organic matter gets dissolved and forms black-alkali soils as organic–clay coatings on soil aggregates and on the soil surface caused by the high pH increased linearly with an increase in ESP (Chhabra 2004; Gupta and Abrol, 1990).

The flocculating power of Calcium is 43 and magnesium is 27 times that of sodium, which – along with its larger ionic size in water – causes the dispersive effect in soil (Figure 1.2). The accumulation of adsorbed Na^+ leads to the dispersion and swelling of soil particles with organic matter, occupying and clogging the soil pores and causing the deterioration of soil–water relations such as hydraulic conductivity and water-holding capacity, thus the loss of soil physical structure and aeration, crusting, compaction, runoff, waterlogging nutrient imbalances and soil erosion (Daba and Qureshi, 2021; Qadir and Schubert, 2002; Quirk and Schofield, 1955).

Sodicity levels are usually determined as the exchangeable sodium percentage (ESP) through the amount of exchangeable Na^+ as a proportion of either the cation exchange capacity (CEC), or the sum of exchangeable cations (Qadir et al., 2007; Sumner et al., 1998), or indirectly estimated by the sodium adsorption ratio (SAR) calculated from the soluble Na^+ relative to the soluble Ca^{2+} + Mg^{2+} concentrations in a soil solution using the formula proposed by Richards et al. (1954), which also is used to characterize the presence of Na^+ in irrigation water (Horneck et al., 2007). Normally, the soil dispersion correlates positively with the soil ESP, mainly when this exceeds 15%. The exchangeable cation ratio (ECR) is an index alternative to ESP, which takes into account the influence of exchangeable K^+ ions on clay dispersion even at a minimum level of exchangeable Na^+ (Marchuk et al., 2014). The cations ratio of soil structural stability (CROSS) is a cation ratio analogous to SAR, which considers the differential dispersive effects of Na^+ and K^+ on clay dispersion and the differential flocculation powers of Ca^{2+} and Mg^{2+} (Rengasamy and Marchuk, 2011). The most used indicators of soil sodicity are summarized in Table 1.1.

The term ‘alkali’ or ‘alkaline’ is usually a synonym of ‘sodic’, generating a certain degree of confusion since sodicity is more related to excess adsorbed Na^+ and alkalinity to the dominance of alkaline salts besides the adsorbed Na^+. Neutral and alkali salts usually determine the distinction between sodicity and alkalinity, so alkali soils normally have excess exchangeable Na^+ and carbonates besides a pH above 8 (Gupta and Abrol, 1990). Sometimes, the presence of Na^+ carbonates passes unnoticed when obtained from paste extract, due to a portion of the dissolved carbonates that reacts with Ca^{2+} and precipitates as $CaCO_3$; moreover, the high solubility of Na^+ salts and the electroneutrality of aqueous solutions mean that the remaining Na^+ charge is either balanced by sulphate ions or included into the exchange sites, which permit the use of efflorescence crusts (pH >8.4, Na/Cl ratio >1) as indicators of Na^+ carbonates (Gupta and Abrol, 1990).

Table 1.1 Indicators/indices used for measuring soil sodicity.

Index/indicator	Equation	Unit	Reference*
Sodium adsorption ratio (SAR)	$\frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$	cations are expressed in $mmol_c\ L^{-1}$	1
Exchangeable sodium percentage (ESP)	$\left(\frac{Na^+}{CEC}\right)100$	Na^+ and CEC are expressed in $cmol_c\ kg^{-1}$	1, 3
Exchangeable sodium percentage (ESP)	$\left(\frac{Na^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+}\right)100$	cations are expressed in $cmol_c\ kg^{-1}$	2, 3
Cation’s ratio of soil structural stability (CROSS)	$\frac{Na^+ + 0.56\,K^+}{\sqrt{\frac{Ca^{2+} + 0.6\,Mg^{2+}}{2}}}$	cations are expressed in $mmol_c\ L^{-1}$	4
Exchangeable cation ratio (ECR)	$\left(\frac{Na^+ + 0.56\,K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+}\right)100$	cations are expressed in $cmol_c\ kg^{-1}$	5

* (1) Richards et al., 1954; (2) Sumner et al. 1998; (3) Qadir et al. 2007; (4) Rengasamy and Marchuk, 2011; (5) Marchuk et al., 2014. CEC = cation exchange capacity.

2.3. Causes and impacts of salinity and sodicity

Some contributing factors to the process of salinization - based on Daba and Qureshi (2021), Choudhary and Kharche (2015) and Marchuck (2013) - are:

- Climate-related factors in arid and semi-arid conditions, such as dryness, insufficient rainfall (< 500mm), and high evaporation/transpiration which exceeds precipitation, among others.
- Soil-water management practices such as the use of low-quality irrigation water, inadequate irrigation methods, poor drainage, unsustainable use of fertilizers, lack of techniques for soil recovery/remediation, and removal of cover and deep-rooted vegetation, among others.
- Geochemical weathering of rocks, saline parent materials, sources such as fossil salts of former marine and lacustrine deposits, atmospheric deposition, and salts brought down from the upstream rivers draining to the plains and subsequent deposition along with alluvial materials.
- Groundwater-associated salinity which mostly occurs in dry lands and is caused by the salt inputs through natural processes of precipitation and the capillary rise from subsoil salt beds or shallow brackish groundwater accompanied by a lack of natural leaching due to topographic situation.
- Non-groundwater associated -or transient- salinity caused by the temporal and spatial variations of salt accumulation in the root zone which mainly occurs in areas dominated by sodic subsoils.
- Accumulation of dissolved Na+ as exchangeable Na+ due to vertical/horizontal leaching mainly in sub-humid regions.

Additionally, Appendix 1.2a illustrates some causes of salinization.

Some effects and impacts of salinity/sodicity - based on Daba and Qureshi (2021), Marchuck (2013), Qadir and Schubert (2002) and FAO (2022) – are:

- A continuous osmotic phase that prevents water uptake by plants due to the osmotic pressure of saline soil solution, followed by a slower ionic phase when the accumulation of specific ions in the plant over some time causes ion toxicity or ion imbalance, leading to poor seedling emergence, limited plant/root growth, and limited plant nutrition due to water and nutrient uptake and gaseous exchange restrictions.
- The increased adsorbed Na^+ content affects the soil aggregation stability because of its dispersive action on soil particles, resulting in a change of the pore size distribution, a decrease of soil volume and soil compaction, thus negatively affecting bulk density, hydraulic conductivity, water-holding capacity, water/air circulation, and consequently the crop productivity.
- Negative impact on soil ecosystem services comprising reduced soil fertility and ability of crops to take up water and the loss of soil-water properties, leading to soil degradation, low agricultural productivity, decrease in income and human quality of life, loss of biodiversity and disturbed ecosystem functions.

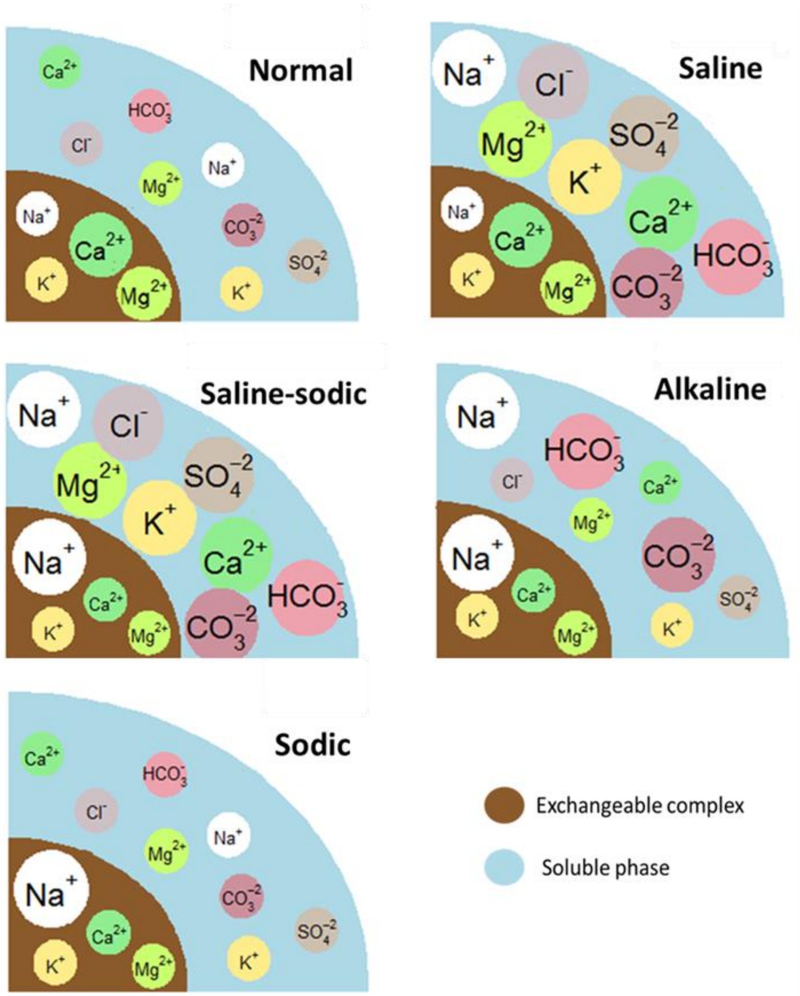

Figure 1.1 Graphical illustration of salt-affected soil types according to their soluble/exchangeable ion composition. Ions' size represents their relative amount/concentration.

2.4. Characterization, classification, and prediction of salt-affected soils

Soil information usually includes the soil characterization in terms of soil profile description, comprising chemical, physical and morphological properties, in addition to geomorphology, pedology, soil formation and landscape processes. Moreover, soil sodicity and salinity variables such as soil ESP, SAR, EC, pH and major ions can be used for classification as the determination of salt-affected soil categories and spatial distribution of saline/sodic soils, as well as for the generation of prediction models, using these properties either as predictor or response variables.

Salt-affected soils can be classified by applying the widely used US Salinity Lab (USSL) classification by Richards et al. (1954). Chhabra et al. (2004) proposed an alternative classification analogous to that of Szabolcs (1989), which includes the ion ratios of $(2CO_3^{2-} + HCO_3^-) / (Cl^- + 2SO_4^{2-})$ and $Na^+ / (Cl^- + 2SO_4^{2-})$ expressed in mol m^{-3}, besides the soil EC_e and ESP, for facilitating the subsequent management of salt-affected soils (Table 1.2). The Australian classification (Rengasamy, 2010/2016) is somewhat analogous to that of the USSL but takes into account the pH levels and a pH threshold value of 8 since at this level the soil becomes alkaline and carbonates dominate the anions, and assumes a soil ESP threshold value of 6% because of the adverse effects of exchangeable Na^+ on soil structure which start at this level in vertisols, due to smectite and montmorillonite as dominant clay minerals, with a higher specific surface area than that of illite and kaolinite, which promote soil dispersion even with a low increase in ESP in arid and semiarid regions (Isbell, 2002; Shainberg & Letey, 1984). The FAO's criterion considers a pH threshold value of 8.2 instead of 8.5 based on the conclusion of Abrol et al. (1980), who affirmed that precipitation of $CaCO_3$ starts at a pH of 8.2 as an indicator of alkaline soil formation. McIntyre (1979) simply differentiated sodic from alkaline soils through the soil ESP and pH, respectively. There are other systems for classifying salt-affected soils based on salinity degree related to the content/composition of toxic salt ions (Pankova et al., 2018), levels of salinity by intervals of EC_e (Richards et al., 1954) and levels of sodicity by intervals of ESP (Abrol et al., 1988).

Table 1.2 Some representative and widely used systems to classify salt-affected soils.

System	Categories	Property / Threshold value
US Salinity Lab[1]	Normal	ESP < 15%, EC_e < 4 dSm^{-1}, pH < 8.5
	Saline	ESP < 15%, EC_e > 4 dSm^{-1}, pH < 8.5
	Saline-sodic	ESP > 15%, EC_e > 4 dSm^{-1}, pH < > 8.5
	Sodic	ESP > 15%, EC_e < 4 dSm^{-1}, pH > 8.5
Alternative[2]	Normal	ESP < 15%, EC_e < 4 dSm^{-1}, pH < 8.2
	Saline	ESP < 15%, EC_e > 4 dSm^{-1}, pH < 8.2, Ratio 1* and Ratio 2† < 1
	Alkali	ESP > 15% (> 6% in vertisols), EC_e < 4 dSm^{-1} (variable), pH > 8.2, Ratio 1* and/or Ratio 2† > 1
Australian[3]	Normal	ESP < 6%, EC_1 < 4 dSm^{-1}, pH 6 - 8
	Saline	ESP < 6%, EC_e > 4 dSm^{-1}, pH < 6 - > 9
	Saline-sodic	ESP > 6%, EC_e > 4 dSm^{-1}, pH < 6 - > 9
	Sodic	ESP > 6%, EC_e < 4 dSm^{-1}, pH < 6 - > 9

(1) Richards et al. (1954), (2) Szabolcs (1989) and Chhabra (2004), (3) Rengasamy (2010).

***** Ratio 1 = $(2CO_3^{2-} + HCO_3^-) / (Cl^- + 2SO_4^{2-})$ † Ratio 2 = $Na^+ / (Cl^- + 2SO_4^{2-})$

Some salinity and sodicity variables can be predicted from each other to lower costs and save time on lab determinations, consequently, some authors evaluated simple linear models to predict ESP, SAR, ESR and EC (Sonmez et al., 2008; Kargas et al., 2020; Chi et al., 2011; Elbashier et al., 2016ab; Seilsepour et al., 2009; Seilsepour and Rashidi, 2008; Al-Busaidi and Cookson, 2003; Harron et al., 1983; Shirmohamm and Heydari, 2020; Annex 4). Moreover, multivariate models using conventional and novel techniques can be an alternative for such purposes. Machine learning (ML), as a process of learning from a system's experience for self-improvement based on resultant information, can be used for obtaining more accurate and complex prediction models. Random Forest (RF)is an ensemble learning method that constructs multiple decision trees during training, which in classification tasks, aggregates the votes and outputs the mode from multiple decision trees to determine the final class prediction and for regression, RF averages the predictions from individual trees to produce a continuous output as the mean (Breiman, 2001). Support Vector Machines (SVM) is a supervised learning algorithm that finds a hyperplane in an N-dimensional space to distinctly classify data points or perform regression; then, in classification finds the hyperplane that best separates classes with the maximum margin (Cortes and Vapnik, 1995), and Support Vector Regression (SVR) finds a hyperplane that best fits the continuous target variable within a certain margin of tolerance (Drucker et al., 1997). Partial Least Squares (PLS) is a statistical method that finds a linear regression model by projecting the predicted variables and the observable variables into a new space; so in classification, PLS Discriminant Analysis (PLS-DA) projects the data onto latent structures and then uses these for classification (Barker and Rayens, 2003), and for regression PLS creates latent variables in the new space to maximize the covariance between the predictor and response variables (Wold, 1966).

Furthermore, some easily obtained variables, such as geo-environmental features including satellite image bands and derived salinity/vegetation indices, geomorphometric and physiographical, among other features, which in turn combined with field/lab measured characteristics such as chemical and physical properties, can be used as explanatory variables or covariates for the training and validation of prediction models for subsequent generation of maps through geostatistical methods as spatial interpolations.

2.5. Remediation of salt-affected soils

Remediation of salt-affected soils normally aims to eliminate the excess soluble salts and exchangeable sodium below the root zone to restore soil productivity and plant growth. Kumar et al. (2022) stated that technological interventions to rehabilitate salt-affected soils can play an important role in increasing agricultural productivity and farmer welfare; therefore, research should target alternative and efficient ameliorants, and suited practices to achieve significant benefits in productivity, profitability, and environment sustainability from salt-affected soils. The amelioration of these soils can be achieved through physical, chemical and biological approaches:

2.5.1. Chemical approaches

The amelioration of saline-sodic and sodic soils usually needs an external source of soluble calcium – ideally applied with non-saline irrigation water – to replace the excess sodium from the cation exchange sites of the rhizosphere (Ahmad et al., 2006), for facilitating the soil flocculation and subsequent improvement of soil structure, pH and nutrient availability. A basic illustration of the saline/sodic soil remediation principle is shown in Figure 1.2. Generally, there are two types of chemical/mineral amendments: Soluble sources of calcium such as Gypsum ($CaSO_4.2H_2O$), calcium chloride ($CaCl_2$) and phospho-gypsum; and acids or acid-formers such as elemental sulphur (S), sulphuric acid (H_2SO_4), sulphates of iron and aluminium, and pyrites; furthermore, if $CaCO_3$ present in the soil, then, needs the application of organic amendments or acid formers to enhance its solubility (Choudhary and Kharche, 2015). Ideally, amendments are applied after cropping and before leaching for initial reclamation and long-term maintenance of the soil. A general reaction of added calcium-based amendment or $CaCO_3$ in soil, for displacing adsorbed sodium is:

$$Na^+ – X + Ca^{2+} (S) = Ca^{2+} – X + 2Na^+ (S) \downarrow,$$

Where, *S* is a solution and *X* is the exchange complex of the soil.

Gypsum and sulphuric acid are widely used because of their relatively low cost and availability (Qadir et al., 2001a). When sulphur is applied to the sodic soil, it is oxidized by microbiological activity to form sulphuric acid, which then dissolves the calcite in the soil, generating the Ca^{2+} needed to remove the exchangeable Na^+. Sulphuric acid can also react directly with Na_2CO_3 in the soil. The soil ESP is normally used to calculate the dose of gypsum necessary to remediate excess Na^+, but it is also influenced by crop tolerance to sodicity and economic conditions. Due to the high pH of alkali soil, most likely as a result of Na_2CO_3, the addition of gypsum provides a source of Ca^{2+}, which precipitates as $CaCO_3$ and Ca $(HCO_3)_2$, leading to a decrease in pH (Wong et al., 2009), besides the reduction of the hydrolysis reactions associated with Na^+ ions on the exchange complex. Moreover, Mahmoodabadi et al. (2013) 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 the properties of calcareous saline-sodic soils.

2.5.2. Biological approaches

The use of organic amendments is an alternative to mineral amendments for reclaiming sodic and saline-sodic soils, as they improve not only salinity/sodicity but also the soil structure through the enhancement of soil-water properties. Organic amendments, such as cattle manure, chicken manure, compost, peat and biochar, among others, promote plant growth thanks to their beneficial effects on the physical, chemical, nutritional and biological properties of the soil and facilitate the leaching of salts in saline/sodic soils, in harmony with the environment (Srivastava et al. 2016; Yaduvanshi and Swarup 2005; Oo et al. 2015). Adding organic amendments in sodic soils usually binds the small soil particles together into large water-stable aggregates, increases porosity and thus improves the physical properties of the soil, and can also reduce input costs as a sustainable and efficient management method for reclaiming salt-affected soils (Srivastava et al., 2016; Chaganti et al., 2015), besides the beneficial impacts on nutritional and biological soil properties. Organic materials help in improving and maintaining soil structure, preventing erosion, supplying essential plant nutrients, and enhancing biological activity, besides reclaiming the sodic soils through their decomposition, which increases the partial pressure of CO_2 and produces organic acids and subsequent increasing electrolyte concentration, mobilizing Ca^{2+} from dissolved soil calcite and facilitating the replacement of exchangeable Na^+ by Ca^{2+} and Mg^{2+}, thus, lowering the soil pH and ESP; therefore, the effectiveness of any organic amendment depends upon the amount of CO_2 produced and the extent of reduction for making the soil porous by maintaining channels and voids which improve water penetration and leaching of the salts out of the root zone, even though, their coarse texture and slow decomposition (Choudhary and Kharche, 2015). Furthermore, Diacono and Montemurro (2015) 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.

Phytoremediation as vegetative bioremediation is a function of four main factors: CO_2 partial pressure within the root zone, root proton release by N_2-fixing plants, improvement of soil porosity by root expansion, and harvested-shoot sodium content (Qadir and Oster, 2004) nonetheless, the latter can be insignificant compared to the ability of some plants to solubilize $CaCO_3$ in calcareous sodic or saline-sodic soils through their root respiration and H^+ release, then, the released Ca^{2+} ions substitute Na^+ ions on the soil cation exchange sites. However, this process is water/irrigation dependent and thus infeasible in arid and semi-arid regions; therefore, shoot-succulent halophytes, which can accumulate enormous Na^+ quantities within their above-ground organs, can be considered for these zones (Shahid, 2002). Furthermore, in areas in which leaching salts with water is unfeasible or costly, planting salt-tolerant crops or forages that can grow under low to moderate saline conditions may be viable (Alemayehu and Haile, 2022), as a relatively recent approach of growing interest known as biosaline agriculture.

2.5.3. Physical approaches

These approaches involve physical and mechanical methods such as deep-ploughing, sub-soiling, profile inversion, sanding, flushing and scrapping to remove the salts and improve permeability, and thereby, internal drainage within the soil profile depth for enhancing the infiltration or transportation of salts dissolved in water to deeper soil layers (Choudhary and Kharche, 2015). Desalination and de-alkalization of soils require proper land drainage and good quality irrigation water to remove dissolved soluble salts from the root zone and maintain the groundwater table, as well as the use of cultural practices such as minimum tillage, surface mulching, organic matter addition, green manures, crop residue management, selection of proper seeding/planting methods, and avoiding lands with a high groundwater table, among others (Daba and Qureshi, 2021).

Leaching excess salts and maintaining a favourable salt balance to prevent detrimental salt accumulation in the soil profile need enough water and proper drainage to leach salts below and out of the root zone but not into groundwater reserves. If drainage is impeded by a shallow water table, hardpan or bedrock, then an artificial drainage must be installed, or another use for the land might be considered. The signs of poor drainage include surface ponding, slow infiltration, or wetness for prolonged periods. The irrigation method and volume of applied water have an impact on salt accumulation/distribution, for instance, flood irrigation and an appropriate leaching fraction generally move salts below the root zone, drip-irrigation moves water away from the emitter and salts concentrate where the water evaporates, furrow-irrigation moves water from the furrow into the bed via capillary flow (Alemayehu and Haile, 2022). For saline soil amelioration, flushing with non-saline water is used to remove excess soluble salts, which involves washing away the surface accumulated salts; however, under shallow water table conditions, salts can again rise and accumulate at the surface through evapotranspiration. Ideally, for a proper reclamation of any salt-affected soil – even through chemical/biological techniques – adequate drainage is indispensable. Moreover, Alemayehu and Haile (2022) state that if soluble salts are leached out of saline-sodic soils even with good quality irrigation water before the exchangeable Na^+ is displaced, the level of this cation and pH would increase, then, the soil would change to adverse characteristics of sodic soils.

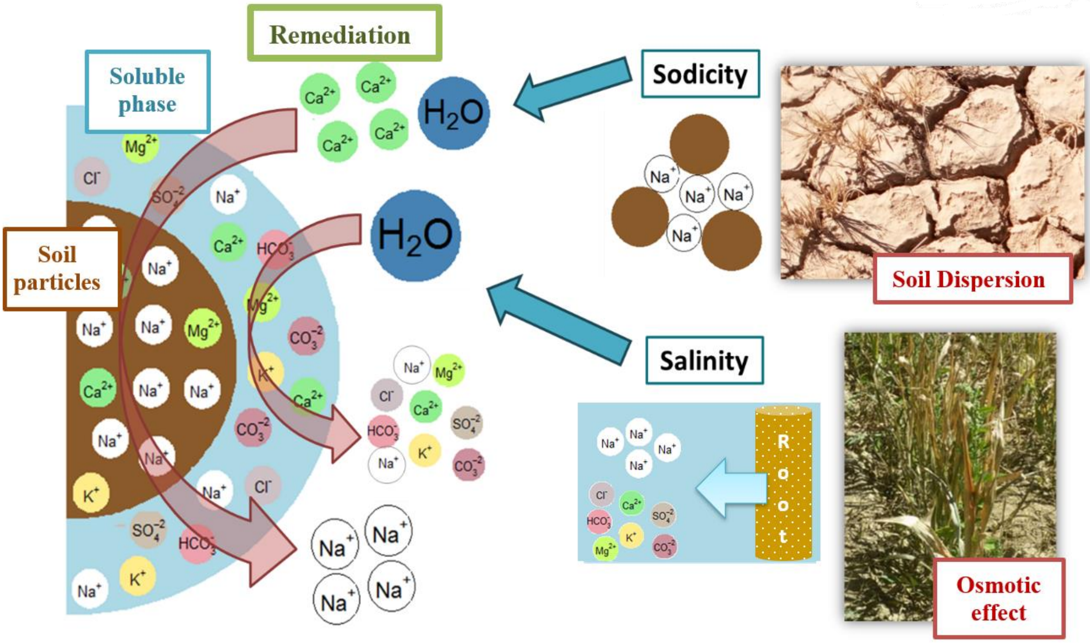

Figure 1.2 Graphical illustration of salinity/sodicity effects and the principle of its remediation. Ions' size represents their relative amount/concentration.

3. Study area: High Valley of Cochabamba

Over the past century, the High Valley of Cochabamba was probably one of the most agriculturally productive valleys in Bolivia; however, it is currently characterized by low productivity as well a large surface of degraded areas mainly affected by soil salinity/sodicity.

3.1. Location

The study area is the High Valley, located in the Department of Cochabamba – Bolivia, between the latitude boundaries of –17°29′47.7″ to –17°39′48.6″ and longitudes of –66°5′16.8″ to –65°45′13.0″ at an average elevation of ~2750 m. The spatial location of the study area is represented in Figure 1.3.

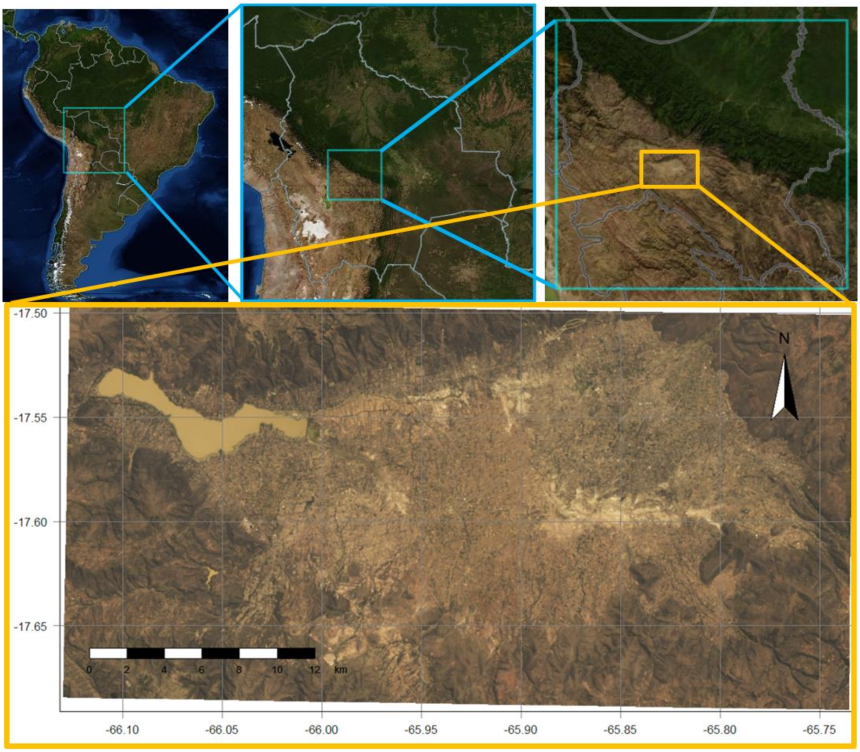

Figure 1.3 Study area location map - High Valley of Cochabamba, Bolivia (Landsat-8 image, 2017 and Google Earth, 2018).

3.2. General description

3.2.1. Climate:

The climate of the valley is semiarid with a mean annual temperature of 14–17 °C and mean annual rainfall of 350–4000 mm. The climatic diagram (Figure 1.4a) for the period from 2000 to 2020 shows maximum annual precipitation in January, a short rainy period and a prolonged drought period from April to mid-November, added to the annual evapotranspiration trend (Figure 1.4b) leads to a significant water deficit. Moreover, there is a tendency to increase inter-annual variability over time, causing more extreme dry years and subsequent higher rainfall periods.

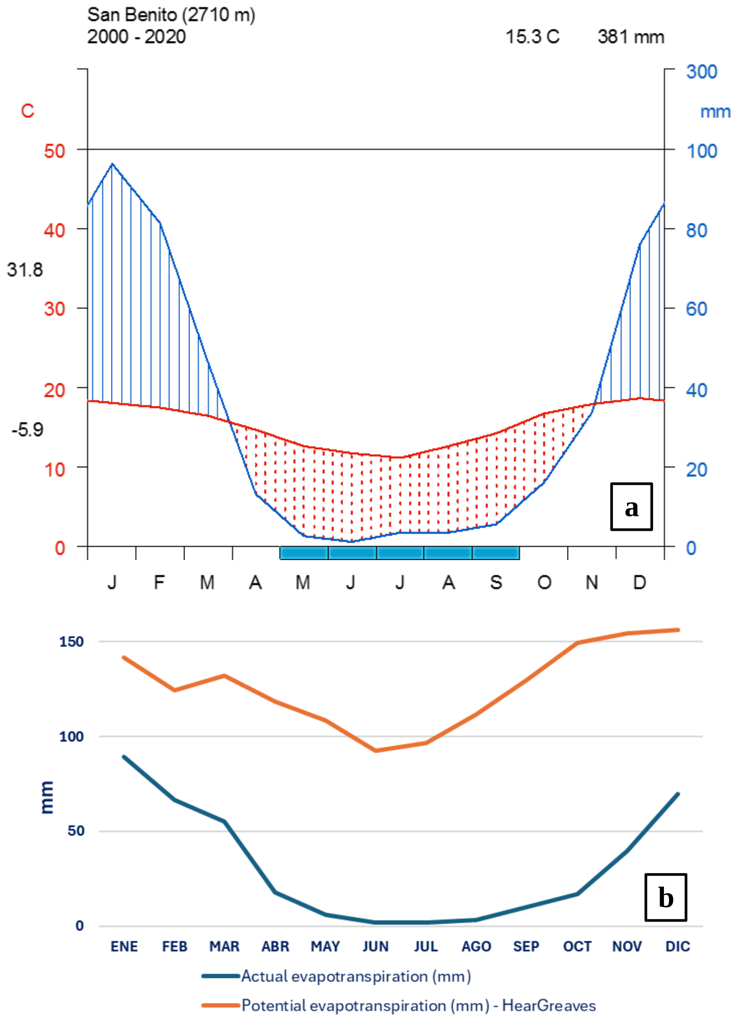

Figure 1.4 Walter & Lieth climatic annual diagram 2000 - 2020 (a), and annual evapotranspiration, 1982 - 2010 (b). Based on data from San Benito Station - High Valley of Cochabamba, provided by SENAMHI – Bolivia.

3.2.2. Geomorphology and geology:

The High Valley belongs to the meso-thermic interandean valleys originated from tectonic depressions filled in by quaternary lacustrine, glacio-lacustrine and alluvio-lacustrine sediments. Regarding the geomorphic characterization of this area, most of the salt-affected soils are in the landscape of a valley with a relief type consisting of lagunary depressions, alluvio-lagunary/lagunary facies, a landform consisting of lagunary flats, and soil associations consisting of Ustalfic Haplargids/Ustochreptic Camborthids and Typic Salorthids/Natric Camborthids (Metternicht and Zinck, 2010/1997). Appendix 1.3 shows the geopedologic map of the High Valley. Soils on alluvial and colluvio-alluvial depositions in piedmont areas exhibit an overall low development, and Entisols dominate on recent and actual fans, Glacis have more developed soils mainly in their proximal and distal parts where Haplargids are predominant, and Calciorthids occur in the proximal part of the dissected depositional Glacis where fragments of the calcic horizon are brought up to the surface as a consequence of ploughing (Metternicht, 1996). The elevation and slope maps are represented in Figures 1.5a and 1.5b.

3.2.3. Hydrography

According to Metternicht (1996), catchment areas have variable extents, and streams are ephemeral and unstable carrying loads of sediments from the highlands during the rainy season, and most of the rivers and brooks have a torrential regime because of the climatic and geomorphic conditions. The Punata basin has its main catchment areas in the southern part, including the Calicanto, Siches, Escalera and Wasa Mayu rivers in Tarata, Cliza, Villa Rivero and Punata districts, respectively. The drainage network is controlled by tectonics, but towards the south of the Punata-Cliza basin, gentler basement subsidence allowed the development of a more extensive and integrated drainage network. In the highlands, the rivers have a dendritic distribution pattern, and in the lowlands, some short streams drain to the lagunary depressions of the Punata-Cliza basin. The Topographic Wetness Index map is shown in Figure 1.6a.

3.2.4. Soils:

An insight into the characterization of soil profiles and the classification of salt-affected soils in the High Valley can be found in Chapter 2.

3.2.5. Vegetation:

Some halophytic (Figure 1.7b, c) salt-tolerant genus such as Portulaca spp, *Suaeda spp*, *Anoda spp*, *Sesuvium spp*, *Chenopodium spp*, *Aizoaceae spp*, *Cynodon spp*, among others, mainly grow in patches at the middle and south of the valley. Additionally, Xerophytic trees, such as *Prosopis spp*, shrubs and cactus, and *Schinus molle* trees, are found as part of patches and hedges.

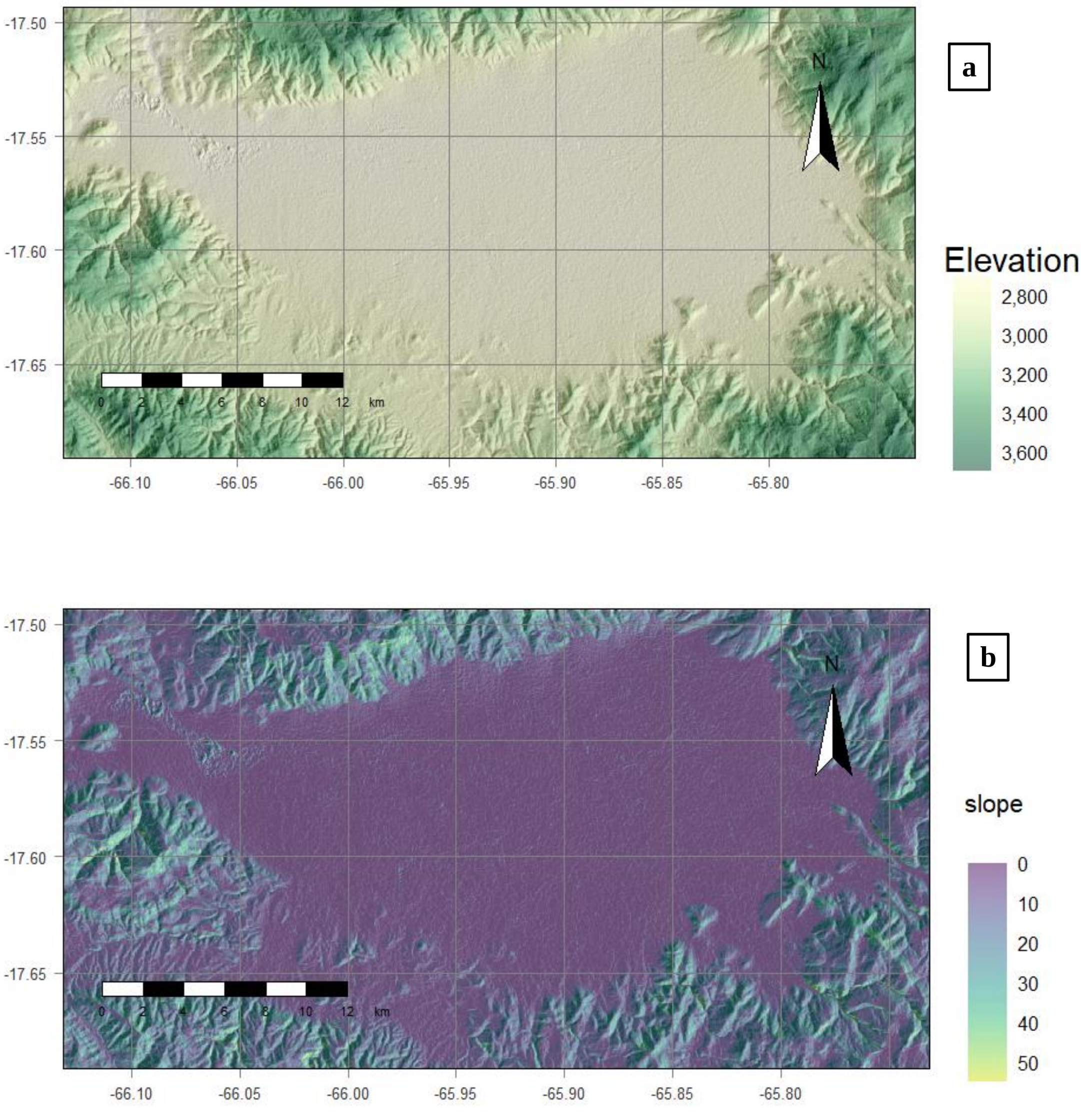

Figure 1.5 Elevation (a), slope (a), and Topographic Wetness Index (c) maps - High Valley of Cochabamba (based on the DEM, 2017)

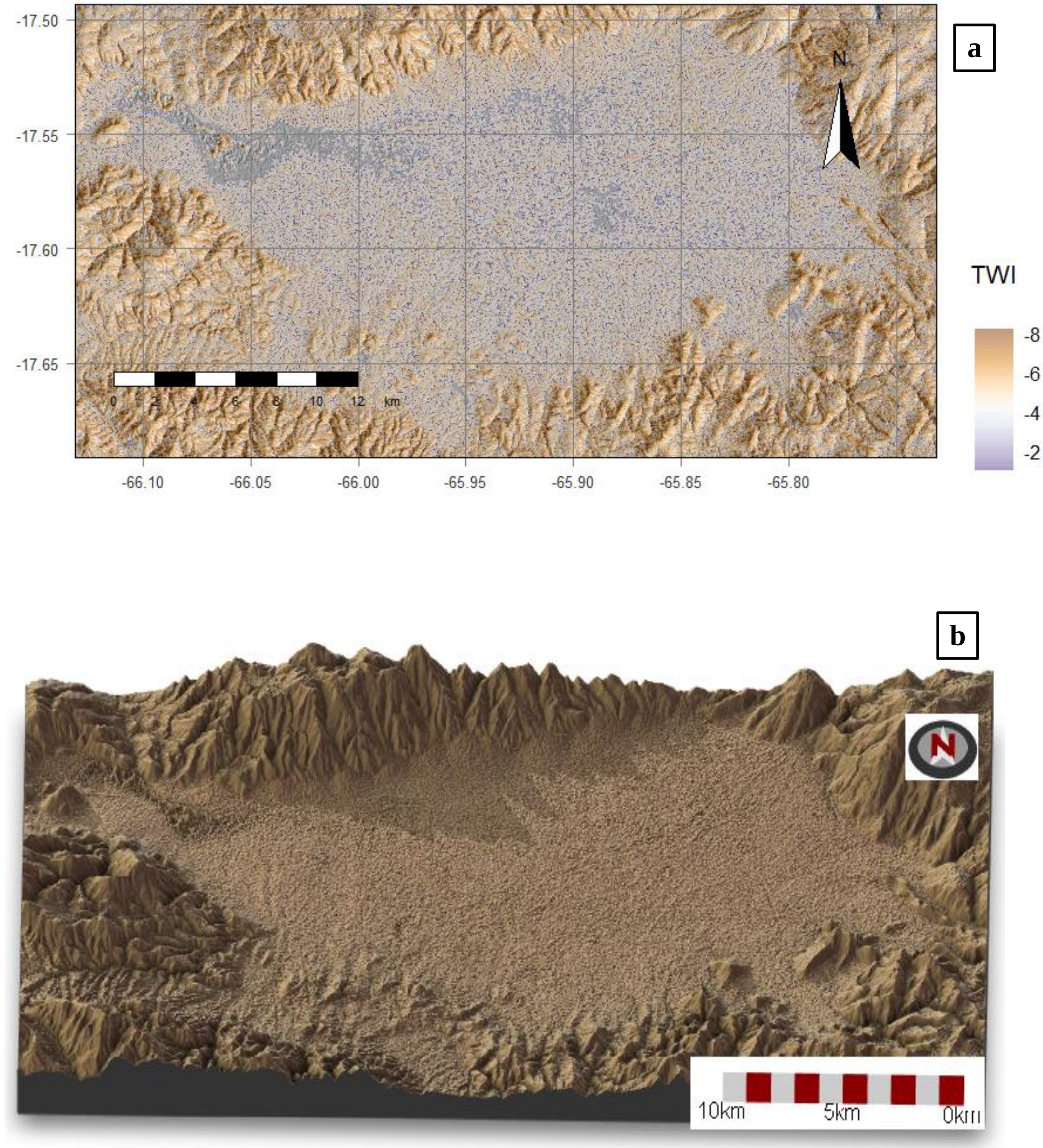

Figure 1.6 Topographic Wetness Index (a) and 3D elevation (b) maps - High Valley of Cochabamba (based on the DEM, 2017).

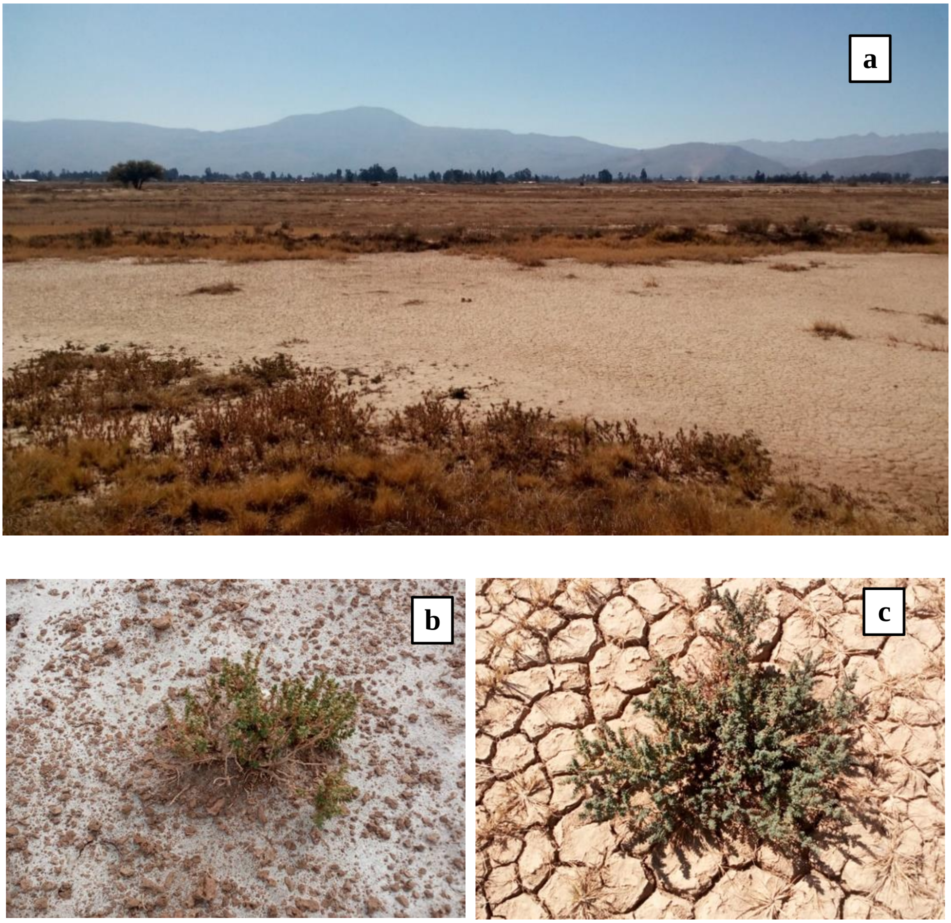

Figure 1.7 Patch of saline-sodic soil in the High Valley (a), and native halophytes (*Suaeda* spp) in soil with salt efflorescence (b) and with cracks (c) due to sodicity.

3.2.6. Agriculture:

The most cultivated agricultural rain-fed/irrigated crops are corn (*Zea mays*), lucerne (*Medicago sativa*), and wheat (*Triticum spp*). Other cereals such as oat (*Avena sativa*), barley (*Hordeum vulgare*) and triticale (X *Triticosecale* Wittmack) are usually cultivated as forage crops. It should be remarked that these crops showed moderate to high tolerance to salinity. The percentage proportions of the agricultural land use about the surface (Figure 1.8a) show the prevalence of cultivation of cereals – mainly corn – and fallow lands normally related to the shifting agriculture; in this regard, the major agricultural land uses in the High Valley (Figure 1.8b) are the intensive and the shifting agriculture mostly linked to rainfed crops and/or under irrigation.

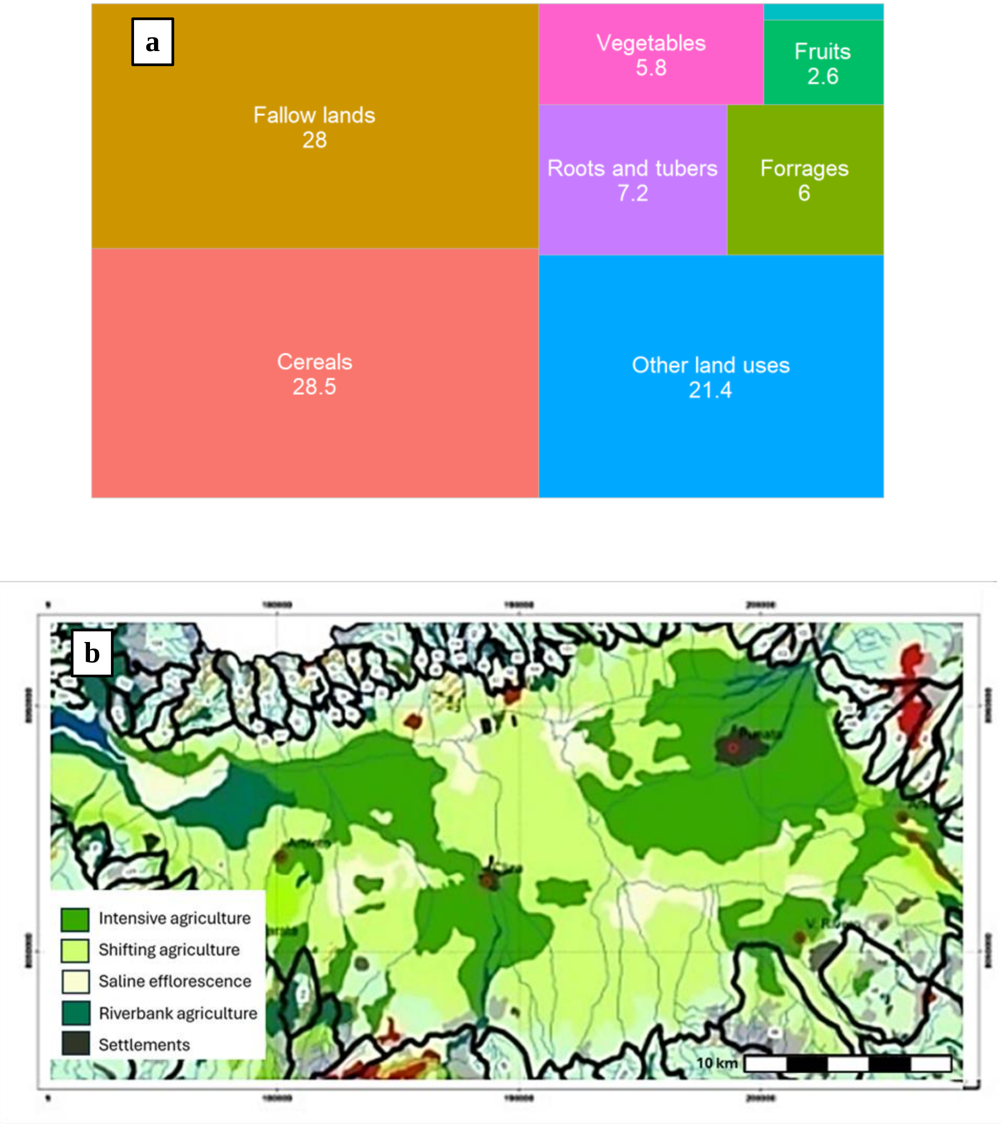

Figure 1.8 Treemap of agricultural land uses (%) in the High Valley, based on the agricultural survey of INE-2015 (a); and broad land use in the High Valley, based on AgroSig-2017 (b).

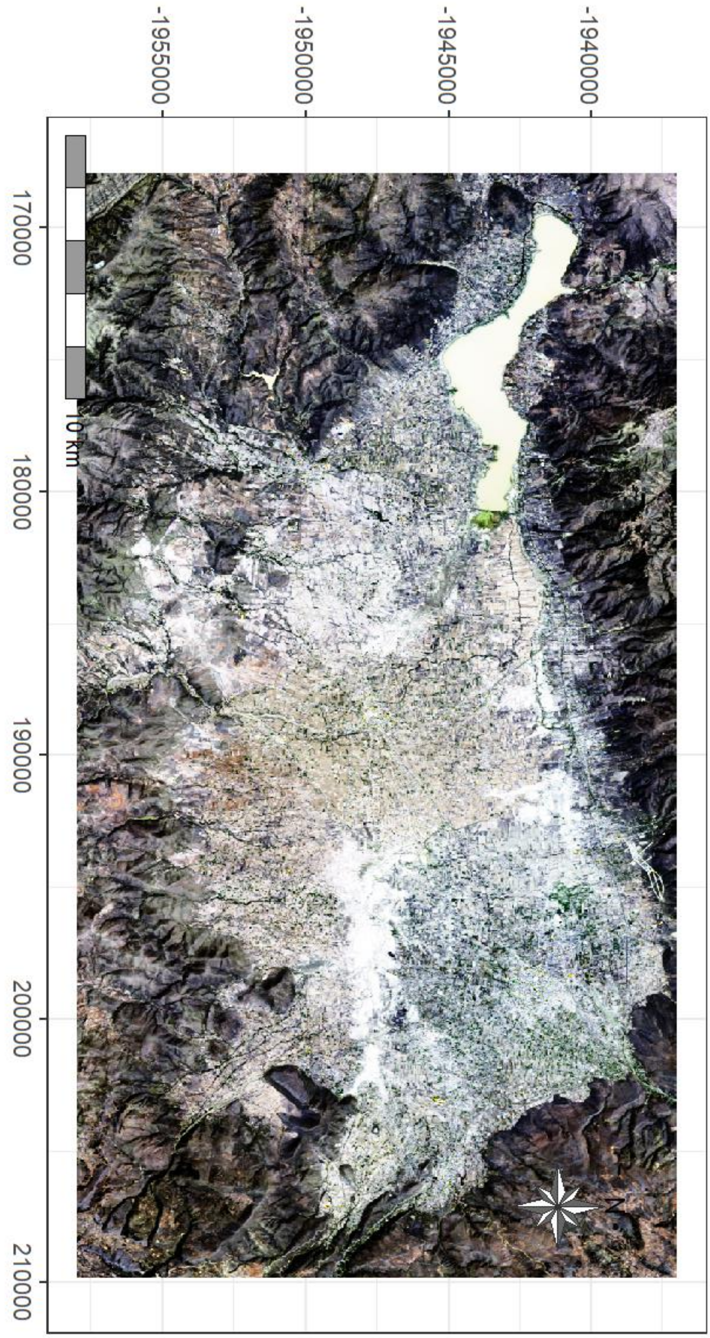

Figure 1.9 Colour composite image - High Valley of Cochabamba - Bolivia (based on Landsat-8 image, 2017).

3.3. Problem identification

The High Valley of Cochabamba was one of the most agriculturally productive valleys in Bolivia during the 20th century; however, nowadays it is characterized by low soil productivity and soil degradation, thus impacting crop yields and farmers' income. In a broad sense, the main driving factor of soil salinity/sodicity in the High Valley of Cochabamba is the semiarid condition characterized by a short rainy period along with a prolonged drought period, thus a climatic water deficit, considering that the formation of salt-affected soils normally occurs as a result of limited rainfall causing an insufficient amount of water to drain away or to groundwater the salts, as well as to meet the evaporation and transpiration needs, leading to a gradual salt accumulation in the soil through the capillary rise; moreover, the geochemical weathering and groundwater associated/non-associated salinization are also prevailing. Some other driving factors in the High Valley related to secondary salinization are the use of brackish or residual water for irrigation, inadequate use of fertilizers and deforestation along with the population increase.

Metternicht (1996) mentioned some aspects which influence the salinization and sodication processes, such as the increase of salt concentration with depth due to the percolation of rainwater through the subsurface alluvio-lacustrine and lacustrine deposits, high concentrations of Na^+ and Cl^- in the groundwater from lacustrine deposits, the dominance of Natric Camborthids and Salorthids in flat landscape areas of lacustrine-lagunary clayey parent materials, sediments with salts which are carried by ephemeral streams from the highlands during the rainy season, and the use of irrigation water, mainly in playas and flat landforms of alluvio-lacustrine origin. Moreover, the Bolivian Society of Soils – in a report of 2015 – stated that this region is subject to salinization processes because salts tend to concentrate in the upper part of the soil and the infiltration of soluble salts is restricted due to low rainfall and the arid regime, which also means that soils are commonly dry for more than six months.

During the phase of the on-site research for this study, some surveys and interviews were carried out in the study area. Among the stakeholders were farmers, agronomists, technicians, researchers and public workers from the agricultural sector, among others; specifically, the persons in charge of agricultural and livestock matter from the municipalities located in the study area, namely Punata, Cliza, San Benito, Arani, Villa Ribero, Tarata and Toco. The most relevant information identified as problems/needs about the impacts of salinity and sodicity in the High Valley were:

- In general, there is a lack of awareness and preparedness for salinization processes and effective management of salt-affected soils among the stakeholders in the study area.
- Insufficient knowledge on causes, effects, characterization and remediation of salt-affected soils not only from farmers but also technicians, decision-makers and policymakers.

- Following the above statement, the frequent erroneous identification of salt-affected soil types and the differentiation between salinity and sodicity, thus of the proper method of amelioration.
- The need for harmonious, comprehensive and updated baseline soil information to facilitate the subsequent management and monitoring of salt-affected soils.
- Insufficient facilities to properly carry out laboratory soil analyses for an adequate soil description, characterization and remediation.
- Some lab measurements such as that of soil ESP are usually costly and time-consuming.
- The necessity of a tailored salt-affected soil classification system which facilitates the management and monitoring of salt-affected soils.
- The determination of some sodicity/salinity variables is time-consuming and expensive, which generates the need for accessible and effective tools, methods and variables under lab and/or field conditions.
- The need for training and validation of site-specific methods for predicting salinity and sodicity, including machine learning-based techniques.
- Lack of insight on accessible reclamation techniques for farmers, including chemical, biological and physical approaches.
- For those amendment-based remediation techniques, a need for alternative low-cost and readily available amendments previously tested under lab and/or field conditions.
- The need for training on the use of monitoring/mapping techniques based on readily obtained features such as remotely sensed data and GIS.
- The absence of a joint program among government entities and farmers' associations for the continuous monitoring of salinity and sodicity.
- The absence of joint research programs between municipalities and research institutions to investigate topics which enhance the management and rehabilitation of salt-affected soils.
- A lack of insight and research on alternative approaches to rehabilitate salt-affected soil such as the strategy of adaptation through value crops highly tolerant to salinity and sodicity.

It should be remarked that the above-mentioned problems were screened and then selected according to the feasibility in function to the research relevance and availability of resources in order to formulate the research question and subsequent objectives; then the output of the filtering somehow represents the scope of the study.

4. Research approach and objectives of the thesis

4.1. Research gaps

Although some studies have already been conducted, mainly focusing on mapping and characterization of salt-affected soils, there are still some gaps in soil knowledge, tools and remediation techniques for the proper management of these soils in the High Valley. In that context and based on the previous on-site research and survey, the following are specific problems/needs as research gaps to be addressed:

- Knowledge to generate awareness and preparedness on salinization processes, characterization, remediation and management of salt-affected soils.
- A comprehensive and updated soil information base to facilitate the subsequent management and monitoring of salt-affected soils.
- The lack of a proper classification system to mitigate erroneous identifications and facilitate the management of salt-affected soils.
- Accessible and effective methods and variables for determining salinity and sodicity to overcome the current use of expensive and time-consuming techniques.
- Training and validation of tailored methods to predict salinity and sodicity variables, such as machine learning-based techniques.
- Some insights into accessible methods to remediate salt-affected soils.
- Evaluation of locally available amendments for saline-sodic and sodic soil remediation, under controlled and/or field conditions.

4.2. Research questions

Some research questions addressed in this study are:

- What is the current context and status in terms of characteristics of salt-affected soils in the study area?
- To what extent can the salt-affected soil classification system influence soil management?
- How effective are machine learning algorithms in predicting salinity/sodicity and salt-affected soil classes from soluble salt ions?
- To what extent can multivariate models accurately predict sodicity/salinity from easily measured/obtained features in the High Valley?
- Which prediction models are suitable to be used and improved in the study area?
- Which variables serve as the most reliable predictors of soil sodicity and salinity?
- How effective are locally available mineral and/or organic amendments in remediating sodic and saline-sodic soils, under controlled conditions?

- How do soil properties change after remediation in response to different amendment treatments under controlled conditions?
- Which mineral and/or organic amendment-based technique(s) is/are best for sodic/saline-sodic soil remediation under controlled conditions?
- How does the addition of organic amendments affect the efficacy of mineral amendments in the remediation of sodic/saline-sodic soils?

Consequently, the following statements were formulated as hypotheses, based on the previous research questions:

- Baseline soil information reveals variation in the levels of salinity and sodicity across different locations in the High Valley, with values ranging from non-saline to highly saline/sodic soils.
- Different classification criteria for salt-affected soils lead to differences in soil categorization, which in turn significantly affect the subsequent selection and efficacy of rehabilitation strategies.
- Prediction models based on both conventional and machine learning methods can accurately predict salinity and sodicity from soluble ions and other easily obtained features, aiding in the management of salt-affected soils.
- At least one amendment-based remediation technique, involving either individual or combined mineral and organic amendment, shows statistically significant improvement in soil salinity/sodicity compared to other treatments, expressed for testing purposes as: H_a: $\overline{X_A} \neq \overline{X_B} \neq \overline{X_C} \neq ... \overline{X_N}$, where, *Ha* is the alternative hypothesis, and $\bar{X}$ is the mean of a given treatment (*A, B, C… N*).

4.3. Objectives of the thesis

This study aims to contribute to the sustainable management and rehabilitation of salt-affected soils in the High Valley of Cochabamba through baseline soil information, models to predict salinity and sodicity, and some insights on amendment-based remediation techniques. In this context, the specific objectives of the study were:

- Generation of soil database information as a baseline for this study and context of the current status of soils in the High Valley.
- Characterization and classification of salt-affected soil samples and profiles.
- Comparison between two salt-affected soil classification systems about their output classes which could impact soil management.
- Performance evaluation of machine learning-based models in predicting salinity, sodicity and salt-affected soil classes from soluble salt ions.
- Accuracy assessment of multivariate models to predict sodicity and salinity variables from easily measured/obtained predictors.

- Selection of the most accurate models and important variables which can be used to predict salt-affected soils in the study area.
- Assessment of the effectiveness of singly/combined mineral and organic amendments with leaching on saline-sodic soil properties under controlled conditions.
- Identification of the most effective organic or mineral amendment(s) and/or their optimal combination(s) for improving soil salinity/sodicity.

4.4. Outline of the thesis

The outline of this research is briefly described in chapters, as follows:

Chapter 1

An introduction to the research including generalities about salinity, sodicity, characterization and remediation of salt-affected soils, as well as a general description of the study area, along with the research approach and objectives of this study.

Chapter 2

Characterization in terms of description of soil profiles in the study area, and the resulting implications of the use of salt-affected soil classification criteria, besides the spatial distribution.

Chapter 3

Performance evaluation of machine learning-based models to predict soil sodicity and salt-affected soil classes from soluble salt ions, as well as of conventional prediction models to estimate salinity and sodicity from other easily obtained features.

Chapter 4

The results from experiments under controlled conditions to evaluate the remediation effect of singly/combined mineral and organic amendment additions with leaching on saline-sodic soil properties.

Chapter 5

A general discussion including the significance and limitations of the findings, future perspectives and recommendations, and overall conclusion.

Figure 1.10 illustrates the structure of the manuscript about the objectives addressed through the research.

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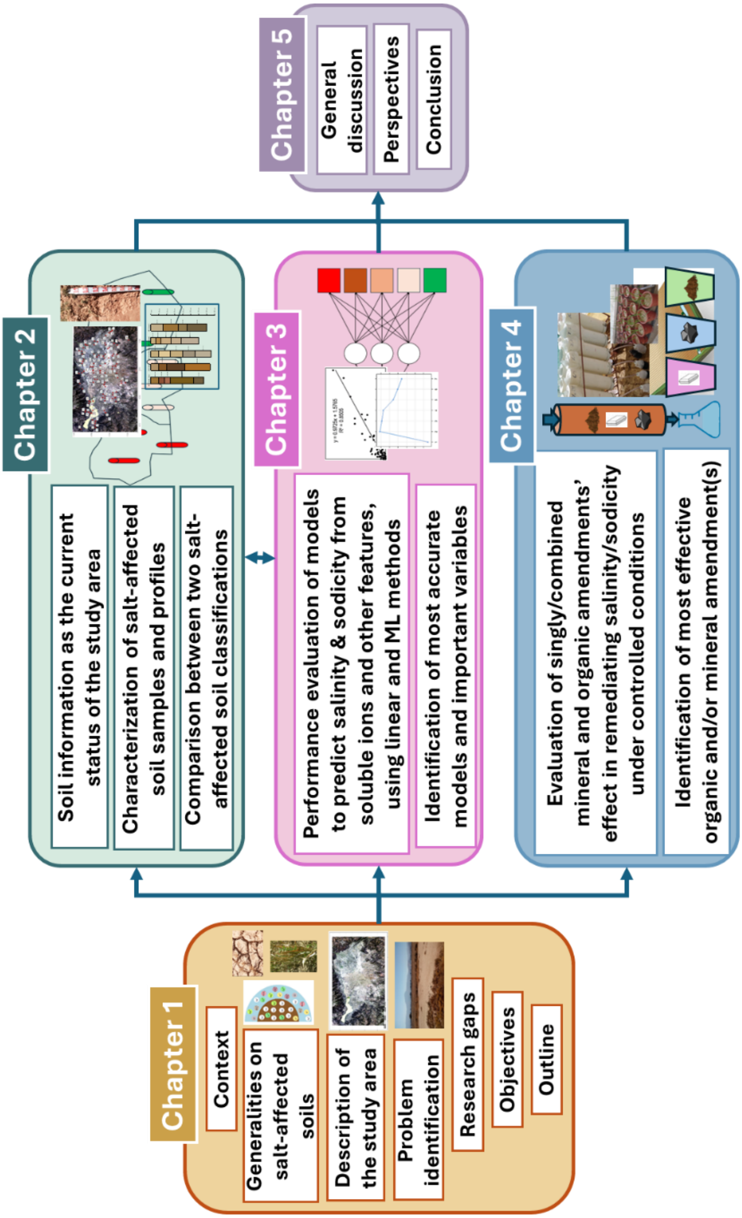


Figure 1.10 Graphical illustration of the structure of the thesis in function to the research objectives and pathway.

Chapter 2

Characterization and classification of salt-affected soils

1. Introduction

A comprehensive knowledge of the soil characteristics in the study area is needed for achieving an effective management and rehabilitation of salt-affected soils besides a better understanding and awareness of driven factors for salinization and sodication processes in the study area. Therefore, a systematic soil survey to obtain a soil information database was carried out to assess soil profiles and to classify soil samples from the High Valley of Cochabamba.

The widely used salt-affected soil classification from the US Salinity Lab (USSL) based on the threshold values of soil EC_e of 4 dS m^{-1}, ESP of 15%, and pH of 8.5, generates the saline, saline-sodic, and sodic soil classes (Figure 2.1a). Chhabra (2004) stated that soil classified as saline-sodic (by the USSL system) comprises, in turn, the alkali soils developed in situ (pH >8.5, ESP >15 and EC_e >4 dS m^{-1}) as well as soils formed due to high residual sodium carbonate (>2.5 mol m^{-3}) irrigation waters (pH >8.5, SAR >13 and EC_e >4 dS m^{-1}), and those formed due to shallow saline water table high in SAR (pH of 7 to 8.5, SAR >13 and EC_e >4 dS m^{-1}); however, the saline-sodic category generates some difficulties for soil management since pH can be not necessarily above the threshold value of 8.5 and because some saline-sodic soils with a high SAR– as saline soils - keep their physical structure and infiltration leading to a simultaneous decrease of EC_e and SAR when are leached of excess soluble salts. This confusion also influences the requirements of leaching to remove soluble salts and/or amendments to lower ESP. In this regard, Chhabra (2004) - based on Szabolcs (1989) - proposed a classification (named Alternative in Figure 2.1b) which generates the saline and alkali categories by considering – besides soil ECe, ESP and pH – the nature of soluble salts, then overcoming the ambiguity of the saline-sodic USSL' category; consequently, if soils classified as saline-sodic by the USSL criterion have the ion ratio of either $(2CO_3^{2-} + HCO_3^-)/(Cl^- + 2SO_4^{2-})$ and/or $Na^+/(Cl^- + 2SO_4^{2-})$ in mol m^{-3} > 1, should be reclaimed as alkali (natric) soils by applying amendments to lower their ESP followed by leaching, since when are leached to decrease excess soluble salts, their pH and ESP increase, causing a decrease in infiltration rate; while if soils have both ratios < 1, then, irrespective of their pH and SAR, should be treated as saline (salic) soils through leaching and/or lowering of the water table to decrease both SAR and EC_e simultaneously.

The term 'alkali' or 'alkaline' is usually a synonym of 'sodic', generating a certain degree of confusion since sodicity is more related to excess sodium and alkalinity to the dominance of alkaline salts. Furthermore, neutral and alkali salts determine the distinction between sodicity and alkalinity, so alkali soils normally have an excess of exchangeable Na+ and carbonates besides a pH above 8 (Gupta and Abrol, 1990). Alkali soils from arid and semiarid lands contain free $CaCO_3$ with concentrations of soluble Na^+ and CO_3^{2-} + HCO^{3-}as the dominant ions, besides a pH above 8 and very low Ca^{2+} and Mg^{2+}; moreover, soil organic matter gets dissolved and forms black-alkali soils due to organic–clay coatings on soil aggregates and on the surface caused by the high soil pH increased linearly with an increase in ESP (Chhabra 2004; Gupta and Abrol, 1990). Additionally, Abrol et al. (1980) reported that alkali soils contain soluble salts capable of alkaline hydrolysis which are predominately CO_3^{2-} and HCO^{3-} of Na^+ leading to an increase in SAR due to precipitation of soluble Ca^{2+} as $CaCO_3$, and also observed that saline soils contain neutral soluble salts of Cl^- and $SO4^{2-}$ of Na^+, Ca^{2+}, and Mg^{2+}; and also that – instead of EC_e – nature of the soluble salts would be a more reliable indicator for differentiating alkali from saline soils.

This component of the study aims to generate soil information comprising the following objectives: Database soil information as a baseline for this study and context of the current state of soils in the High Valley, characterization and classification of salt-affected soil samples and profiles, looking for variations in the levels of salinity and sodicity across different locations in the High Valley, besides a comparison between two salt-affected soil classification systems about the differences which could impact on the subsequent management.

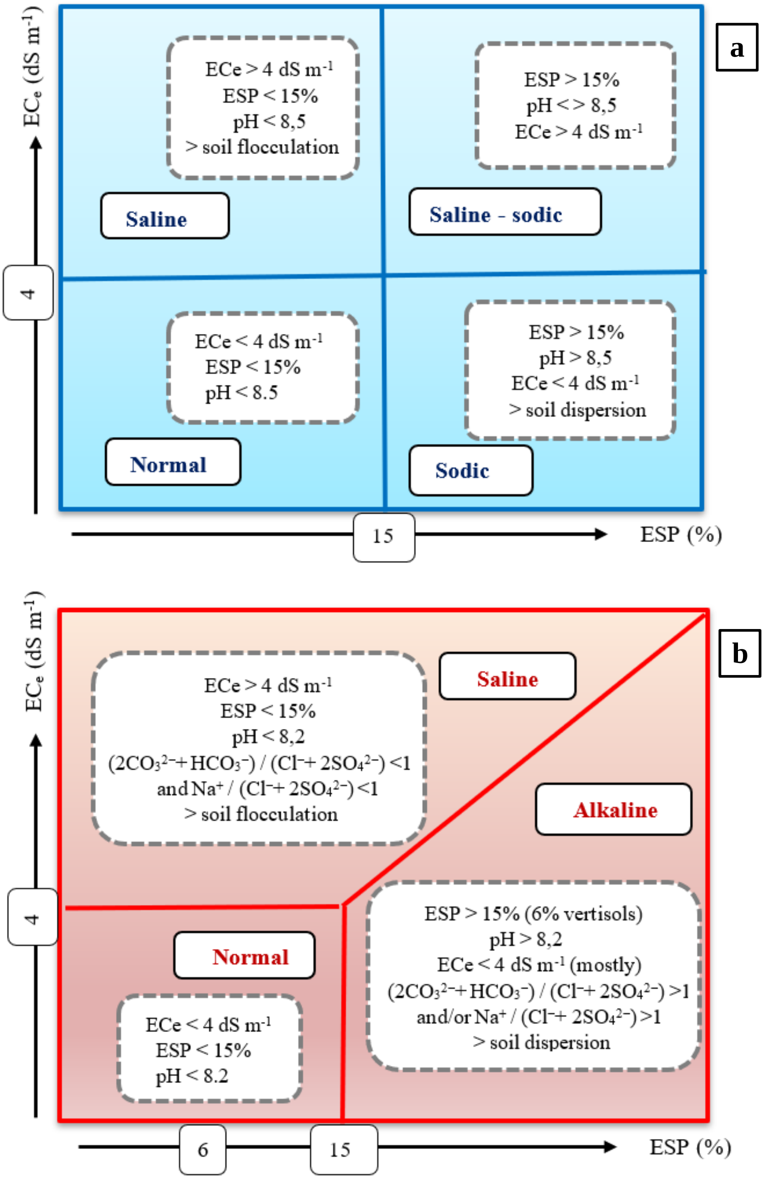


Figure 2.1 Graphical illustration of the USSL (Richards et al., 1954) (a), and the Alternative (Chhabra, 2004; Szabolcs, 1989) (b) salt-affected soil classification systems.

2. Methodology

The study area was the High Valley of Cochabamba - Bolivia, located between the boundaries of latitude –17°29′47.7″ to –17°39′48.6″ and longitude of –66°5′16.8″ to –65°45′13.0″, at an elevation of ~2750 m. The soil survey including sampling and description of profiles was performed in May 2017 at the end of the autumn season, under the framework of the study by Weber (2018).

Eight soil profiles (five salt-affected and three non-salt-affected) were assessed, and their dimensions were approximately one, two and 1.5-2.0 m in width, length and depth, respectively. The spatial location of the profiles (Appendix 2.1) was defined to somehow encompass the geomorphic landforms/soils (Appendix 1.3), municipalities and land uses. A composite sample made up of three subsamples was taken from each horizon, and turned into only one lab measurement due to technical and cost restrictions; in this regard, it can be noted the limitation in terms of reliability of the soil properties information, description and classification. For the soil sampling, 135 valid samples were collected at a depth of ~25 cm as composite soil samples from five cores taken at a square surface of 3 x 3 m. The determination of the number of samples was based on the formula suggested by Legros (1996) and following the recommendation by Hengl (2007), a systematic random sampling method was applied. The spatial location of the soil samples is shown in Appendix 2.2.

The soil pH, EC_e and the composition of soluble ions were measured in the extracted solution following the standard procedures of Richards et al. (1954) including the use of atomic absorption spectrometry (AAS) for cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), titration and H_2SO_4 0.01N for carbonates (CO_3^{2-}) and bicarbonates (HCO^{3-}), titration and $AgNO_3$ 0.005N for chlorides(Cl^-), and the turbidimetric method and $BaCl_2$ for sulphates (SO_4^{2-}), at the Soil-Water Lab, Faculty of Agricultural and Livestock Sciences – 'Universidad Mayor de San Simón' (Bolivia). The exchangeable cations were determined through a derived ISO 22171 method and AAS at the 'Station Provinciale d'Analyses Agricoles' Lab (Belgium) considering the remark of So et al. (2006) for overcoming the overestimation caused by the extractable cations. The sodium adsorption ratio (SAR) was calculated by using the formula (Eq. 1) proposed by Richards et al. (1954). The soil ESP was determined through the percentage ratio of Na^+ to the sum of cations (Eq. 2) instead of the cation exchange capacity (CEC), following the recommendation of Qadir et al. (2007) and Sumner et al. (1998). The total organic carbon (TOC) was measured through the Walkley-Black method based on ISO 14235, the bioavailable elements using the Lakanen and Erviö method (AA and EDTA at a pH of 4.65) and AAS for Ca^{2+}, Mg^{2+} and K^+; colourimetry for P, and soil CEC by a modified Metson method at a pH of 7. The soil texture was obtained following the standard method NF X 31-107. Some morphological properties of soil profiles' horizons and soil surface were described by using a field form (summarized in Appendix 2.3) based on the Guidelines for soil description of FAO (2006). Finally, the profiles were classified in terms of taxonomy based on the WRB for soil resources

(IUSS Working Group WRB. 2022) and Keys to Soil Taxonomy (Soil Survey Staff, 2022).

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad (Equation\ 1)$$

Where cations are expressed as a concentration in $mmol_c\ L^{-1}$

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

Where cations are expressed as a concentration in $cmol_c\ kg^{-1}$.

For comparison purposes, the salt-affected soil samples were classified by applying the USSL (Richards et al., 1954) and an alternative (Chhabra, 2004; Szabolcs, 1989) classification systems, which indicators and threshold values are listed in Figure 2.1. To avoid unclassified observations, a margin of +/- 10% was fixed for the threshold values of the Alternative classification. To generate the salinity and sodicity classifications, the saline-sodic class from the USSL system was reclassified as a saline or sodic class to be compared to the categories from the Alternative classification. Spatial distributions and predictions through some interpolation techniques were performed. Finally, the TOC and salt-affected soil categories were quantified on the soil texture triangle from the USDA system. The R software v.4.1.3 (R Core Team, 2013) was used for statistical and geostatistical analysis together with some R packages such as *soilassesment* (Omuto, 2020), *soiltexture* (Moeys, 2018), *aqp* (Beaudette et al., 2013), *raster* (Hijmans, 2023), *geoR* (Ribeiro et al., 2024), *sf* (Pebesma, 2018), *ggmap* (Kahle and Wickham, 2013), *tmap* (Tennekes, 2018), *rgdal* (Bivand et al., 2023), *rayshader* (Morgan-Wall T, 2024), among others for data preparation, analysis and visualization.

3. Characterization of salt-affected soils

3.1. General description

In terms of geomorphic characterization of this area, most of the salt-affected areas are in the landscape of a valley with a relief type consisting of lagunary depressions, alluvio-lagunary/lagunary facies, a landform consisting of lagunary flats, and soil associations consisting of Ustalfic Haplargids/Ustochreptic Camborthids and Typic Salorthids/Natric Camborthids (Metternicht and Zinck, 1997). Some relevant geographical and physiographical features for the salt-affected (SP 1 – SP 5) and non-salt-affected (SP 6, SP7, SP 8) soil profiles are listed in Table 2.1.

Table 2.1 Relevant geographical and physiographical characteristics of the soil profiles.

SP	Location	Longitude	Latitude	Elevation	Slope	Geomorphology*
1	Santa Ana	-65.861651	-17.544048	2714	<1%	The old cone of the boundary between the central and distal part
2	Cliza	-65.899188	-17.607761	2717	2%	Lagunary depression low (limit with the distal part of a glacis)
3	San Benito	-65.907701	-17.528609	2708	<1%	Glacis (distal part)
4	Aramasí	-65.859688	-17.597974	2713	<1%	Playa
5	Arani	-65.805878	-17.588081	2720	<1%	Lagunary depression low (limit with the central part of a glacis)
6	Tarata	-66.007495	-17.608299	2743	<2%	Glacis (distal part)
7	Punata	-65.824014	-17.526634	2758	5%	Active dejection cone
8	Cuchumuela	-65.795681	-17.652989	2874	8%	Glacis (proximal part)

* Based on Metternicht and Zinck (1997)

3.2. *Chemical properties*

Salinity/sodicity variables and exchangeable cations of the five salt-affected soil profiles are listed in Table 2.2, and the same information is shown in Appendix 2.4a for the non-salt-affected soil profiles.

Table 2.2 Soil chemical properties: salinity/sodicity variables and exchangeable cations for each horizon of the salt-affected soil profiles.

Soil profile	Horizon	Exchangeable cations ($cmol_c\ kg^{-1}$)				Soil salinity/sodicity variables			
		Na^+	K^+	Ca^{2+}	Mg^{2+}	pH	EC_e $dS\ m^{-1}$	ESP* %	Class †
SP 1 Santa Ana	Ap	9.45	0.23	5.75	0.63	9.56	28.52	58.8	Saline-sodic
	A2	5.13	0.16	5.60	0.72	9.80	21.96	44.2	Saline-sodic
	B	10.78	0.13	4.95	0.91	9.95	18.23	64.3	Saline-sodic
	C1	5.69	0.07	3.50	0.56	10.09	13.51	57.9	Saline-sodic
	2C2	4.99	0.09	2.30	0.44	9.90	7.98	63.8	Saline-sodic
SP 2 Cliza	A	14.46	2.01	13.85	1.00	7.87	3.44	23.6	Sodic
	Bt1	7.70	1.61	3.25	0.59	9.43	9.41	46.2	Saline-sodic
	Bt2	9.50	0.87	5.80	1.09	10.03	9.66	58.5	Saline-sodic
	C	3.22	0.10	4.45	0.98	9.81	13.20	55.0	Saline-sodic
SP 3 San Benito	A	8.15	0.18	6.35	0.51	7.71	21.81	36.8	Saline-sodic
	AB	13.29	0.60	10.50	1.79	9.80	10.07	56.9	Saline-sodic
	C	13.15	0.59	12.35	1.83	9.82	7.45	53.6	Saline-sodic
	2C	27.90	1.55	7.45	0.41	9.64	8.86	50.8	Saline-sodic
	2C2	19.28	0.83	6.60	0.38	9.89	10.19	47.1	Saline-sodic
SP 4 Aramasí	A	25.93	0.80	8.75	0.44	9.68	69.28	74.8	Saline-sodic
	A2	21.77	1.13	12.00	1.54	10.10	48.79	71.2	Saline-sodic
	C	0.64	2.50	11.15	4.06	10.00	26.76	77.0	Saline-sodic
	C1	0.92	0.27	4.85	2.19	10.00	27.83	72.2	Saline-sodic
	2C2	0.63	0.14	7.90	2.30	9.50	13.18	59.7	Saline-sodic
SP 5 Arani	Ap	0.40	1.27	29.70	2.00	7.28	1.45	3.5	Normal
	Bw	0.17	0.98	28.20	2.00	7.50	0.94	11.2	Normal
	C	0.07	0.50	35.35	2.22	7.56	2.91	5.7	Normal
	C2	0.05	0.40	25.75	2.03	7.98	5.50	49.0	Saline-sodic

* Corrected values of exchangeable sodium percentage, considering the difference between extractable and exchangeable cations (So et al., 2006).

† Salt-affected soil classes according to the US Salinity Lab classification (Richards et al., 1954)

Most of the profiles' horizons are saline-sodic (according to the USSL classification) with high levels of soil ESP, ECe and pH, except that of Arani (SP 5). The distribution of soil ESP, EC_e and pH levels (Table 2.2) in each salt-affected soil profile is graphically shown in Figure 2.2. The soil profiles of Santa Ana (SP 1), Aramasi (SP 4) and San Benito (SP 3) showed high levels of soil ESP and pH along the depth of their horizons and high soil EC_e in their topsoil horizons.

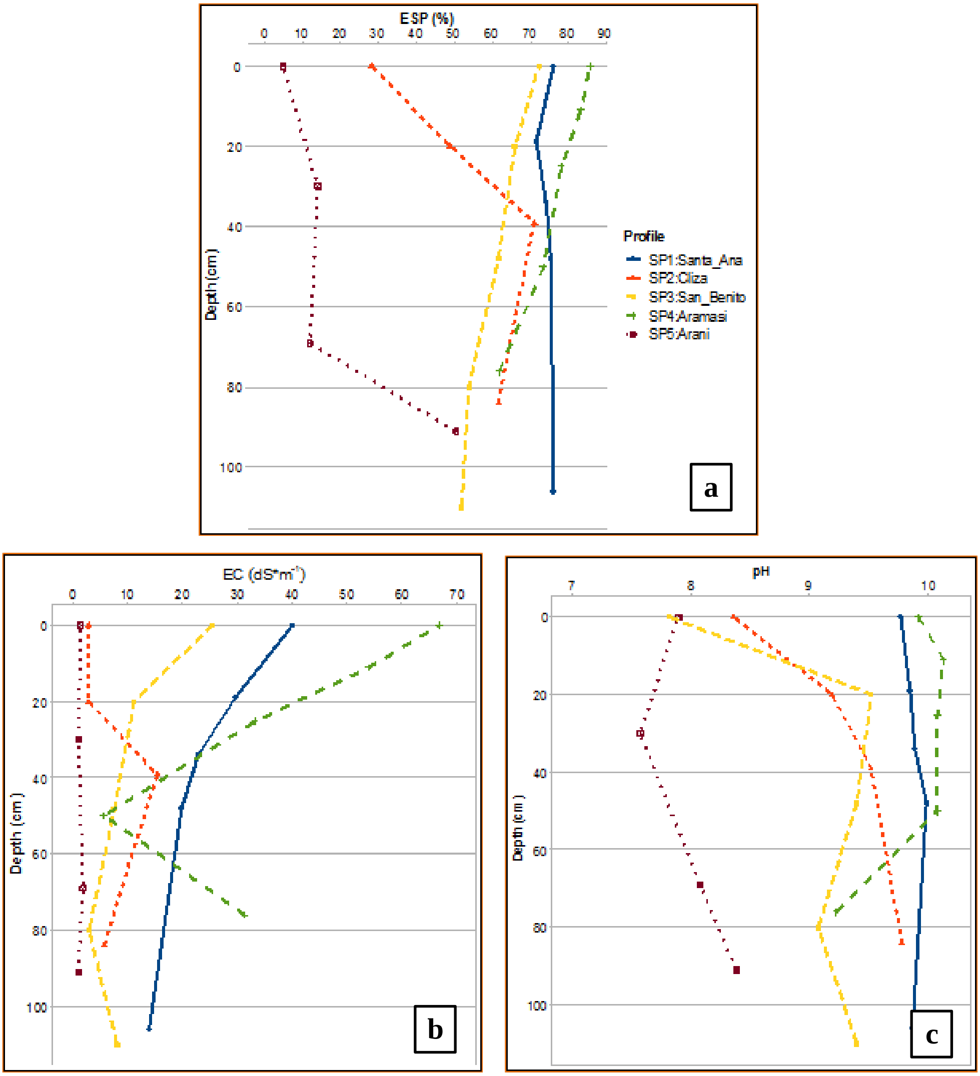


Figure 2.2 Variation of soil ESP (a), EC_e (b), and pH (c) in the salt-affected soil profiles.

The major soluble salt ions and the sodium adsorption ratio (SAR) by horizons for the salt-affected soil profiles are listed in Table 2.3, and the same information for the non-salt-affected soil profiles are listed in Appendix 2.4b. The upper horizons of the Santa Ana (SP 1) and Aramasí (SP 4) profiles are saturated with Na^+ in the soil solution. Additionally, a graphical illustration of the distribution of soluble cations and soluble anions along the depth in the salt-affected soil profiles is shown in Appendix 2.5.

Variables related to plant nutrition are listed in Table 2.4 and the same information for the non-salt-affected soil profiles is listed in Appendix 2.4c. Overall, the nutrient status is variable, and the total organic carbon (TOC) indicates a low soil organic matter (SOM) content. Soil profiles of Santa Ana (SP 1) and Arani (SP 5) are located within agricultural lands. Additionally, an illustration of the cation exchange capacity (CEC) values by horizons is shown in Appendix 2.6b.

3.3. Physical properties

Soil physical properties, namely, texture, colour and bulk density for each horizon of the salt-affected soil profiles are listed in Table 2.5. Most soil profiles' horizons are silty-loam and/or silty-clay-loam. The Munsell colour values for each horizon of the salt-affected soil profiles (Table 2.5) are graphically shown in the morphological description of each soil profile (Figures 2.3 – 2.7). Soil physical properties of the non-salt-affected soil profiles are listed in Appendix 2.4d.

3.4. Morphological description

At the time of the soil profile assessment (May 2017) was the end of the autumn season during the drought period, the days were sunny with no clouds and partially cloudy. Some relevant morphological characteristics are described for each salt-affected soil profile in sections 3.4.1 to 3.4.5.

Table 2.3 Soil chemical properties: soluble ions and sodium adsorption ratio for each horizon of the salt-affected soil profiles.

Soil profile	Horizon	Soluble Ions ($cmol_c\ L^{-1}$)								SAR*
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	
SP 1 Santa Ana	Ap	3.39	0.01	0.00	0.01	1.85	0.71	0.40	0.60	450.9
	A2	3.26	0.01	0.00	0.01	0.95	0.55	0.52	0.30	409.8
	B	1.87	0.00	0.00	0.01	0.63	0.68	0.61	0.25	256.5
	C1	2.08	0.01	0.00	0.01	0.53	0.37	0.69	0.34	286.5
	2C2	1.17	0.01	0.00	0.01	0.28	0.38	0.39	0.27	178.4
SP 2 Cliza	A	0.24	0.01	0.00	0.01	0.15	0.05	0.00	0.10	32.4
	Bt1	0.47	0.02	0.00	0.01	0.15	0.50	0.15	0.04	64.1
	Bt2	1.65	0.02	0.00	0.01	0.35	0.18	1.01	0.20	237.0
	C	0.87	0.02	0.00	0.00	0.10	1.17	0.40	0.20	146.6
SP 3 San Benito	A	3.27	0.00	0.14	0.09	0.65	2.31	0.02	0.08	96.4
	AB	1.30	0.01	0.02	0.01	0.25	1.11	0.00	0.08	107.3
	C	0.93	0.02	0.01	0.01	0.15	0.85	0.00	0.06	85.3
	2C	0.52	0.01	0.00	0.00	0.05	0.97	0.00	0.18	121.6
	2C2	0.83	0.00	0.00	0.00	0.10	0.30	0.39	0.10	170.5
SP 4 Aramasí	A	8.70	0.04	0.02	0.01	0.90	0.40	3.00	0.00	814.4
	A2	5.65	0.02	0.00	0.01	2.50	0.30	4.00	0.15	913.8
	C	0.39	0.02	0.00	0.01	2.00	0.24	0.89	0.22	64.3
	C1	0.54	0.01	0.00	0.00	2.05	0.14	1.34	0.07	93.9
	2C2	0.55	0.01	0.03	0.01	1.00	0.02	0.20	0.20	41.9
SP 5 Arani	Ap	0.08	0.02	0.05	0.01	0.08	0.02	0.00	0.07	4.6
	Bw	0.08	0.01	0.02	0.01	0.03	0.05	0.00	0.05	6.3
	C	0.23	0.01	0.00	0.01	0.10	0.12	0.00	0.08	36.3
	C2	0.16	0.01	0.02	0.00	0.08	0.05	0.00	0.03	15.6

* Sodium adsorption ratio was calculated through the formula obtained by Richards et al. (1954).

Table 2.4 Soil chemical properties: available nutrients, organic carbon and CEC for each horizon of the salt-affected soil profiles.

Soil profile)	Horizon	CEC * $cmol_c\ kg^{-}$	TOC %	Nutrient bioavailability ($g\ kg^{-1}$)			
				P	K	Ca	Mg
SP 1 Santa Ana	Ap	9.3	0.28	0.06	0.08	1.66	0.12
	A2	9.0	0.29	0.03	0.06	1.61	0.13
	B	9.3	0.18	0.01	0.05	2.06	0.19
	C1	6.4	0.09	0.01	0.03	1.03	0.10
	2C2	3.2	0.04	0.04	0.03	1.04	0.08
SP 2 Cliza	A	8.0	0.45	0.02	0.18	2.28	0.12
	Bt1	22.4	0.31	0.30	0.65	5.20	0.19
	Bt2	13.8	0.41	0.14	0.53	1.17	0.11
	C	8.6	0.08	0.06	0.30	1.98	0.20
SP 3 San Benito	A	10.60	0.54	0.02	0.04	1.10	0.14
	AB	12.80	0.33	0.05	0.06	2.24	0.14
	C	10.90	0.15	0.10	0.07	2.05	0.10
	2C	18.60	0.34	0.11	0.20	9.25	0.55
	2C2	15.40	0.21	0.11	0.20	7.02	0.48
SP 4 Aramasí	A	19.20	0.54	0.13	0.50	3.65	0.13
	A2	13.10	0.26	0.13	0.27	3.05	0.10
	C	10.80	0.19	0.09	0.18	1.76	0.06
	C1	16.40	0.25	0.15	0.26	4.14	0.10
	2C2	21.60	0.24	0.19	0.31	8.07	0.43
SP 5 Arani	Ap	15.00	1.24	0.58	0.82	3.90	0.63
	Bw	8.30	0.29	0.02	0.11	1.17	0.29
	C	9.30	0.16	0.03	0.06	2.92	0.34
	C2	12.80	0.11	0.08	0.09	3.91	0.42

* Some differences between the CEC values and the sum of exchangeable cations (Table 2.2) were mainly due to the inherent error of the measurement.

Table 2.5 Soil physical properties for each horizon of the salt-affected soil profiles.

Soil profile	Horizon	Colour	Depth (cm)	Bulk density (g cm^{-3})	Soil fractions – texture			
					Clay %	Silt %	Sand %	Textural class *
SP 1 Santa Ana	Ap	10YR 5/6	0 -19	1.24	19.3	54.9	25.8	SiLo
	A2	2.5YR 4/6	19 - 34	1.40	20.3	53.3	26.3	SiLo
	B	2.5YR 5/6	34 - 48	1.38	23.6	51.4	25.0	SiLo
	C1	2.5Y 4/6	48 - 106	1.56	15.4	47.8	36.9	Lo
	2C2	2.5Y 4/3	106 - 132	1.47	11.5	24.3	64.3	SaLo
SP 2 Cliza	A	10YR 6/4	0 -20	1.38	18.3	40.4	41.3	Lo
	Bt1	7.5 YR 4/6	20 - 39	1.56	41.5	46.2	12.4	SiCl
	Bt2	7.5YR 3/4	39 - 84	1.40	37.8	46.6	15.7	SiClLo
	C	7.5YR 5/8	84 - 148+	1.39	23.7	41.8	34.5	Lo
SP 3 San Benito	A	2.5Y 7/4	0 -20	1.45	22.2	53.7	24.1	SiLo
	AB	2.5Y 8/4	20 - 48	1.42	27.7	59.2	13.1	SiClLo
	C	2.5Y 7/4	48 - 80	1.50	24.7	57.8	17.5	SiLo
	2C	2.5Y 6/2	80 - 110	1.51	39.8	54.4	5.8	SiCl
	2C2	2.5Y 7/2	110 - 150+	1.60	37.2	61.1	1.6	SiClLo
SP 4 Aramasí	A	2.5Y 7/4	0 -11	1.61	33.4	63.8	2.8	SiClLo
	A2	10YR 6/6	11 -25	1.54	25.2	70.4	4.5	SiLo
	C	10YR 7/4	25 - 50	1.32	18.6	74.9	6.6	SiLo
	C1	10YR 7/3	50 - 76	1.53	33.0	62.2	4.8	SiClLo
	2C2	10YR 7/2	76 - 120+	1.61	53.6	37.7	8.8	Cl
SP 5 Arani	Ap	2.5Y 7/3	0 -30	1.32	28.5	59.7	11.8	SiClLo
	Bw	10YR 5/6	30 - 69	1.36	20.0	46.0	34.0	Lo
	C	2.5Y 5/4	69 - 91	1.44	22.1	45.1	32.9	Lo
	C2	2.5Y 4/3	91 – 140+	1.4	27.4	46.9	25.7	Lo

* Determination of textural classes through the USDA system.

3.4.1. Soil profile in Santa Ana (SP 1)

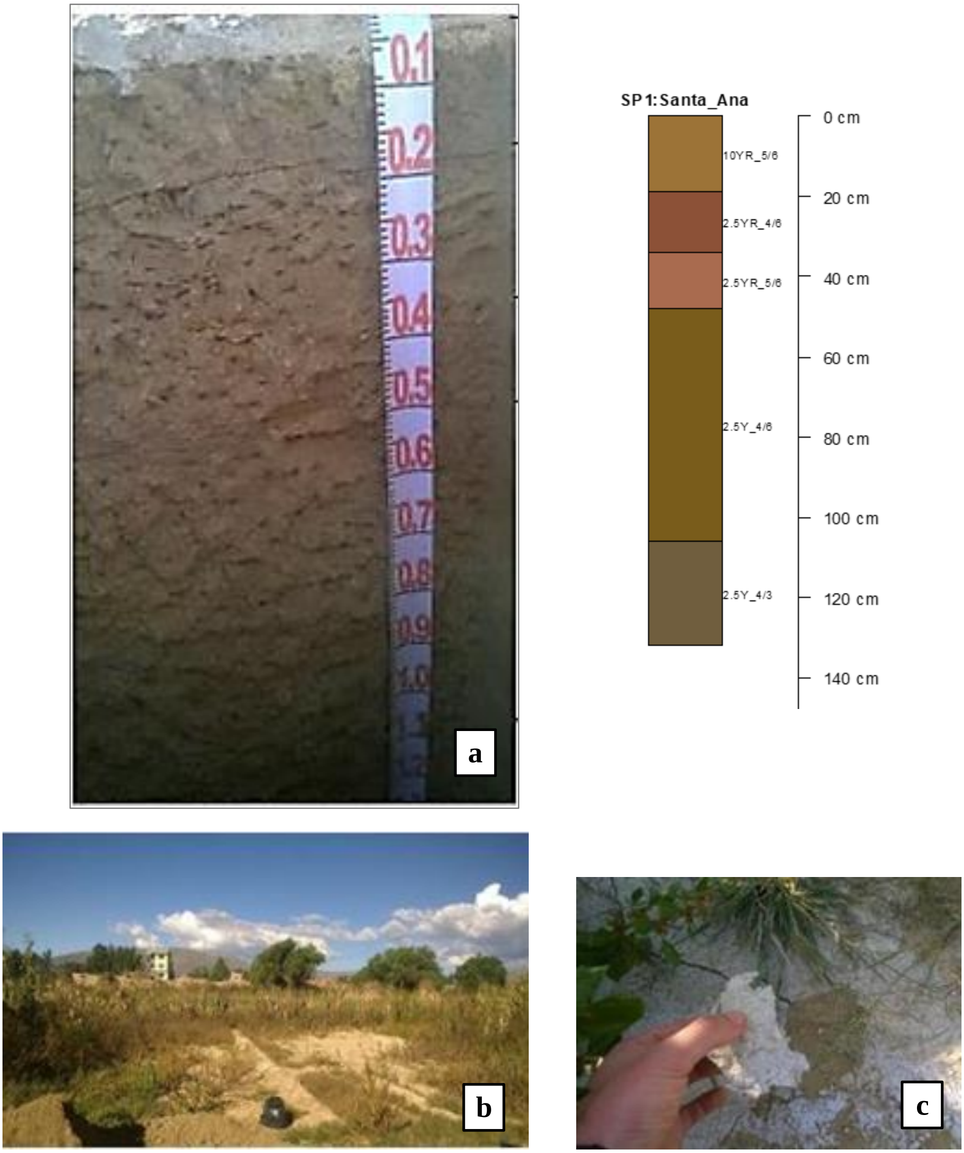


Figure 2.3 Soil profile in Santa Ana (a), its landscape (b) and surface salt crust (c)

Table 2.6 Description of the soil profile in Santa Ana (SP1)

Horizon	Depth	Colour	Main characteristics
Ap	0 -19	10YR 5/6	Polyhedral and laminar structure. Salic horizon
A2	19 - 34	2.5YR 4/6	
B	34 - 48	2.5YR 5/6	Slightly humid and massive structure
C1	48 - 106	2.5Y 4/6	Humid, massive structure and soft consistency
2C2	106 - 132	2.5Y 4/3	Salic horizon and oxidation spots at 2 C2 horizon
Surface: Saline efflorescence of thickness < 2 mm covering ~ 40% surface. Gravel covering < 2% surface and thin cracks of wide < 1 cm. Rock outcrops (2 - 5%) and coarse fragments covering 5 - 15% surface. Moderate water erosion. Agricultural land, which is irrigated with temporary flooding and wastewater, for cultivating corn and forage. Presence of halophytes.			
Whole profile: High salinity and sodicity along the profile (Table 2.2). Gravels up to 2% of the soil volume. Reaction to HCl 1M with low effervescence.			

3.4.2. Soil profile in Cliza (SP 2)

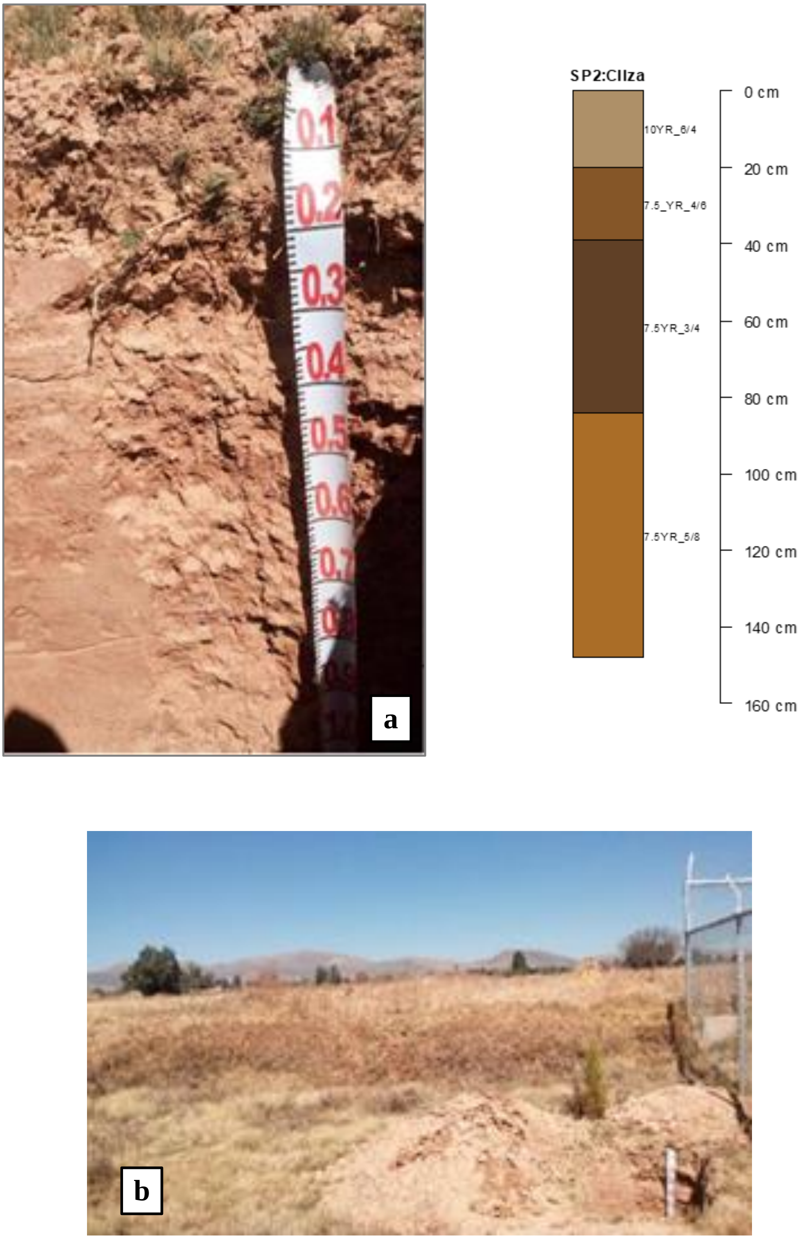


Figure 2.4 Soil profile in Cliza (a) and its landscape (b).

Table 2.7 Description of the soil profile in Cliza (SP 2)

Horizon	Depth	Colour	Main characteristics
A	0 -20	10YR 6/4	Moderately developed blocky structure. Slightly hard consistency and dryness
Bt1 Bt2	20 - 39 39 - 84	7.5 YR 4/6 7.5YR 3/4	Massive structure, hard consistency, with clay coatings and dryness
C	84 - 148+	7.5YR 5/8	Poorly developed, massive structure and very hard consistency
Surface: Gravel covering < 2% surface. Surface cracks of depth < 2 cm, wide 1 - 2 cm and spaced between 0.5 - 2 m. Saline crusts with a thickness < 2 mm covering up to 15% surface. The vegetation is herbaceous and covers over 50% surface.			
Whole profile: High sodicity and moderately high salinity along the profile except A horizon (Table 2.2). Gravel up to 5% of the volume (except A horizon). Roots of diameter 0.5 - 5 mm. Reaction to HCl 1M with a no effervescent foam (except A horizon). Carbonates spots < 15% as dispersed powder (except A horizon).			

3.4.3. Soil profile in San Benito (SP 3)

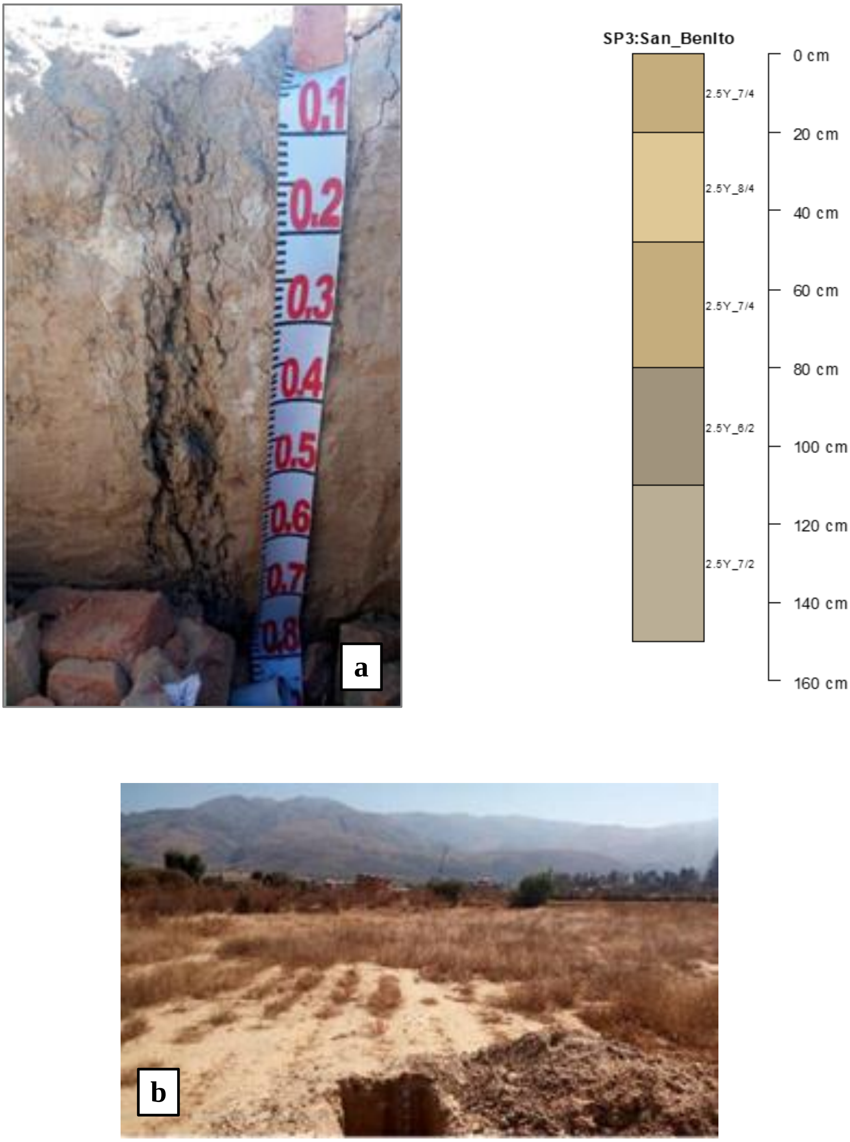


Figure 2.5 Soil profile in San Benito (a) and its landscape (b).

Table 2.8 Description of the soil profile in San Benito (SP 3)

Horizon	Depth	Colour	Main characteristics
A	0 -20	2.5Y 7/4	Slightly hard consistency, granular structure, dryness and presence of some roots of diameter < 0.5 mm
AB	20 - 48	2.5Y 8/4	Moderately hard consistency, dryness, and small concretions
C	48 - 80	2.5Y 7/4	Hard consistency, moderate degree of wetness and blocky structure
2C1	80 - 110	2.5Y 6/2	
2C2	110 - 150+	2.5Y 7/2	

Surface: Herbaceous vegetation and residues of a former cultivation of forage crops. An artisan brick factory is next to the pit. Gravel covering < 2% surface. Thin cracks of wide < 1 cm, deep < 2 cm and spaced between 0.5 - 2 m.

Whole profile: High salinity and sodicity along the profile (Table 2.2). Gravel covering < 5% of soil volume. Reaction to HCl 1M with a no effervescent foam (except A horizon). Carbonates spots < 15% as dispersed powder (except A horizon).

3.4.4. Soil profile in Aramasí (SP 4)

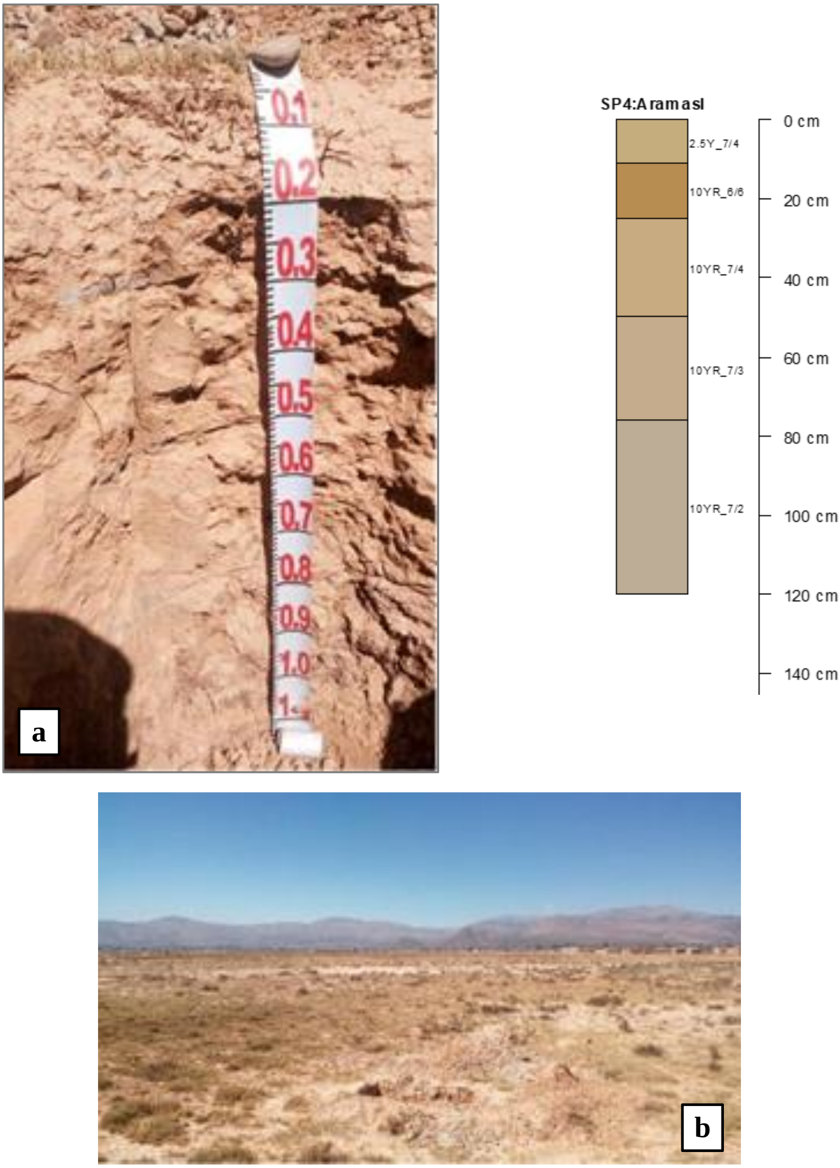


Figure 2.6 Soil profile in Aramasí (a) and its landscape (b).

Table 2.9 Description of the soil profile in Aramasí (SP 4)

Horizon	Depth	Colour	Main characteristics
A	0 -11	2.5Y 7/4	Hard consistency, slightly lamellar structure, marked dryness and roots of diameter < 0.5 mm
A2	11 -25	10YR 6/6	
C	25 - 50	10YR 7/4	Poorly developed, very hard consistency and massive structure, reaction to HCl 1M as foam without effervescence, and small carbonate concretions
C1	50 - 76	10YR 7/3	
2C2	76 - 120+	10YR 7/2	

Surface: Vegetation is sparse with native halophytes and small bushes. Slightly hard crusts of thick < 2 mm. Saline crusts of thick < 2 mm covering up to 10% surface. Gravel covering up to 2% surface. Fine cracks of wide < 1 cm, depth up to 2 cm and spaced < 20 cm.

Whole profile: Very high salinity and sodicity/alkalinity along the profile (Table 2.2). Dryness, low sand content and gravel < 2% of soil volume. Low porosity, high compaction and carbonate concretions (except A and A2 horizons).

3.4.5. Soil profile in Arani (SP 5)

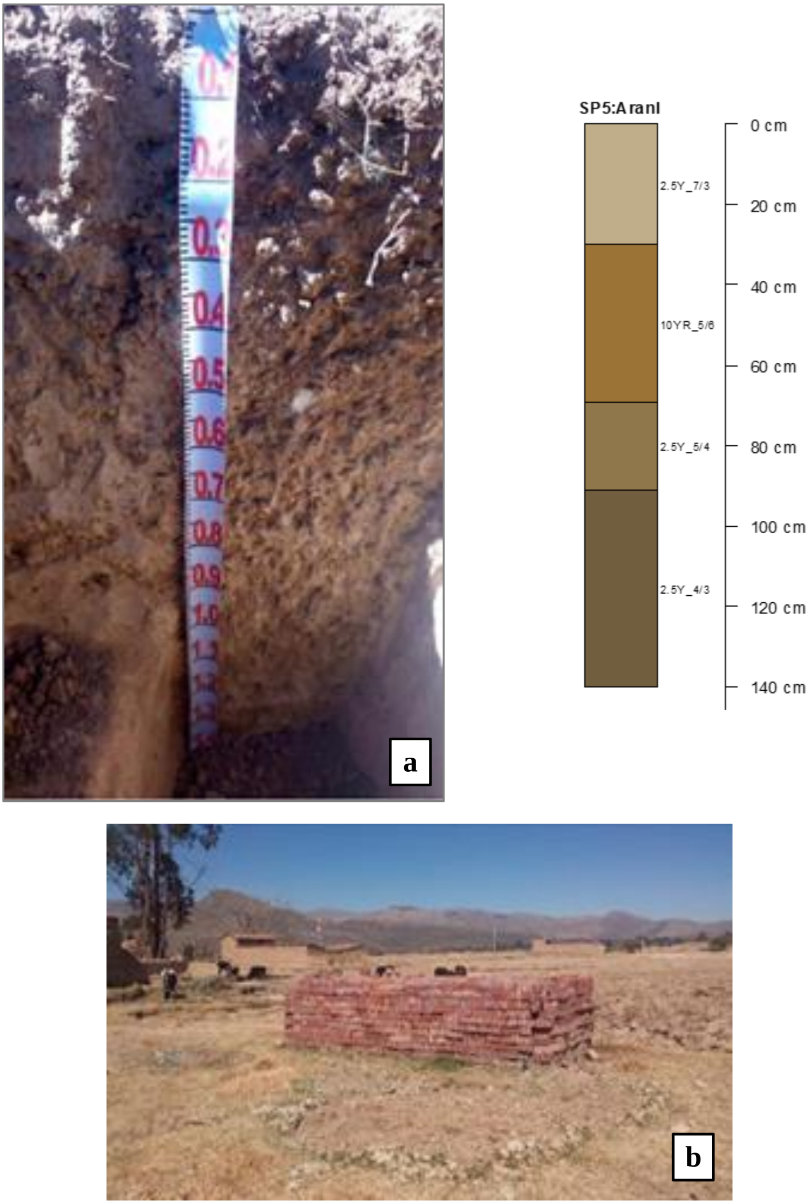


Figure 2.7 Soil profile in Arani (a) and its landscape (b).

Table 2.10 Description of the soil profile in Arani (SP 5)

Horizon	Depth	Colour	Main characteristics
Ap	0 -30	2.5Y 7/3	Polyhedral structure, dryness and roots of diameters between 0.5 and 5 mm
Bw	30 - 69	10YR 5/6	
C1	69 - 91	2.5Y 5/4	Massive structure, wetness and oxidation spots, weak reaction to HCl 1M with no effervescence
C2	91 – 140+	2.5Y 4/3	

Surface: Agricultural land under preparation before ploughing. Gravel covering < 2% surface. Fine cracks of wide < 1 cm, depth < 2 cm and spaced between 2 - 5 meters. Saline efflorescence covers up to 2% surface.

Whole profile: Only the C2 horizon shows slight salinity and high sodicity (Table 2.2). Gravel covering < 2% of soil volume. (except Ap horizon).

3.5. Taxonomic classification

Taxonomic soil classifications of the soil profiles based on the soil's chemical, physical and morphological properties, following the guidelines of the WRB for soil resources (IUSS Working Group WRB. 2022) and the Keys to Soil Taxonomy (Soil Survey Staff, 2022) are listed in Table 2.11 and Table 2.12, respectively.

Table **2.11** Taxonomic classification of the salt-affected soil profiles according to the WRB for soil resources (IUSS Working Group WRB. 2022).

Profile	Location	Classification
1	Santa Ana	Sodic **Solonchak** (Hypersalic, Siltic)
2	Cliza	Salic Sodic **Vertisol** (Calcaric)
3	San Benito	Salic **Solonetz** (Natric, Siltic)
4	Aramasí	Salic **Solonetz** (Hypernatric, Siltic, Protocalcic)
5	Arani	**Cambisol** (Loamic, Aric, Endosodic)
6	Tarata	Fragic Fluvic **Cambisol** (Loamic)
7	Punata	Leptic **Fluvisol** (Fluvic)
8	Cucuchumuela	Calcic **Regosol** (Clayic)

Table **2.12** Taxonomic classification of the salt-affected soil profiles according to the soil taxonomy (Soil Survey Staff, 2022)

Profile	Location	Classification
1	Santa Ana	Typic Natrustalid
2	Cliza	Salic Haplotorrerts
3	San Benito	Typic Natrargids
4	Aramasí	Calcic Natrargids
5	Arani	Haplocambids
6	Tarata	Haplic luvisol
7	Punata	Typic Udifluvents
8	Cucuchumuela	Typic Ustorthents

4. Classification of salt-affected soils

4.1. Salt-affected soil classification

Some descriptive statistics of the soil properties for all the samples used for the classification are listed in Appendix 2.7. The average ionic concentrations are graphically represented in Appendix 2.8. The salinity/sodicity variables (SAR, ESP, Ec_e, pH, ECR and CROSS) as well as the salt-affected soil classes for the soil samples are listed in Appendix 2.9. The distribution of samples by classes according to the USSL classification (Figure 2.8a) comprises non-salt-affected (27.4%), saline (28.1%), saline-sodic (28.1%) and sodic (16.3%) soils, and resulting from the Alternative classification (Figure 2.8b), are non-salt-affected (40%), saline (36.3%) and alkali (23.7%); these frequencies also illustrate the count imbalance generated by the fewer number of sodic/alkali soil samples in the dataset. These frequencies represent the differences between the output counts from both classification systems, due to the ambiguity and consequent redistribution of the USSL's saline-sodic class within the categories of the Alternative method, caused by the differences between both criteria in terms of indicator variables and their threshold values (Figure 2.1). Therefore, because of the confusion generated by the saline-sodic – USSL – category, it is essential to consider the approach from the Alternative classification method to foresee if a saline-sodic soil behaves – in terms of soil/plant affection – as saline or sodic/alkaline, then to be treated through leaching of excess soluble salts and/or by adding amendments to lower the soil ESP.

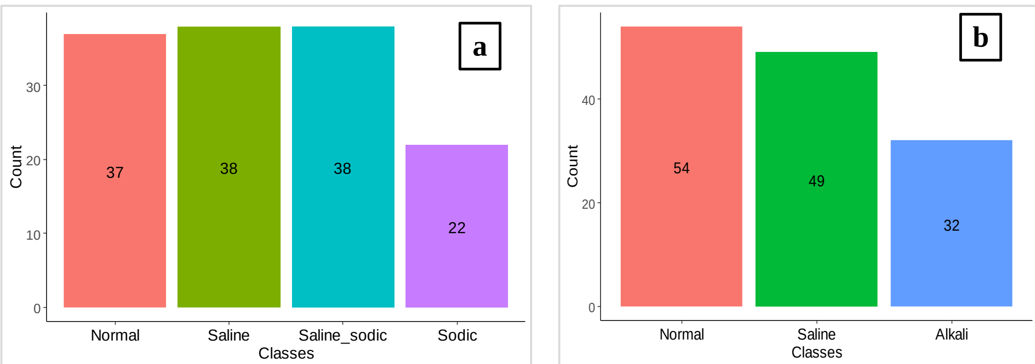
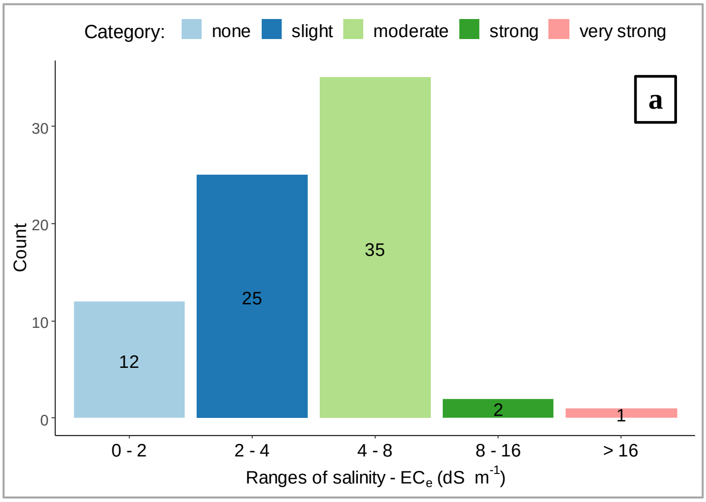


Figure 2.8 Distribution of salt-affected soil classes according to the US Salinity Lab (a) and the Alternative (b) classification systems.

The classification of soil salinity (Figure 2.9) according to the EC_e intervals proposed by Richards et al. (1954) shows evident differences between the counts generated by the USSL and those by the Alternative classification systems, mainly within the intervals of 2 to 4 and 4 to 8 dS m^{-1}, which could lead to misinterpretations in management of salinity. Besides the ambiguity of the saline-sodic – USSL – class, these differences can be explained by the fact that the Alternative system prioritizes the alkali/neutral salt ions ratio ($[2CO_3^{2-} + HCO_3^-] / [Cl^- + 2SO_4^{2-}]$) above the soil EC to classify a soil as saline in contrast to the USSL method which only considers the EC; in this regard, Abrol et al. (1980), affirm that the nature of soluble salts would be a more suitable indicator than EC_e for differentiating alkali from saline soils.



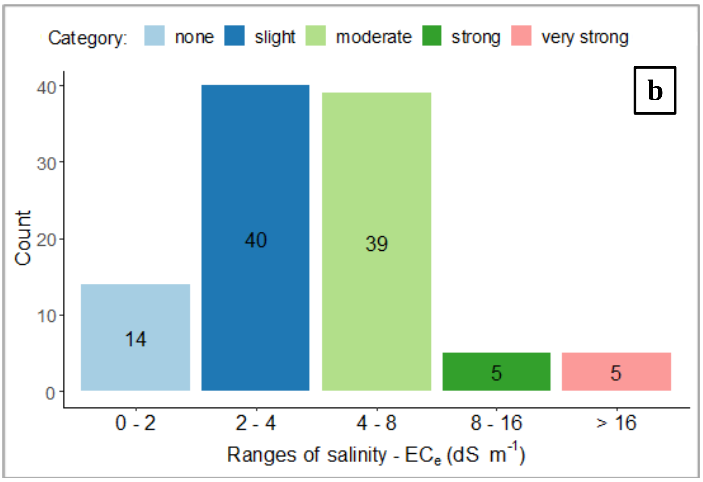


Figure 2.9 Classification of salinity by intervals using the saline soil categories from the USSL (a) and the Alternative (b) classification systems.

The classification of sodicity (Figure 2.10) based on the soil ESP intervals proposed by Abrol et al. (1988) shows lower differences between the counts generated from both systems compared to those for salinity classification (Figure 2.9). As for the classification of salinity, these differences were because the Alternative classification considers the ratio of alkaline salts ($2CO_3^{2-} + HCO_3^-$) and Na^+ to neutral salts (Cl^- +

$2SO_4^{2-}$) along with ESP and pH for classifying soil as alkali in contrast to the USSL system which only uses the ESP and sometimes the pH to categorize a soil as sodic, also leading to the ambiguity of its saline-sodic class.

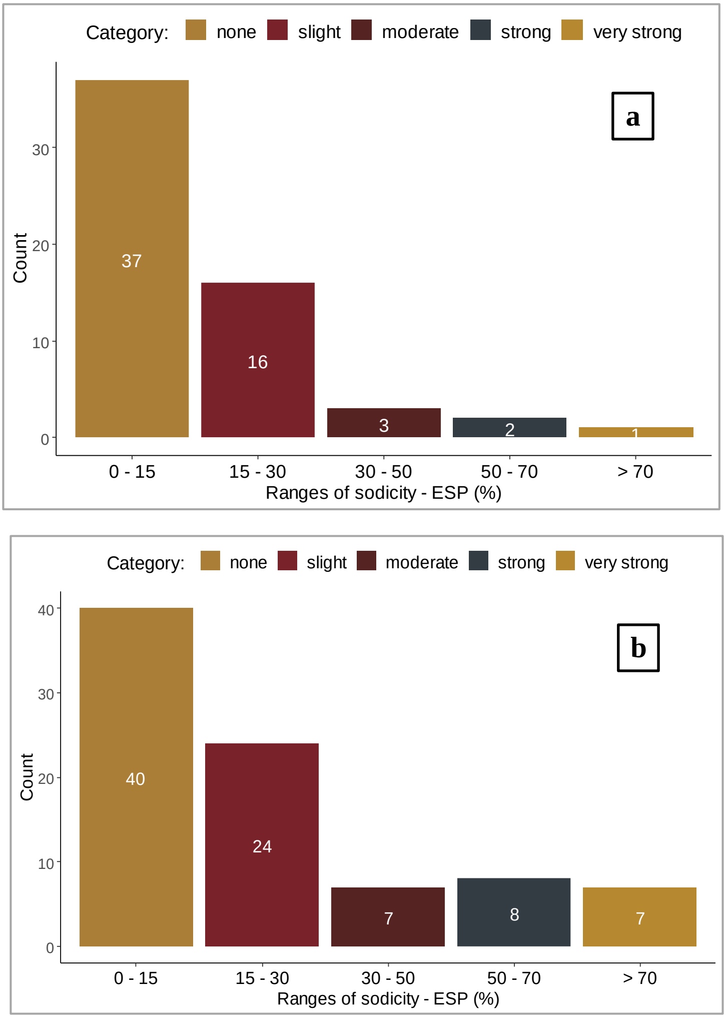
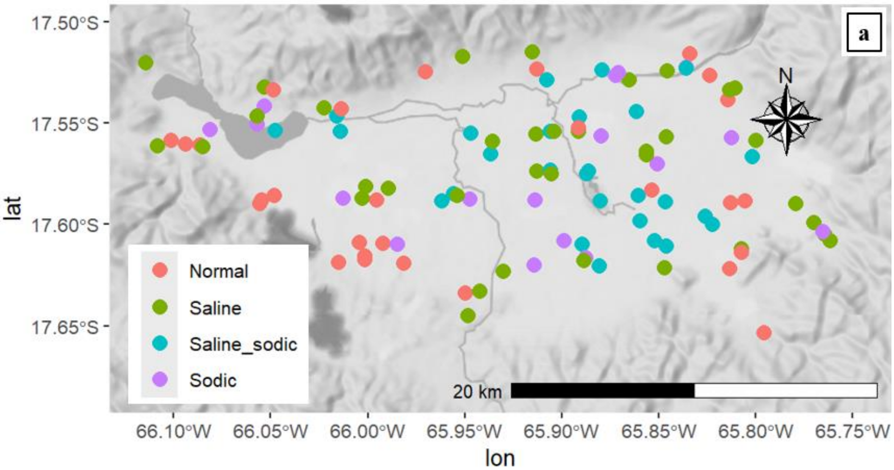


Figure 2.10 Classification of sodicity by intervals using the sodic/alkaline categories from the USSL (a) and the Alternative (b) classification systems.

4.2. Spatial distribution and interpolation

The spatial locations of the salt-affected soil classes generated through the USSL (Figure 2.11a) and the Alternative (Figure 2.11b) classification systems illustrate the previously mentioned differences between both criteria' outputs, which could generate some distortions when mapping salinity and sodicity, potentially affecting the effectiveness of soil management and remediation.



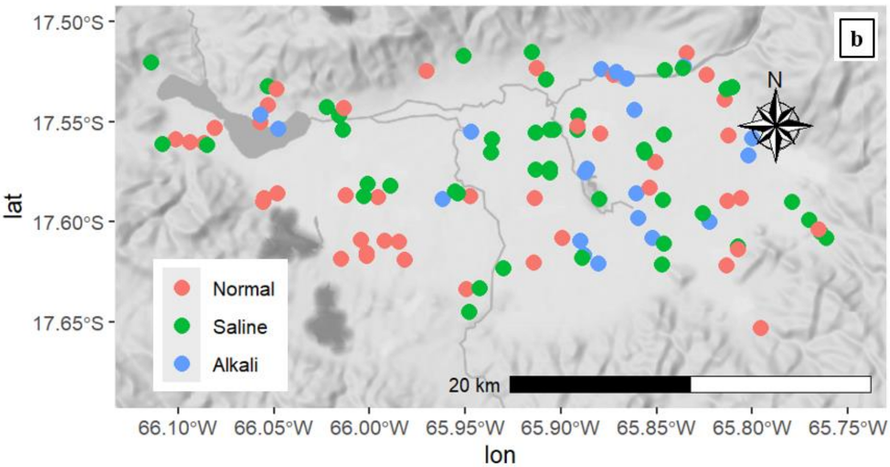


Figure 2.11 Spatial distribution of salt-affected soil categories, classified by the USSL (a) and the Alternative (b) classification systems (Background image: terrain/Stadia-Map, 2023)

The spatial interpolation was not satisfactory (Appendix 2.11) because of the insufficient spatial correlation of soil ESP and EC mainly due to a relatively small number of observations to represent the study area and somehow related to the imbalance caused by the excess non-salt-affected soil samples. Although this insufficiency, a graphical representation of the spatial prediction of salinity as soil EC and sodicity as soil ESP by using the interpolation methods of ordinary kriging, universal kriging, simple kriging, inverse distance weighting (IDW) and nearest neighbour, is shown in Figure 2.12. The cross-validation metrics of *RMSE* and *MAE* of the interpolations show that the kriging methods are relatively better than IDW and nearest-neighbour for both soil ESP and EC (Table 2.12). A complementary spatial interpolation of soil ESP and EC by using ordinary kriging is shown in Appendix 2.13.

Table 2.13 Errors from cross-validation of some interpolation methods.

Variable	Metric	Ordinary kriging	Universal kriging	Simple kriging	IDW	Nearest neighbor
ESP	*RMSE*	19.2	19.4	19.2	21.4	20.6
	MAE	14.2	14.2	14.2	14.3	15.5
EC	*RMSE*	13.8	13.8	13.7	16.1	14.7
	MAE	7.2	7.2	7.1	7.5	7.0

RMSE = Root mean squared error, MAE = mean absolute error IDW = inverse distance weighting, ESP = exchangeable sodium percentage, EC = electrical conductivity

Some spatial predictions were generated under the framework of the survey by Weber (2018), who generated maps of soil salinity/sodicity variables from samplings, such as soil ESP and EC based on the inverse distance weighted interpolation method (Appendix 2.12) since the spatial scales show very abrupt and localized variations leading to a non-satisfactory prediction for kriging. The study of spatial prediction of salinity/alkalinity based on regression kriging in the High Valley by Araujo (2009), showed that saline soils are dominant (57.9%), followed by saline-sodic soils (18.8%) and according to the salinity and sodicity classification, 25.7% and 56.5% are slightly saline and slightly sodic, respectively. Metternicht (1996) combined remote sensing data and field-measured observations at a multi-scale level to estimate the intensity, rate and spatial distribution of salt-affected soils in the High Valley as well as to assess a synergistic approach for mapping and monitoring land degradation, then concluded that detailed discrimination of type and intensity of the degradation processes requires increased synergy among remotely-sensed, field and lab data, especially in salinity/alkalinity studies.

4.3. Soil texture classification

Textural classes for all the observations grouped by salt-affected soil – USSL – classes for the soil EC_e and ESP were placed on the USDA textural triangle (Figure 2.13), which also show the ambiguity of the saline-sodic class with high values of soil ESP and EC; additionally, a similar illustration for the Alternative classification is shown in Appendix 214. It can be observed that most samples belong to the loam, silty-loam, clay-loam and silty-clay-loam textural classes.

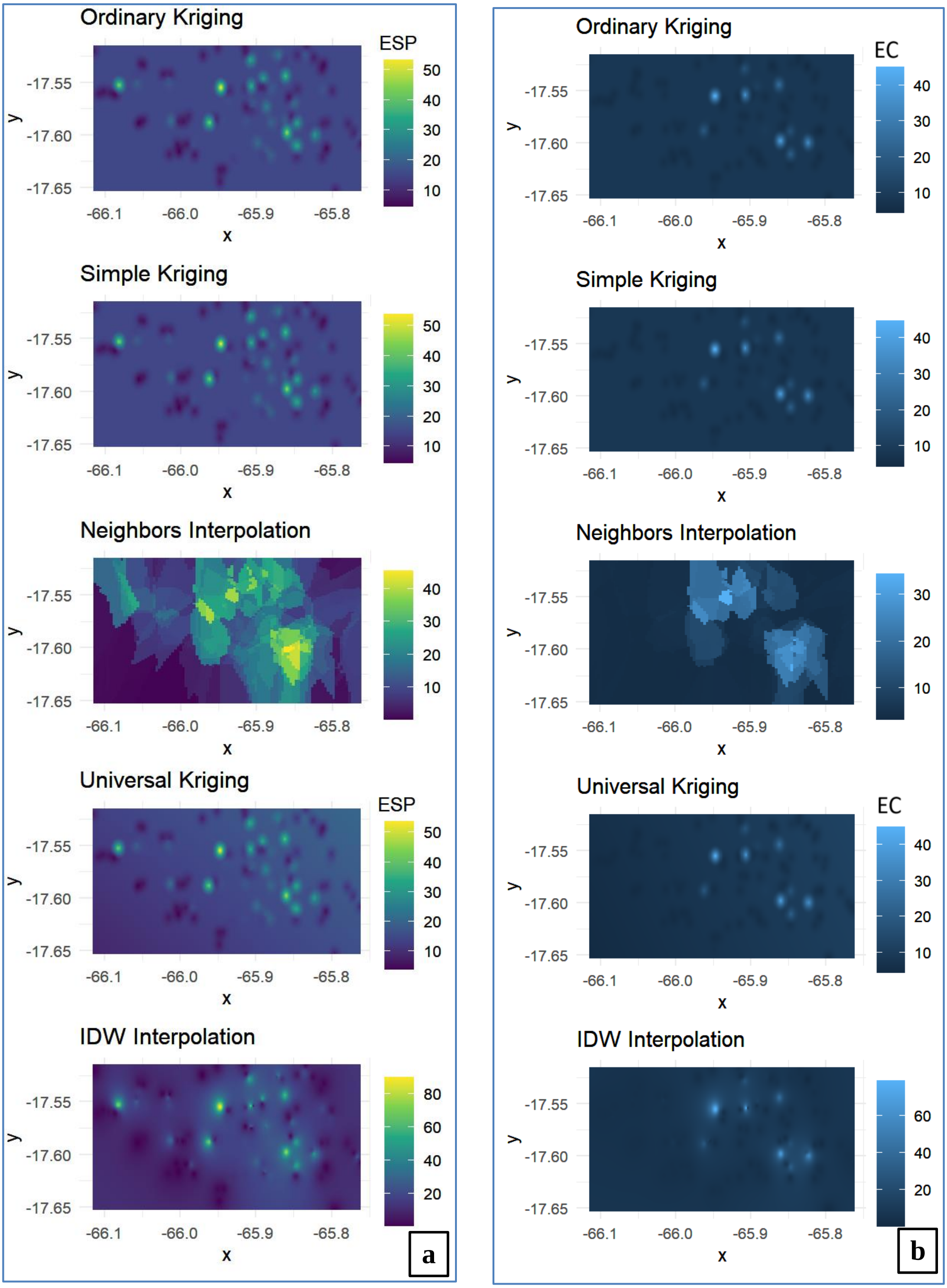


Figure 2.12 Spatial prediction of soil ESP (a) and EC (b) through various interpolation methods.

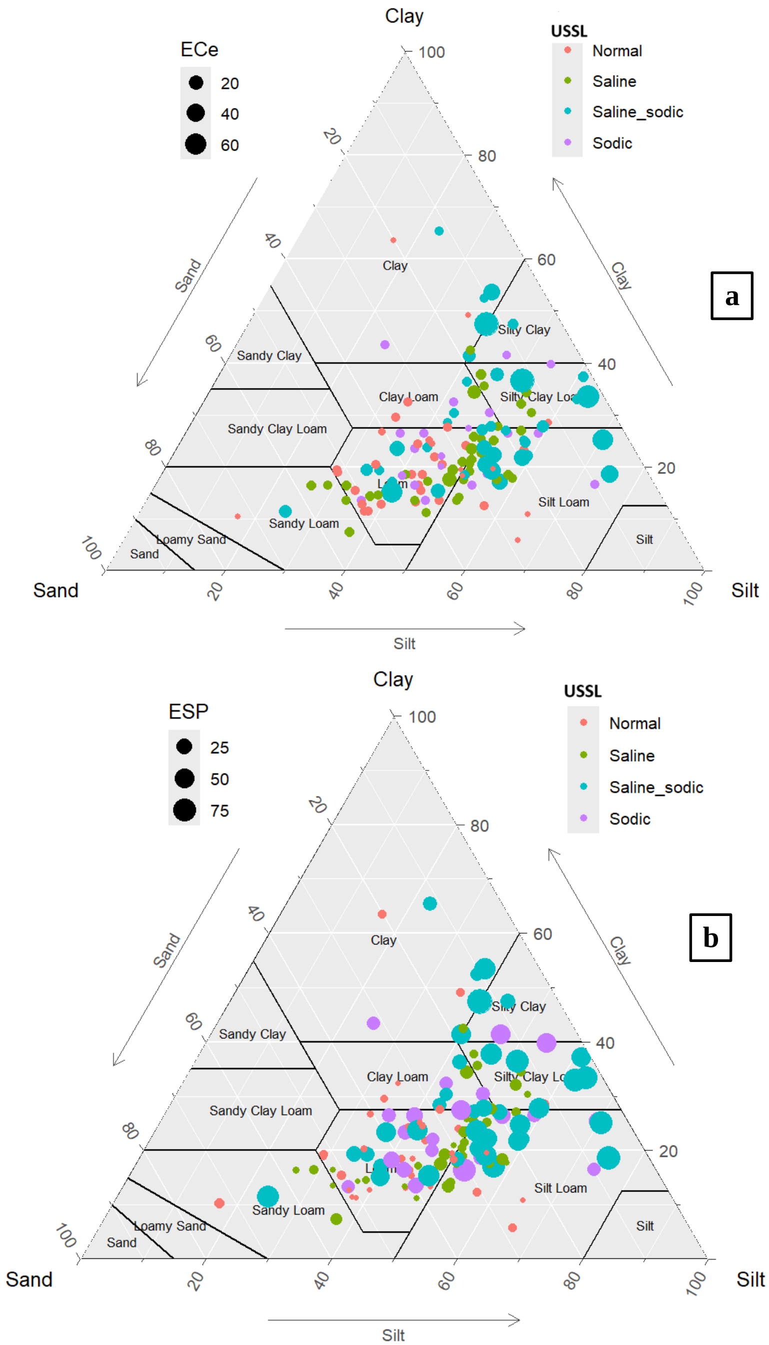


Figure 2.13 Textural classes by salt-affected soil (USSL) classes for the soil EC$_e$ (a) and ESP (b) of the sampling, on the soil textural triangle (USDA system).

Based on the total organic carbon (TOC) levels in the soil samples (Figure 2.14) and assuming that soil organic matter (SOM) contains ~58% of carbon, it can be mentioned that some soils in the High Valley contain on average ~1.26% of SOM, which is a low content considering that most of the surface is dedicated to agriculture and the fact that organic matter can enhance the soil properties and the dissolution of soil calcite to form Ca^{2+}, which in turn contributes in lowering the Na^{+} in the exchangeable complex (Srivastava et al. 2016; Choudhary and Kharche, 2015).

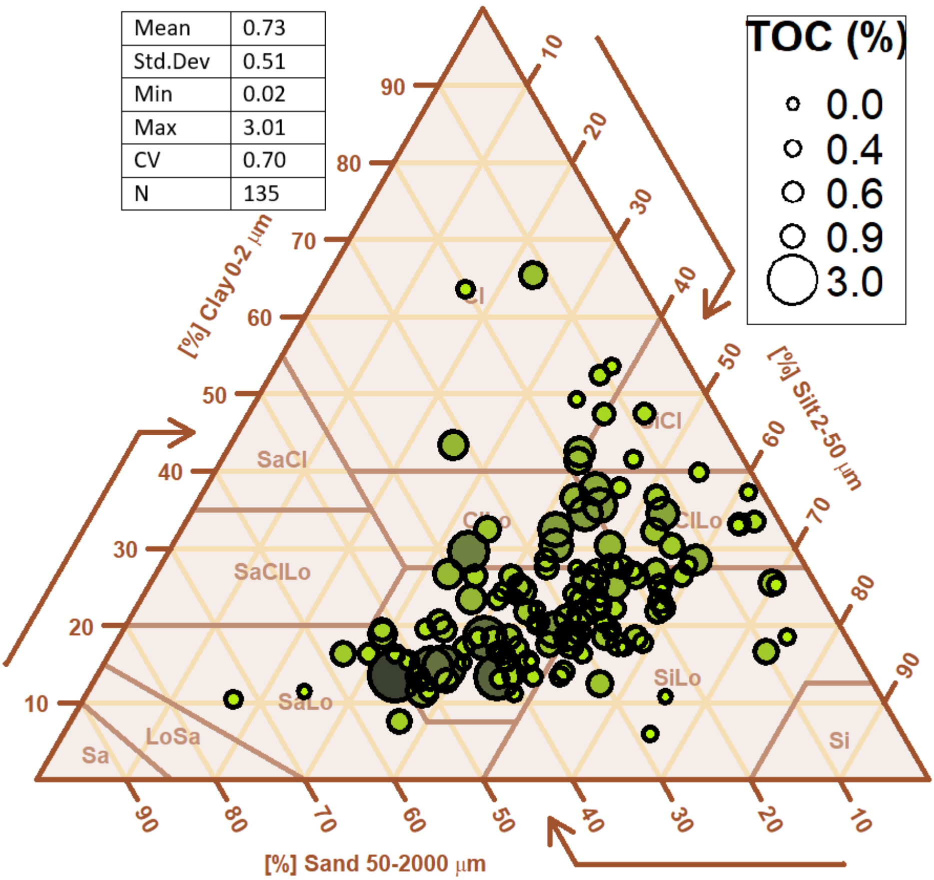


Figure 2.14 Total organic carbon (%) in the soil samples, mapped on the soil texture triangle (USDA system).

5. Conclusions

Five salt-affected and three non-salt-affected soil profiles from the High Valley of Cochabamba were described and characterized. Most of the salt-affected profiles' horizons showed high levels of salinity, sodicity and soil pH. The salt-affected profiles located in Santa Ana, Cliza, San Benito, Aramasí and Arani, were taxonomically classified – based on the WRB-SR 2022 – as Solonchak (Hypersalic, Siltic), Salic Sodic Vertisol (Calcaric), Salic Solonetz (Natric, Siltic), Salic Solonetz (Hypernatric, Siltic, Protocalcic) and Cambisol (Loamic, Aric, Endosodic), respectively; as well the non-salt-affected profiles of Tarata, Punata and Cucuchumuela were categorized as Fragic Fluvic Cambisol (Loamic), Leptic Fluvisol (Fluvic) and Calcic Regosol (Clayic), respectively. The dominant classes among the salt-affected soil samples were saline-sodic and saline.

The saline-sodic class from the USSL classification (Richards et al., 1954) could impact the salt-affected soil management since soils under this category mostly behave as saline or alkaline, then need to be leached of excess soluble salts and/or treated with amendments to lower ESP; such confusion is overcome by the Alternative classification (Szabolcs, 1989; Chhabra, 2004) which considers – besides ESP, EC_e and pH – the nature and ratios of soluble salt ions. After applying both classification criteria in soils from the High Valley, some differences in their derived salinity/sodicity distributions were found. The spatial interpolation was unsatisfactory due to the insufficient spatial correlation. Textural classes of silty-loam and silty-clay-loam were dominant, and a low soil organic matter content was noticed in the sampling.

Further characterization with additional soil samples and profiles is recommended to enhance the representativeness of the soil information database for improving the classification and spatial prediction of salt-affected soils, as well as further validation of the classification criteria and threshold values to define a tailored classification for proper soil management in the study area.

Chapter 3

Prediction of soil salinity/sodicity from soluble salt ions, soil properties, and other features

Adapted from:

soil systems
an Open Access Journal by MDPI (Annex 1)

Andrade Foronda, D.; Colinet, G. Prediction of Soil Salinity/Sodicity and Salt-Affected Soil Classes from Soluble Salt Ions Using Machine Learning Algorithms. *Soil Syst*. 2023, 7, 47. https://doi.org/10.3390/soilsystems7020047

Abstract

Tailored models to predict salinity and sodicity variables are essential for the classification, mapping and management of salt-affected soils. This study aimed to evaluate the performance of three machine learning (ML) algorithms, namely Partial Least-Squares (PLS), Support Vector Machines (SVM), and Random Forests (RF), in predicting soil exchangeable sodium percentage (ESP), electrical conductivity (EC_e), and salt-affected soil classes, from the major soluble salt ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}) determined in soil samples from the High Valley. Additionally, some multivariate regressions to estimate soil sodicity and salinity from some soil properties and easily obtained features were assessed. According to the ML models' evaluations, the SV and RF regressions performed the best for predicting the soil EC_e, as well as the RF model for estimating the soil ESP. The random forest algorithm was superior in predicting the salt-affected soil categories. Soluble Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and HCO_3^- were the most important variables for all models. The random forests and SVR models can be used to predict soil EC_e and ESP, as well as the salt-affected soil classes from soluble ions in the study area. Regression models to estimate ESP from EC + SAR and EC + pH + SAR performed relatively well and slightly better than the simple regression to predict ESP from SAR. Multivariate models to predict soil ESP and EC from easily obtained geomorphometric and remote sensed features showed a regular performance. The obtained models might contribute to the monitoring and management of salt-affected soils in the High Valley; however, additional soil samples and explanatory features are needed to improve their performances.

1. Introduction

The determination of soil ESP from exchangeable cations is often time-consuming and cost-expensive, in contrast to the measurement of soluble ions-based variables in paste extract, which are often used to indirectly estimate sodicity. Regression models can be fitted and validated to predict salinity/sodicity variables and classify soil categories. Some investigations focused on simple regression models for predicting soil ESP from SAR (Chi et al., 2011; Elbashier et al., 2016ab, Seilsepour et al., 2009; Annex 4), SAR from EC (Seilsepour and Rashidi, 2008; Al-Busaidi and Cookson, 2003), ESR from SAR (Harron et al., 1983; Shirmohamm and Heydari, 2020), and soil EC measured in paste extract from EC measured in soil: water ratios (Sonmez et al., 2008; Kargas et al., 2020). Alternatively, some easily obtained features, such as satellite bands, salinity/vegetation indices, geomorphometric features, and other environmental covariates can be used to predict salt-term soil properties as well as to improve the performance of field-measured data-based models including physical and chemical soil–water properties.

Data mining can be described as the capacity to identify patterns from data to establish relationships and models through data analysis, and machine learning (ML) is a process of learning from a system's experience for self-improving based on resultant information. Moreover, supervised learning models the relationships and dependencies between the target prediction output and the input data/features to predict the output values for new data. Partial Least-Squares (PLS) - Discriminant Analysis (DA) is a supervised version of principal component analysis (PCA) which achieves dimensionality reduction with complete cognizance of the classes, arriving at a linear transformation that converts the data to a lower dimensional space with as small an error as possible (Ruiz-Perez et al., 2020); and the PLS regression combines features from PCA and multiple regression, allowing the reduction of the dimensionality while focusing on covariance. The Support Vector Machines (SVM) seek to design a decision surface and separate the margin between the different levels, finding this hyperplane using support vectors and margins; then, the SVM with linear kernel function fits an optimal hyperplane between the classes, making linear and separable small samples (Mohan et al., 2020), while support vector regression fits a line as the hyperplane with the maximum number of points. Breiman and Cutler's Random Forests (RF) algorithm is a tree-based ensemble which generates trees built on resampled subsets of data, with each tree depending on an ensemble of random variables. The Random Forests algorithm combines the trees by unweighted voting and chooses the most voted class over all the tree ensembles at training time if the response is categorical or combines the resulting trees by unweighted averaging if the response is continuous (Cutler et al., 2012; Breiman, 2001). Machine Learning methods have been used to classify soils based on various features such as chemical, physical, and biological soil properties, as well as on specific criteria. Within the framework of ML algorithms, many methods have been progressively developed to automate the soil classification process, such as Decision Trees, k-Nearest Networks, Artificial Neural Networks, and SVM (Chandan, 2018); in that context, some investigations on various soil type classifications using ML methods were carried out by Kovačević et al. (2010), Harlianto et al. (2017), Bhargavi and Jyothi, (2011), and Raza Ansari (2018). The review on ML and soil sciences by Padarian et al. (2019) concludes that the modelling of continuous and categorical soil properties is based on their relationships with environmental covariates and is mainly focused on mapping. Some key findings in the compilation by Motia and Reddy (2021) were that: the implementation of soil classification uses more ML methods than soil regression; the assessment of soil salinity still shows a low contribution from ML; SVM and RF methods are widely used in ML predictions of soil variables and classifications; and the *RMSE* and R^2 are the top metrics used for performance evaluation of ML prediction models in soil analysis. Apart from simple/multivariate regression-based models, most of the studies based on ML methods in predicting and mapping salinity use variables from remote sensing such as spectral bands and derived indices and combined with other environmental covariates such as those related to the elevation, geology, hydrology, morphometry, and climate (Allbed and Kumar, 2013; Kaplan et al., 2023; Wang et al., 2021; Wu et al., 2018; Zarei et al., 2021; Zurqani et al., 2018; Li et al., 2023; Boudibi et al., 2021; Merembayev et al., 2022; Nabiollahi et al., 2021; Vermeulen and Van Niekerk, 2017; Wang et al., 2020), and to predict ESP from SAR compared to generalized regression neural networks (Gharaibeh et al., 2021). Furthermore, field-measured data (physical and chemical soil–water properties), which are used to a lesser extent, may improve the prediction performances for soil salinity, even more if alternative salt-related variables are considered.

Prediction models may considerably vary in function to the soil properties and local conditions, thus the need for affordable and site-specific models to facilitate the characterization and management of salt-affected soils. In this sense, the objectives of this study were to assess the performance of machine learning-based models in predicting salinity, sodicity and salt-affected soil classes from soluble salt ions, evaluate the accuracy of classical multivariate models to predict sodicity and salinity variables from easily measured/obtained predictors and find out the most important variables and best models which can be used to predict salt-affected soils in the study area, thus aiding in the management of these soils. Moreover, the use of machine learning algorithms for predicting salinity/sodicity from soluble ions is somehow related to the alternative classification (addressed in Chapter 2) since prioritizes the nature and ratios of the major soluble salt ions above the soil ESP, EC and pH.

2. Methodology

The soil samples were collected at a depth of ~25 cm from the High Valley of Cochabamba - Bolivia. Lab measurements, determination and calculations of soil properties were described in the methodology of Chapter 2 (section 2.2). Some descriptive statistics of the dataset are shown in Appendix 3.1a.

Some multivariate models for predicting soil ESP, EC and salt-affected soil categories as response variables from soluble salt ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{-2}) as explanatory variables, were calibrated and validated through three supervised ML algorithms, namely Partial Least-Squares (PLS) and Support Vector Machines (SVM) with linear kernel function as discriminating methods, and Random Forests (RF) as a tree-based method, for the respective regression (PLS-R, SV-R, RF-R) and classification (PLS-DA, SVM, RF-C) methods. The multivariate linear regressions to estimate soil ESP from soil chemical/physical properties (EC, pH, SAR, ions and texture) and those generated from some easily obtained features (remote sensing and elevation derived) were calibrated by using the mathematical multiple regression equation (Eq. 3). Additionally, a simple model to predict soil ESP from SAR was fitted through the linear regression mathematical formula (Eq. 4).

$$Y = X\beta + \epsilon \qquad \text{(Equation 3)}$$

where Y is a n-dimensional vector, X is a n × p matrix, β is a p-dimensional vector, and ϵ is the n-dimensional (uncorrelated) error term.

$$Y = b0 + b1 * x \qquad \text{(Equation 4)}$$

where Y is the dependent variable, *b0 and b1* are the linear regression beta coefficients for the intercept and slope, respectively, and x is the independent variable.

For the multivariate linear regressions and machine learning-based models, outliers were removed by applying a threshold value through the Mahalanobis distance from the principal component analysis (PCA). The Factor Analysis was performed to search for similar covariates regarding their mutual correlation and dimensionality reduction. For testing purposes, an internal validation was applied to overcome the possibility of hidden dependencies of the cross-validation (CV), by partitioning the model's dataset into calibration (75%) and validation (25%) datasets. When necessary, data were scaled, and normalization was not needed. The flow process for the ML regression/classification models is shown in Figure 3.1. The models were trained with tenfold groups, and CV was repeated five times. The specific tuning of training parameters and CV of the models is shown in Appendix 3.1b. Subsequently, the prediction was applied to the testing datasets for each trained ML model, then the metrics performances were determined and compared. For the multivariate linear models, the independent variables were reduced by using the stepwise regression algorithm as a step-by-step iterative model construction through the *Akaike information criterion* (AIC) as an estimator of the prediction error.

The satellite Landsat 8 image (ID: LC08.L2SP.232072.20180910.20200830.02. T1, Datum: WGS84, UTM zone: 20, year: 2018, resolution: 30 m) was used to extract six bands, namely, B2 (Blue), B3 (Green), B4 (Red), B5 (NIR), B6 (SWIR1) and B7 (SWIR2), and to calculate some salinity indices (Table 3.1) and vegetation indices (Appendix 3.2). Additionally, some geomorphometric factors (Appendix 3.3) namely elevation, slope, topographic position index (TPI), terrain ruggedness index (TRI), topographic wetness index (TWI) and flow direction were determined based on the digital elevation model (DEM). Subsequently, all these features together with soil properties (pH and soil texture), were used as predictor variables to fit the multivariate models for estimating the soil ESP and EC.

The metrics used to assess the regression models' performance were: the coefficient of determination - R^2 (Eq. 5) which tells how well the predictor(s) can explain the variation in the response variable, the root mean square error – *RMSE* (Eq. 6) as the residuals' standard deviation for the predictions, the mean absolute error – *MAE* (Eq. 7) as the average magnitude of the errors, and the residual standard error – *RSE* (Eq. 8) as the standard deviation of the residual. For the ML classification models, the metrics were the overall accuracy (Eq. 9) as the correct classification of the data obtained by executing the model, and Cohen's kappa statistics (Eq. 10) like the strength of the agreement as the extent to which the data are correct representations of the measured variables (McHugh, 2012). Additionally, the measures of sensitivity and specificity as the proportions of true positives and true negatives correctly predicted, respectively, were calculated for classification.

The relative importance of the variables was assessed through the RF measures, namely per cent increase in mean square error (*%incMSE*) as the prediction error of each variable if omitted from the analysis and the increase in node purity as how much the model error increases when a particular variable is randomly permuted or shuffled, for regression models; and Mean Decrease Accuracy as how much accuracy the model losses by excluding each variable and Mean Decrease Gini as a measure of how each variable contributes to the homogeneity of the nodes and leaves, for classification models. To overcome the imbalance caused by the sodic category, the resampling method 'Synthetic Minority Over-Sampling Technique' was applied through the *Smote* function (Chawla et al., 2002). The stability of the models was assessed in function to three different data partitions (per cent calibration datasets of 70, 75 and 80) as an indicator of the change in the level of performance. Finally, the models were assessed with additional explanatory variables, namely, soil pH, EC_e, total organic carbon (TOC), and soil texture.

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(p_i - o_i)^2}{\sum_{i=1}^{n}(\bar{o} - o_i)^2} \quad \text{(Equation 5)}$$

$$RMSE = \left[n^{-1}\sum_{i=1}^{n}(p_i - o_i)^2\right]^{1/2} \quad \text{(Equation 6)}$$

$$MAE = n^{-1}\sum_{i=1}^{n}|(p_i - o_i)| \quad \text{(Equation 7)}$$

$$RSE = \left[(n-2)^{-1}\sum_{i=1}^{n}(p_i - o_i)^2\right]^{1/2} \quad \text{(Equation 8)}$$

where *n* is the number of observations, *pi* is the predicted values, *oi* is the observed data, and $\bar{o}$ is the mean for *oi*.

$$Accuracy = \sum_{i=1}^{n}\frac{True\ classification}{Total\ cases} \quad \text{(Equation 9)}$$

$$Kappa = \frac{P_o - P_e}{1 - P_e} \quad \text{(Equation 10)}$$

where *n* is the number of classes, P_o is the total agreement probability, and P_e is the agreement probability due to chance.

Statistical analyses were performed by using the R software v.4.1.3 (R Core Team, 2013). The multivariate and ML regression and classification models were trained and evaluated through the R package *caret* (Kuhn, 2022), *randomForest* (Liaw and Wiener, 2002), *MASS* (Venables and Ripley, 2002), car (Fox and Weisberg, 2019), among others for data preparation, analysis and visualization.

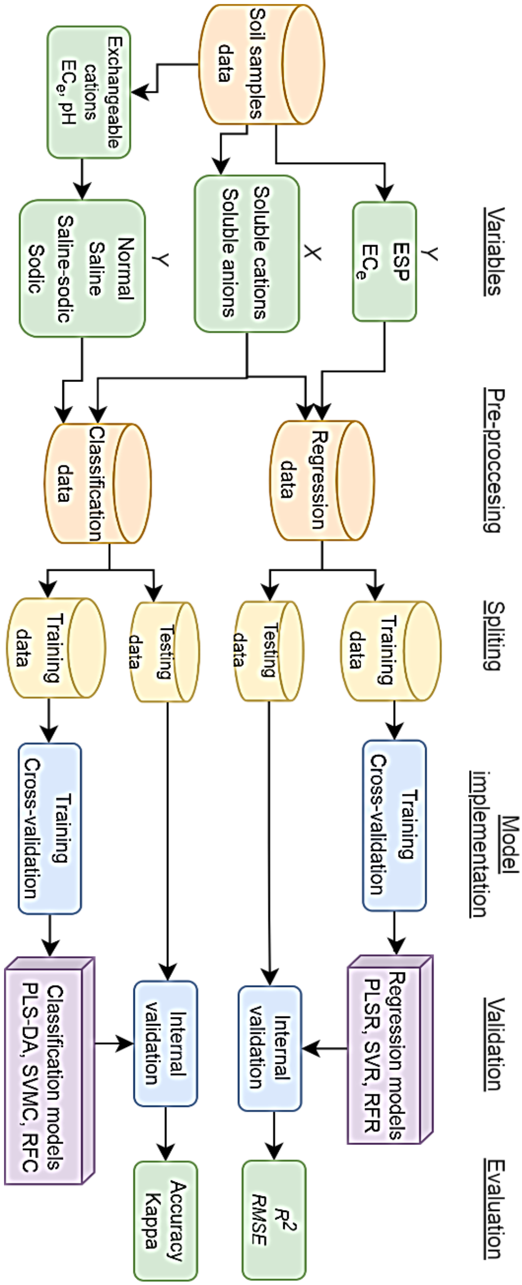


Figure 3.1 Flow chart of the methodological path of the study.

Table 3.1 Salinity indices derived from the satellite image bands, and their equations.

Index	Abbreviation	Equation*	Reference†
Salinity Index 1	SI1	$\sqrt{G * R}$	2, 3, 4, 5, 6
Salinity Index 2	SI2	$\sqrt{B * R}$	1, 3, 4, 5
Salinity Index 3	SI3	$\sqrt{B + R}$	4
Salinity Index 4	SI4	$\sqrt{G^2 + R^2}$	1, 2, 3, 4
Salinity Index 5	SI5	$\sqrt{G^2 + R^2 + NIR^2}$	1, 2, 4, 5, 6
Salinity Index 6	SI6	$\frac{R}{NIR}\ x\ 10$	1, 2
Salinity Index 7	SI7	$\frac{B * R}{G}$	3, 4, 5
Salinity Index 8	SI8	$\frac{R * NIR}{G}$	4, 5
Salinity Index 9	SI9	$\frac{G * R}{B}$	4
Salinity Index 10	SI10	$\frac{B}{R}$	2, 4, 5
Salinity Index 11	SI11	$\frac{B - R}{B + R}$	2, 4
Normalized Salinity Index	NDSI	$\frac{R - NIR}{R + NIR}$	1, 2, 6
Salinity Ratio Index	SAIO	$\frac{R - NIR}{G + NIR}$	2

* B = B2 (blue), G = B3 (green), R = B4 (red), NIR = B5.

† 1) Li Yanan 2021, 2) Wang F. et al. 2019, 3) Aksoy et al. 2022, 4) Wang J. et al. 2021, 5) Bouaziz et al. 2018, 6) Moreira et al., 2015. These references are not necessarily the original sources for the above-listed indices.

3. Results and discussion

The correlation matrix of the explanatory variables (soluble ions, EC, SAR, pH and texture) and response variables (ESP and EC) used to calibrate/validate the machine learning-based and classical multivariate models, is shown in Figure 3.2. A correlation matrix for the remote sensing-based and geomorphometric variables as predictors is shown in Appendix 3.4.

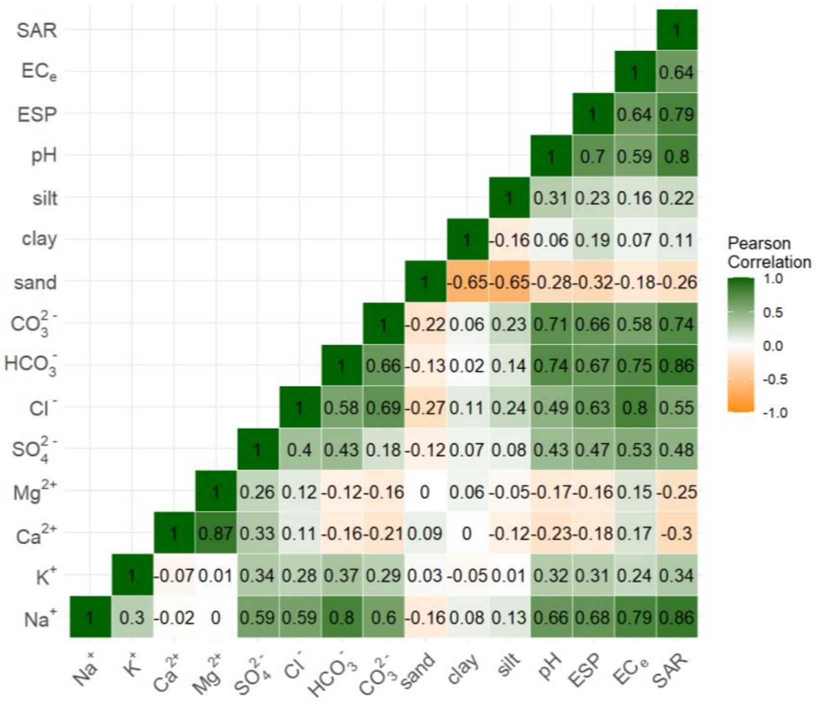


Figure 3.2 Correlation matrix for the predictors and response variables of the multivariate regressions.

3.1. *Machine learning regression models*

Among the assessed ML regression models to predict soil EC_e, the SV-R and RF-R algorithms performed the best with relatively similar values of R^2 and *RMSE*, followed by the ML-R and PLS-R models, which, in contrast, showed good cross-validation performances (Table 3.2). The overall high proportions of soil EC_e variance explained by the soluble ions agree with the fact that the soluble major ions complex is a good predictor for the soil EC_e and vice versa, coinciding with the high correlations between soil EC_e and soluble ions as total dissolved salts (Simón and García, 1999; Chang et al., 1983). As a partially related study, Wang, S. et al. (2019) found that RF regression performed comprehensively better than SV-R among other ML models in predicting salinity from field-measured spectral and salinity data.

Regarding the validation performances, the RF-R model was superior for estimating the soil ESP followed by the rest of the models with similar results; even so, they obtained relatively good cross-validation performances (Table 3.2); these results are partly related to the relationships between SAR, ESP and exchangeable sodium ratio (ESR) (Appendix 3.1c) and have some correspondence to the results obtained by Chi et al. (2011), Elbashier et al. (2016a,b), Seilsepour et al. (2009), and Annex 4, to predict the soil ESP form SAR, and also concur with those to estimate the ESR from SAR by Harron et al (1983) and Shirmohamm and Heydari (2020). Gharaibeh et al. (2021) obtained a very accurate prediction of ESP from easy-to-obtain soil features using generalized regression neural networks. Furthermore, the low performance of the PLS-R model agrees with the fact that it is better in cases where the number of explanatory variables is high or where multicollinearity is an issue.

Table 3.2 Regression models' performances for estimating EC_e and ESP from soluble ions.

	EC_e			***ESP***		
Method	***RMSE***	***MAE***	***R^2***	***RMSE***	***MAE***	***R^2***
PLS-R	2.9 (3.3)	2.1 (2.0)	0.82 (0.72)	19.0 (13.6)	12.7 (10.5)	0.41 (0.63)
SV-R	1.9 (3.5)	1.2 (1.9)	0.92 (0.74)	18.4 (14.0)	11.0 (9.6)	0.40 (0.65)
RF-R	2.1 (3.7)	1.2 (1.8)	0.91 (0.66)	12.6 (12.4)	10.0 (9.2)	0.71 (0.60)
ML-R	2.4 (2.8)	1.6 (-)	0.88 (0.81)	19.1 (13.6)	13.0 (-)	0.40 (0.54)

Values in parentheses mean the cross-validation results. *RMSE* = root mean square error, *MAE* = mean absolute error, R^2 = coefficient of determination, PLS = partial least squares, SV = support vector, RF = random forests, ML = multivariate linear, R = regression.

According to the RF measures of percent increase in MSE and the increase in node purity, Na^+ is the most important variable followed by Ca^{2+} for predicting the soil ESP and Na^+ followed by Cl^- and HCO_3^- for estimating the soil EC_e (Figure 3.3). Despite the relatively low importance of K^+ in predicting soil ESP (Figure 3.3b), it might be important to keep this cation for modelling because it influences soil dispersion, as demonstrated through the exchangeable cation ratio (ECR) by Marchuk et al. (2014) and the cation ratio of soil structural stability (CROSS) by Rengasamy and Marchuk (2011) as alternative indicators for soil ESP and SAR, respectively.

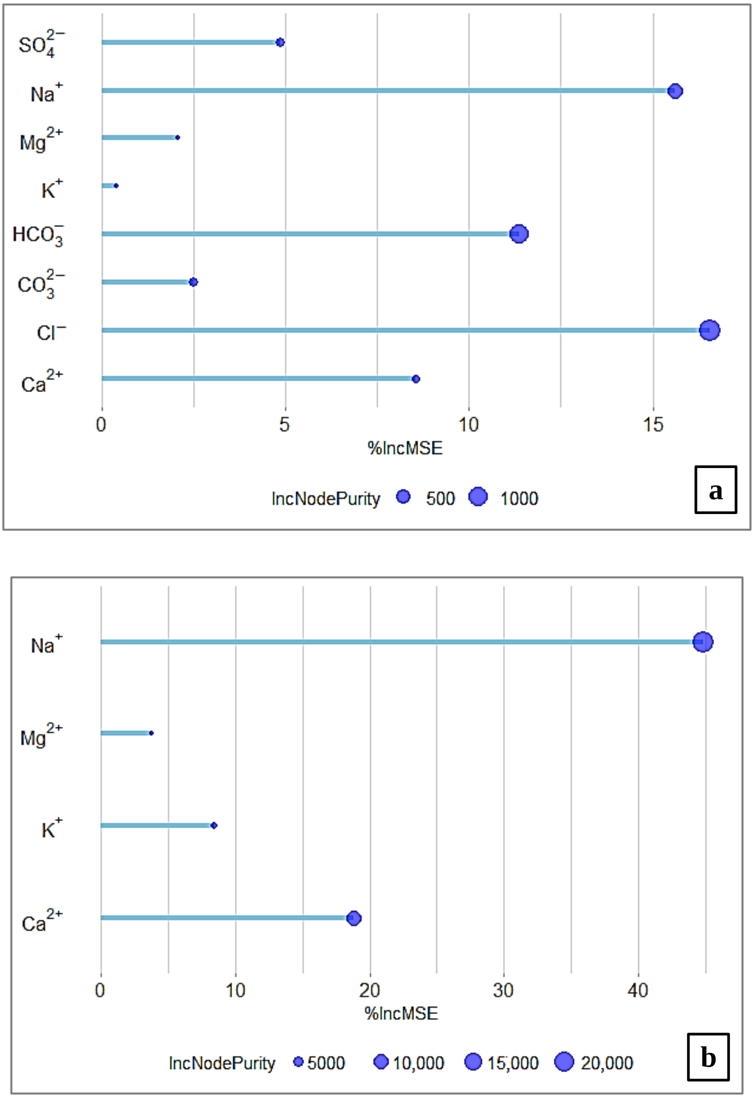


Figure 3.3 Variable importance as the per cent increase in mean square error (*%IncMSE*) and the increase in node purity (*IncNodePurity*) from the RF algorithm for the soil EC_e (a) and ESP (b).

Despite the relatively strong relationships among chemical variables (Figure 3.2) it should be considered that ML algorithms deal with multicollinearity through regularizations and by focusing the prediction and accuracy instead of the influence among variables. Correlations between the contents of cations in the soil sorption complex and those in the soil–water solution are relatively low (Appendix 3.1c) in contrast to the findings of Porębska and Ostrowska (2016).

3.2. Machine learning classification models

The distribution of samples according to the salt-affected soil classes was relatively balanced, except for the sodic soil category (Figure 3.4a). According to the PCA, around 98% of the variance was explained by seven out of eight components. The components are not so good for discriminating the clusters (Figure 3.4b); consequently, for a complete separation of the soil categories, ML classification algorithms were performed.

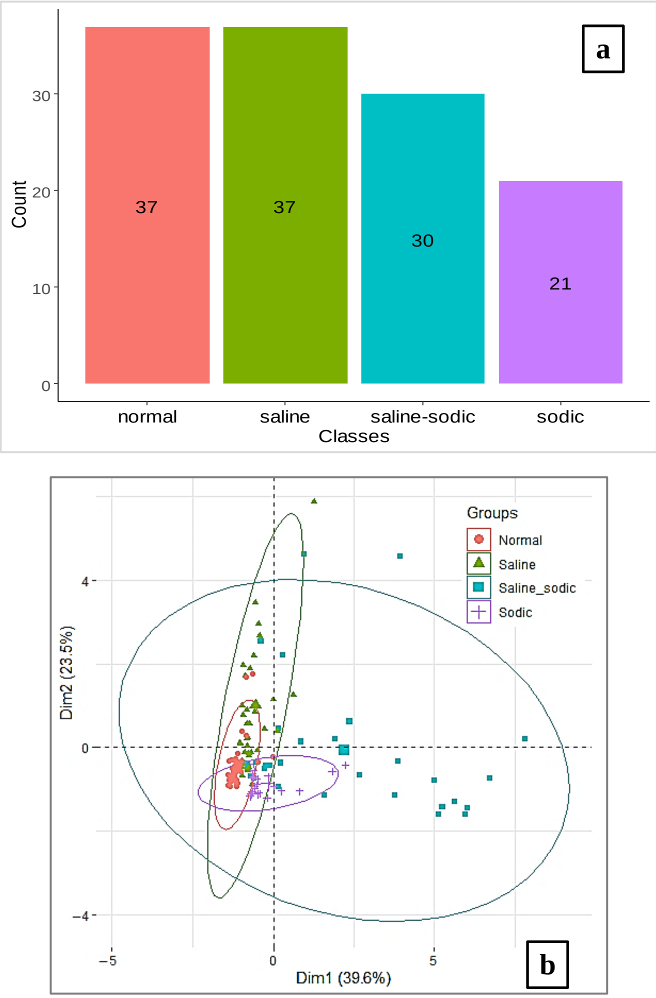


Figure 3.4 Distribution of the observations (a), and PCA plot of observations (b) grouped by salt-affected soil categories.

According to the internal validation, the RF-C model obtained the best performance with the highest prediction accuracy indicating a good classification with a significant strength of agreement beyond chance, followed by the SVM and PLS-DA models, both with a regular classification accuracy and moderate agreement, and according to the cross-validation analysis, the RF-C and SVM algorithms performed better than the PLS-DA model with relatively similar results (Table 3.3).

Table 3.3 Classification models' performances for predicting salt-affected soil classes from soluble ions.

Method	Calibration-CV		Validation	
	Accuracy	**Kappa**	**Accuracy**	**Kappa**
PLS-DA	0.55	0.37	0.67	0.52
SVM	0.63	0.49	0.70	0.58
RF-C	0.61	0.47	0.87	0.82

CV = cross-validation, Accuracy = correct classification of the data, Kappa = strength of the agreement, PLS-DA = partial least squares – discriminant analysis, SVM = support vector machines, RF-C = random forests classification.

The overall Out of Bag (OOB) error of the RF bootstrapping was 37.9%, and the error classes were 0.29, 0.38, 0.26, and 0.68 for normal, saline, saline-sodic, and sodic soil, respectively (Figure 3.5). The misclassification of sodic soil was mainly due to its imbalance as fewer counts in contrast to the other categories. The soil pH used to classify the soil may influence the quality of the classification models because it is not directly related to the soluble/exchangeable cations, as the soil EC_e and ESP are. Based on the predictions in the confusion matrixes (Appendix 3.5a), the measure of sensitivity as the true positive rate was regular to good for predicting the normal, saline, and saline-sodic classes but poor for the sodic class; in addition, the RF-C model generated higher values of sensitivity than those of the SVM and PLS-DA models (Appendix 3.5b).

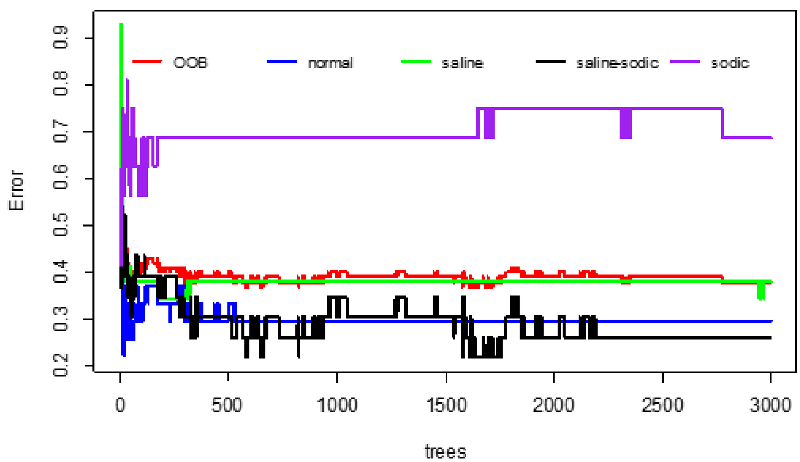


Figure 3.5 RF overall out-of-bag and class errors in function to the number of trees.

Regarding the estimation of the variables' relative importance using the RF *Mean Decrease Accuracy* and *Mean Decrease Gini* calculations, the soluble Na^+ was the most relevant variable for classifying salt-affected soils, followed by Ca^{2+}, Mg^{2+}, and Cl^- (Figure 3.6). These ranks coincide with the variable selection through RF backward elimination and become important for eventually discarding the less important variables if and when the performance of the model is improved. These importance estimations have some correspondence to the SAR and the relevance of neutral salts over alkali salts for these soils.

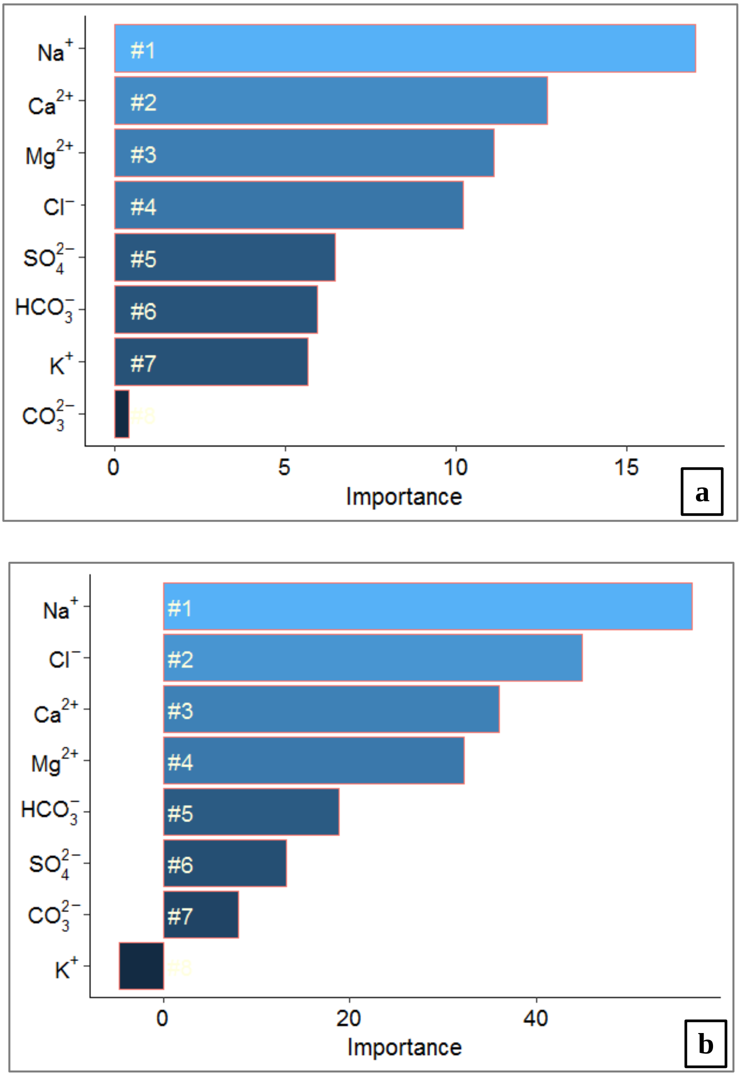


Figure 3.6 Random forest's relative importance of the explanatory variables according to the measures of *MeanDecreaseAccuracy* (a) and *MeanDecreaseGini* (b).

Once the models were trained a second time by using the *Smote* function to overcome the imbalance generated by the sodic category as a minority class, the validation results showed a slight improvement for the SVM model, but a decrease in accuracy and kappa values for the RF-C model (Table 3.4), compared to those without resampling (Table 3.3).

Table 3.4 Classification models' performances for predicting salt-affected soil classes from soluble ions after applying the *Smote* function.

Method	Calibration-CV		Validation	
	Accuracy	Kappa	Accuracy	Kappa
PLS-DA	0.55	0.39	0.60	0.48
SVM	0.61	0.46	0.73	0.62
RF-C	0.60	0.45	0.77	0.68

CV = cross-validation, Accuracy = correct classification of the data, Kappa = strength of the agreement, PLS-DA = partial least squares – discriminant analysis, SVM = support vector machines, RF-C = random forests classification.

Additional classification models were performed based on the Alternative classification (Szabolcs, 1989; Chhabra, 2004) used in Chapter 2. The three algorithms (RF-C, SVM and PLS-DA) showed relatively similar effectiveness for predicting the three categories (normal, saline and alkali) generated by the Alternative classification (Table 3.5), and were relatively more accurate than those obtained to predict the soil classes from the USSL classification.

Table 3.5 Classification models' performances for predicting salt-affected soil classes from soluble ions after using the Alternative classification.

Method	Calibration-CV		Validation	
	Accuracy	Kappa	Accuracy	Kappa
PLS-DA	0.67	0.45	0.77	0.62
SVM	0.68	0.48	0.80	0.68
RF-C	0.72	0.57	0.80	0.68

CV = cross-validation, Accuracy = correct classification of the data, Kappa = strength of the agreement, PLS-DA = partial least squares – discriminant analysis, SVM = support vector machines, RF-C = random forests classification.

By adding the soil pH, EC_e, TOC, clay, silt, and sand to the matrix of predictor variables, only the validation performances of the PLS and SV regressions to predict soil ESP showed a significant improvement (Table 3.6) compared to those in Table 3.2. These results are partly related to those of Keshavarzi et al. (2016) who applied the AI-based models Multi-Layer Perceptron and Adaptive Neuro-Fuzzy Inference

System for predicting ESP from EC_e, pH, and clay. Although the RF classification model obtained a significant increase in performance (Table 3.6) compared to those in Table 3.3, it should be noted the redundancy caused by the soil EC_e and pH as explanatory variables and – at the same time – as classifiers of the explained soil categories; however, their further inclusion might be pertinent if more easily measured features are used, such as EC and pH determined in soil–water suspensions.

Table 3.6 Models' performances after adding features to the matrix of explanatory variables.

Method	Regression—ESP			Method	Classification	
	RMSE	***MAE***	***R^2***		**Accuracy**	**Kappa**
PLS-R	12.5 (13.9)	10.5 (10.7)	0.62 (0.61)	PLS-DA	0.61 (0.56)	0.45 (0.39)
SV-R	12.1 (14.6)	9.9 (11.0)	0.63 (0.61)	SVM	0.61 (0.60)	0.47 (0.45)
RF-R	12.7 (12.7)	10.2 (9.4)	0.62 (0.64)	RF-C	0.90 (0.78)	0.87 (0.69)

Values in parentheses indicate the cross-validation results.

The model stability showed that RF regression models for predicting soil EC_e and ESP obtained lower differences between performances of the three calibration data amounts than those of SV-R and PLS-R, whereas, for the classification models, PLS-DA followed by the SVM method was more stable than the RF-C model in predicting soil categories (Table 3.7).

Table 3.7 Validation performances from the stability assessment of the ML models.

Model / Metrics	Method	Percent of Calibration Dataset			Difference*
		70%	**75%**	**80%**	
EC_e - Regression (*RMSE*/*R^2*)	PLS-R	3.5/0.68	2.9/0.82	2.3/0.92	1.2/0.24
	SV-R	3.4/0.71	2.0/0.92	1.9/0.95	1.5/0.24
	RF-R	2.9/0.79	2.1/0.91	3.0/0.88	1.7/0.15
ESP - Regression (*RMSE*/*R^2*)	PLS-R	15.1/0.52	18.9/0.41	14.9/0.57	7.8/0.27
	SV-R	15.5/0.54	18.4/0.40	15.5/0.58	5.8/0.32
	RF-R	12.6/0.65	12.6/0.71	11.1/0.78	1.5/0.13
Classification (*Accuracy/Kappa*)	PLS-DA	0.65/0.51	0.67/0.52	0.71/0.57	0.06/0.06
	SVM	0.70/0.58	0.70/0.58	0.79/0.69	0.09/0.11
	RF-C	0.78/0.70	0.87/0.82	0.79/0.71	0.17/0.23

* Difference = sum of absolute differences among the metric values of the three partitions.

Considering that it is important to apply tailored reclamation techniques based on proper classifications and predictive models for site-specific salt-affected soils (Shaygan and Baumgartl, 2022), these models become important tools for the monitoring and management of salt-affected soils in the study area, and as a source of alternative covariates for further modelling. Additional observations might be included in their datasets to improve the performance and stability of the classification/regression models, and for overcoming class imbalances and reinforcing the selection of variables. Additionally, the input of additional features such as remote sensing/derived data and field-measured soil properties can also be useful for improving the effectiveness of the models.

3.3. Multivariate regression models

The Pearson correlation values among the explanatory and response variables are shown in the correlation matrix (Figure 3.2). The maximum-likelihood factor analysis applied on the covariance matrix concerning their mutual correlation (Table 3.8), shows the notorious association between the soil ESP as response variable and EC, SAR and pH as predictors. In this case, soluble salt ions are somehow redundant with EC and SAR and then were discarded from the regression analysis. The factor analysis for the remote sensed-based and geomorphometric features is shown in Appendix 3.6.

Table 3.8 Factor analysis for the multivariate regressions to predict soil sodicity.

Analysis* (Loadings > 0.5)

	Factor1	Factor2	Factor3
Na_so	0.89		
SO4	0.53		
Cl	0.65		
HCO3	0.90		
CO3	0.75		
pHe	0.80		
ESP	0.79		
ECe	0.77		
SARe	0.94		
Sand		-0.70	-0.70
Silt		0.99	
Clay			0.99
K_so			
Ca_so			
Mg_so			

Variance

	Factor1	Factor2	Factor3
SS loadings	5.83	1.64	1.55
Proportion Var	0.39	0.11	0.10
Cumulative Var	0.39	0.50	0.60

* Factor analysis was performed through the R function *Factanal* (Varimax rotation). Var = variance

The multivariate regression models predicting soil ESP in function to soil EC + pH + SAR (initial) and EC + SAR (final) obtained through stepwise selection, showed relatively good performances, similar to that of the simple regression estimating ESP from SAR, indicating that EC and pH did not significantly improve the prediction effectiveness of SAR alone (Table 3.9). Although these predictors (pH, EC and SAR) are relatively easy to determine in contrast to the soil ESP and performed relatively well, their use as predictors for the study area should be subject to further improvement and validation. Complementary, a previous performance evaluation of the simple univariate model to predict ESP from SAR is summarized in Annex 4.

Table 3.9 Performance evaluation of the multivariate regressions to predict ESP from soil chemical properties.

Model	Calibration		Validation		
	RSE	***R^2***	***RMSE***	***MAE***	***R^2***
$ESP = 0.58\,EC + 1.38\,pH + 2.69\,SAR - 7.46$ (initial model - stepwise selection)	12.3	0.62	12.0	9.2	0.72
$ESP = 0.59\,EC + 2.87\,SAR + 3.04$ (final model - AIC = 483.7)	12.2	0.63	12.3	9.3	0.70
$ESP = 3.32\,SAR + 4.97$ (simple regression)	12.5	0.62	13.3	10.6	0.64
$ESP = 1.11\,EC + 13.34\,pH - 97.97$	14.0	0.51	11.8	10.3	0.70

RSE = residual standard error, RMSE = root mean square error, MAE = mean absolute error, R^2 = coefficient of determination, ESP = exchangeable sodium percentage, SAR = sodium adsorption ratio, EC = electrical conductivity.

Despite the relatively low performance of multivariate regression models to predict soil ESP and EC from easily obtained features (Table 3.10), these models can be improved through supplementary sampling, geostatistical filtering, and additional geo-environmental features. The relatively low accuracy of these models was mainly due to the imbalanced dataset in terms of excess non-salt-affected soil samples which negatively affect the strength of the expected relationships, for instance between low elevation/slope and salinity/sodicity or salinity/vegetation indices.

Table 3.10 Screening and evaluation of multivariate models to predict soil ESP and EC from some easily obtained features.

Initial model *	Final model**	AIC†	*RSE*	R^2
ESP = green + red + NIR + SWIR1 + SWIR2 + SI1 + SI2 + SI3 + SI5 + SI6 + SI7 + SI8 + SI9 + SI10 + SI11 + SI13 + NDSI + SAIOI + ELEV + TPI + TRI + FLD + SLOPE	*ESP = green + red + SWIR2 + NIR + + SI1 + SI3 + SI6 + SI7 + SI8 + NDSI + SAIOI + ELEV + FLD*	509.1	11.7	0.46
EC = green + red + NIR + SWIR1 + SWIR2 + SI1 + SI2 + SI3 + SI5 + SI6 + SI7 + SI8 + SI9 + SI10 + SI11 + SI13 + NDSI + SAIOI + ELEV + TPI + TRI + FLD + SLOPE	*EC = green + red + NIR + SWIR1 + SWIR2 + SI1 + SI2 + SI3 + SI5 + SI6 + SI8 + SI9 + SI10 + SI11 + ELEV*	390.2	6.4	0.45

* Predictors: satellite bands, salinity indices (Table 3.1), vegetation indices (Appendix 3.2), and geomorphometric factors (Appendix 3.3).

** Estimated coefficients and P(>|t|) for the final models (Appendix 3.7).

† Smallest *Akaike* information criterion values from the stepwise variable selection.

4. Conclusions

The support vector (SV) and random forests (RF) regressions showed the best performances for predicting the soil EC_e, whereas the RF model was superior for estimating the soil ESP. The RF classification algorithm showed the best prediction accuracy, followed by the support vector machines (SVM) and partial least squares (PLS-DA) models. The most important explanatory variables for all the prediction models were Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and HCO_3^-. The sodic class was poorly predicted, and the applied resampling method for overcoming its imbalance did not significantly improve the classification performances. The stability analysis showed that the amount of training data generated less impact on the RF regression models and the SVM and PLS-DA classifications. Additional explanatory variables somehow improved the PLS and SV regressions to predict ESP and the RF classification. It can be concluded that the RF and SV regression algorithms can be suitable to estimate the soil EC_e and ESP, as well as the RF and SVM classification models to predict salt-affected soil classes from soluble salt ions.

Multivariate regressions to predict soil ESP in function to SAR, EC and pH showed a satisfactory performance, in turn relatively similar to that of the simple regression to predict ESP from SAR. Multivariate models to predict soil ESP and EC from easily obtained features showed a relatively low performance.

The assessed models might contribute to the monitoring, mapping, and management of salt-affected soils in the High Valley; however, additional samples and geo-environmental features can be considered for improving their performances.

Chapter 4

Use of mineral and organic amendments to remediate salt-affected soils

Adapted from:

(Annex 2)

Andrade Foronda, D.; Colinet, G. Combined Application of Organic Amendments and Gypsum to Reclaim Saline–Alkali Soil. Agriculture 2022, 12, 1049. https://doi.org/10.3390/agriculture12071049

(Annex 3)

Andrade Foronda, D. Reclamation of a Saline-Sodic Soil with Organic Amendments and Leaching. Environ. Sci. Proc. 2022, 16, 56. https://doi.org/10.3390/environsciproc2022016056

Reclamation of saline-sodic soils with gypsum & sulphur in: FAO. (2022). Halt soil salinization, boost soil productivity - Proceedings Global Symposium on Salt-affected Soils. 20–22/10/2021. p.175-176. Rome. doi: 10.4060/cb9565en

Abstract

Two soil column experiments were carried out to evaluate the effectiveness of singly/combined organic and mineral amendments with leaching in remediating saline-sodic soils from the High Valley of Cochabamba. First, mineral amendments (gypsum and sulphur) at two doses (50 and 100%) and organic amendments (cattle manure, chicken manure, biochar and peat) at two levels (1 and 2% of OM w/w) with leaching besides no/amendment, were evaluated. The properties of the soil before were exchangeable sodium percentage (ESP) of 66.6%, electrical conductivity (EC_e) of 20.5 dS m^{-1}, and pH of 8.55. Gypsum at a dose of 100% of the requirement was the most effective, followed by gypsum at 50% in improving the soil ESP and EC_e; in contrast, sulphur was more efficient than gypsum in lowering the soil pH. Cattle manure at a dose of 2% performed the best in decreasing the soil ESP but, without reaching the threshold value of 15%, and any treatment was more effective than only water in lowering EC_e below 4 dS m^{-1}. Peat at a dose of 2% was efficient in lowering pH to 7.76. Gypsum was more effective than sulphur in lowering soil ESP because of its calcium content which facilitates the displacement of sodium and improvement of soil-water properties; and sulphur was less efficient than gypsum, probably due to the short time for incubation. Cattle manure was superior in reducing soil ESP and EC_e mainly due to its organic matter and divalent cations content which can improve the soil structure and infiltration, whereas peat and biochar reduced the infiltration rate. Subsequently, cattle manure and chicken manure combined with gypsum at four levels (0, 50, 75, and 100%) were assessed through a second experiment. The soil-before properties were ESP 52.8%, EC_e 24.1 dS m^{-1}, and pH 9.6. Combined treatments (manure + gypsum) at any dose were more effective than those of sole gypsum at any level in reducing the initial soil ESP to below 5%, in turn, gypsum at a dose of 100% performed the best; EC_e was lowered to below 1.6 dS m^{-1} by any combination and sole gypsum at any dose, except sole water; and any combination of manure with gypsum lowered the pH to below 8.7. The addition of cattle manure or chicken manure might enhance the effect of gypsum due to their synergistic effect on Na^+ displacement by their Ca^{2+} contribution and subsequent improvement of soil structure through the organic matter, leading to an enhancement of the leaching process. Soluble salts and Na^+ were considerably reduced by any treatment at the first leaching. These studies suggest that either sole gypsum or cattle/chicken manure – or even better – combined, can be used for ameliorating saline-sodic soils. However, further investigation is needed considering intermediate doses, different soil types, and validation through field experiments.

1. Introduction

Salinity affects root/plant growth through the osmotic effect due to the excess soluble salts. Sodicity causes many adverse effects, such as changes in exchangeable and soluble ions ratios, increase of soil pH, destabilization of soil structure, deterioration of soil hydraulic properties, increase in susceptibility to crusting, runoff, soil erosion, and osmotic-specific ion effects on plants (Qadir and Schubert, 2002). Leaching with non-saline water is used to remove excess soluble salts from saline soils, and mineral/organic amendments are usually added with leaching to remediate soils affected by sodicity.

The amelioration of saline-sodic and sodic soils normally needs an external source of soluble Ca^{2+} to replace the excess Na^+ from the cation exchange sites of the rhizosphere, and this is most effective with non-saline irrigation water (Ahmad et al., 2006); 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 (Qadir et al., 2001a), leading to soil flocculation and improvement of soil structure, pH and nutrient availability. Gypsum ($CaSO_4.2H_2O$) and sulphuric acid (H_2SO_4) are widely used because of their relatively low cost and availability (Qadir et al., 2001a). Gypsum application counters reduced hydraulic conductivity in Na^+- dominated soils through $Na^+ – Ca^{2+}$ exchange, hydrolysis of Na^+ through the ionic strength effect, and enhancing electrolytic concentration (Ahmad et al., 2016). Due to the high pH of alkali soil, most likely because of Na_2CO_3, the addition of gypsum provides a source of Ca^{2+} which precipitates as $CaCO_3$ and Ca $(HCO_3)_2$ leading to a decrease in pH (Wong et al., 2009). The soil ESP is normally used to determine the dose of gypsum necessary to displace excess adsorbed sodium.

The chemical reactions of added gypsum and sulphur in the sodic or saline-sodic soil - based on Choudhary and Kharche (2015) - are as follows:

Gypsum:

$CaSO_4$ + 2Na [clay micelle] = Ca [clay-micelle] + Na_2SO_4 (Leachable) ↓

and/or $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ (leachable) ↓

Sulphur:

Previous biological oxidation of elemental sulphur mainly by *Thiobacillus*

$2S + 2H_2O + 3O_2 = 2H_2SO_4$ (sulphofication)

$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2$

or $H_2SO_4 + 2CaCO_3 = CaSO_4 + Ca\ (HCO_3)_2$

Then, $CaSO_4$ reacts with the adsorbed Na^+ and/or Na_2CO_3 as above for gypsum.

The chemical amelioration strategy itself has become cost-intensive as an effect of increases in amendment costs (Qadir et al., 2001a); moreover, using organic instead of inorganic materials can reduce input costs as a sustainable and efficient management method to reclaim salt-affected soils (Chaganti et al., 2015). Therefore, organic amendments can be considered either an alternative or a complement to mineral amendments. 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 improving their physical properties by increasing the aggregate stability (Lax et al., 1994). Furthermore, Mahmoodabadi et al. (2013) 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 the properties of calcareous saline-sodic soils. An illustration of the influence of biochar – as a referent of organic amendments – on the physical/biological properties of salt-affected soils is shown in Appendix 4.1.

Soil salinity and sodicity negatively affect the crop yields and consequently the farmers' income; therefore, readily available and low-cost amendments are needed for reclaiming sodic/saline-sodic soils. Some local experiments under controlled conditions were carried out using soils from the study area (Annexes 2, 3, 5 and 6) and somehow showed that manures or gypsum alone was effective in improving soil sodicity and salinity. Amendment-based techniques were prioritized above other restoration methods because: (1) Mineral amendments are widely used because of their direct effect on Na^+ displacement; (2) however, sometimes are cost-intensive, therefore organic amendments can be an alternative either for replacing or enhancing the effect of mineral amendments by improving the soil-water properties; and although (3) shoot-succulent halophytes can accumulate significant Na^+ quantities within their above-ground organs, these can be insignificant compared to the ability of some plants to solubilize $CaCO_3$ then release Ca^{2+} ions ; (4) which is also water/irrigation dependent and thus infeasible in arid and semi-arid regions; and then, (5) despite mineral amendments are also water-dependent, their amelioration effect is normally higher and accomplished in a shorter time than that of phytoremediation (Qadir et al, 2007; Qadir et al., 2001b; Shahid, 2002).

Therefore, some soil-column experiments were carried out to evaluate the effect of individual/combined mineral and organic amendments with leaching in remediating soil salinity/sodicity and to identify the most effective organic or mineral amendment(s) and/or their combination(s). In terms of hypothesis, the assessment looks to accept or reject that at least one amended-based remediation technique, involving either individual or combined mineral and/or organic amendment, shows statistically significant improvement in soil salinity/sodicity compared to other treatments under controlled conditions, expressed for testing purpose as the alternative hypothesis: H_a: $\overline{X_A} \neq \overline{X}_B \neq \overline{X_C} \neq ... \overline{X_N}$, where, and $\bar{X}$ is the mean of a given treatment (*A, B, C… N*).

2. Materials and methods

The soils were collected from a location in the High Valley (17°32′38.6” S, 65°51′41.9” W) at an elevation of 2750 m and a depth of ~25 cm. The experiment was carried out at the Faculty of Agricultural and Livestock Sciences – UMSS (17°27′2.9” S, 66° 7′59.7” W). It should be remarked that even though the target soils are saline-sodic – based on the USSL classification –, both behave as sodic/alkali according to the Alternative classification system (Chapter 2); moreover, considering that the soil in columns is closer to the soil under natural/field condition than that in the pots, the soil-column experiments are described next and the pot experiments' results are summarized in Annexes 5 and 6.

2.1. Singly mineral and organic amendments

The soil properties before remediation are shown in Table 4.1. The purity of gypsum was 92% (18.5 % Ca^{2+}) and the purity of sulphur was 97.5%. The gypsum requirement as a dose of 100% to reduce the initial soil ESP to 15% was calculated through the equation of Hoffman and Shannon (2007) and the sulphur requirement was determined by using a conversion factor (5.38 times gypsum requirement) as suggested by Richards et al. (1954). The organic amendments used to remediate the soil were: cattle manure locally collected, tropical peat as tree fern fibre from the tropical area, and biochar branded by Greenpoch SA (Belgium). Some properties of the organic amendments are listed in Table 4.2.

Table 4.1 Chemical and physical properties of the soil before remediation.

Property	Value	Soluble ion	Value ($mmol_c$ L^{-1})
ESP (%)	66.6	Na^{+}	339.2
EC (dS m^{-1})	20.5	Mg^{2+}	0.7
pH	8.55	K^{+}	1.5
Clay (%)	18.2	HCO_3^{-}	40.3
Silt (%)	52.1	CO_3^{2-}	20.0
TOC (%)	0.3	Cl^{-}	185.0
CEC ($cmol_c$ kg^{-1})	5.0	SO_4^{2-}	71.1

TOC = total organic carbon, CEC = cation exchange capacity.

Following the protocol of Ahmad et al. (2016), simulated soil columns (Figure 4.1a, Appendix 4.2) were assembled using PVC tubes (15 cm diameter), each one filled with 6.7 kg of 4 mm sieved soil in two layers, so the upper layer was mixed according to each treatment. The dose of the amendments was calculated on a dry weight soil basis (w/w) to reach one and two per cent of organic matter content. Distilled water was used for the leaching process to simulate the rainwater and was calculated as a pore volume (PV) using the formula provided by Kahlon et al. (2013) and Ahmad et al. (2016). After an initial soil saturation of 3/4 PV, two to four lixiviations (each of one PV=2L) were applied. The soil ESP was calculated using the formula (Eq. 2 – Chapter 2). The design was completely randomized, and the treatments were the combinations between mineral amendment (gypsum and sulphur) and dose (50 and 100%) as well as between organic amendment (cattle manure, biochar and peat) and dose (1 and 2%) besides no amendment or only-leaching. The LSM-Tukey adjustment test was used to determine the significant differences between treatments at $p < 0.05$.

Table 4.2 Some properties of the organic amendments (cattle manure, biochar, and peat).

Property	Cattle Manure	Biochar*	Tropical Peat †
Na^{+} ($cmol_c\ kg^{-1}$)	0.1	0.0	0.0
Ca^{2+} ($cmol_c\ kg^{-1}$)	4.7	0.5	1.5
Mg^{2+} ($cmol_c\ kg^{-1}$)	7.7	0.4	3.1
$EC_{1:1}$ ($dS\ m^{-1}$)	3.7	0.3	0.7
$pH_{1:1}$	8.5	9.7	3.6
TOC (%)	23.7	33.0	22.5

* Additional biochar properties are listed in Appendix 4.1.
† Swelling capacity of 1.85 w/w (g water/g dry peat)

2.2. Combined amendments

The properties of the soil before remediation are listed in Table 4.3, and those of the organic amendments are shown in Table 4.4. The protocol to simulate soil columns by Ahmad et al. (2016) was adapted by using PVC tubes (height 100 cm and diameter 10 cm) with five cm of gravel, glass fibre and plastic mesh were placed at their bottoms (Figure 4.1b, Appendix 4.2). The gypsum requirement at a level of 100% (8 g gypsum kg^{-1} soil) needed to reduce the initial soil ESP to 15%, was calculated through the equation used by Lebron et al. (2002). The saline-alkali soil, gypsum 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 soil to a height of 35 cm based on bulk density, then the treated soil was placed in the upper layer (height of 20 cm). The properties of the leaching water were EC of 0.2 dS m^{-1}, pH of 8.1, and Na^+, Ca^{2+} and Mg^{2+} concentrations of 0.9, 0.6 and 0.5 meq L^{-1}, respectively. The pore volume (PV) of 1060 ml water was determined through the formula given by Kahlon et al. (2013). 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 (Appendix 4.4b), and then the reclaimed soil was collected.

Table 4.3 Chemical and physical properties of the saline–alkali soil before remediation.

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

Values in $mmol_c$ L^{-1} and $cmol_c$ kg^{-1} are from soluble ions and exchangeable cations, respectively.
* Remeasured values (difference between CEC and the sum of exchangeable cations represent an inherent error)

The soil pH was determined in a 1:5 soil–water suspension through a derived ISO 10390. The soil EC_e and soluble ions were measured in the paste extract by using the standard procedures of Richards et al. (1954). Exchangeable cations were obtained through a derived ISO 22171 at a pH of 7 and AAS. The soil ESP was determined by applying the formula (Eq. 2 - Chapter 2), the estimated percentage of displaced Na^+ was calculated through Equation (11) and the SAR using the formula (Eq. 1 - Chapter 2).

$$Na^+{}_{displaced} = 100 - \left(\frac{Na^+{}_{SA}}{Na^+{}_{AM}+Na^+{}_{SB}}\right)100 \qquad \text{(Equation 11)}$$

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

Table 4.4 Some properties of the organic amendments and gypsum.

Property	Cattle Manure	Chicken Manure	Gypsum*
Na+ (cmolc kg−1)	20.7	12.7	0.2
Ca2+ (cmolc kg−1)	10.7	6.6	424.7
Mg2+ (cmolc kg−1)	4.5	3.4	0.8
EC (dS m−1)	11.4	5.2	2.6
pH	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 $CaCl_2$) and EC (1:5 suspension).
* Purity of gypsum: 91.7%

The experimental design was completely randomized with four replicates. The treatments comprised the combinations of amendments (cattle manure, chicken manure and no manure) and gypsum levels (GY levels (50, 75 and 100%), besides the only leaching treatment. The effects on soil ESP, EC_e, pH and displaced Na^+ as response variables were evaluated by using the Scott–Knott clustering algorithm (p = 0·05). Statistical analysis was performed using the R software v.4.1.3 (R Core Team, 2013). Additionally, a field experiment (Annex 7) assessing the same amendments was carried out at the same location where the target soil was collected for this study.

Figure 4.1 Soil column experiment to assess singly (a) and combined (b) organic and mineral amendments.

3. Results and discussion

3.1. Mineral amendments

Significant differences were found for the combined effect together mineral amendment (gypsum and sulphur) with dose (50% and 100%) and organic amendment (cattle manure, peat and biochar) along with dose (1% and 2% of OM w/w), significant differences were found. The treatment of gypsum at a dose of 100% performed the best in decreasing the initial soil ESP (66.6%) by 65.5% followed by 50% gypsum (by 55.2%), 100% sulphur, 50% sulphur and only water (Figure 4.2a). The treatments of gypsum at doses of 50 and 100% were more effective in reducing soil EC_e from 20.5 to 0.9 and 1.6 dS m^{-1}, respectively (Figure 4.2b). The soil pH showed a reduction from 8.55 to 7.5 and 7.8 for the treatments of sulphur at doses of 50 and 100%, respectively, followed by gypsum and only water (Figure 4.2c).

The effectiveness of gypsum in lowering the soil exchangeable sodium may confirm the influence of Ca^{2+} on displacing Na^+ and improving the soil infiltration, in addition to the effect on leaching soluble salts through lixiviation. Sulphur was less efficient than gypsum probably due to insufficient incubation time and low soil organic matter content, but more effective for improving soil pH, maybe due to its acidic counteracting effect. The results about the effectiveness of gypsum were congruent with those obtained by Qadir et al. (1996), Tavares et al. (2012), and Ahmed et al. (2016); in contrast Manzano Banda et al. (2014) who found that leaching with water reduced soil salinity and sodicity to adequate levels for conventional crops, with and without the application of cattle manure, gypsum and sulfuric acid.

The sodium concentration in the leachates was higher at the first lixiviation (900–1200 $mmol_c$ L^{-1}) for all treatments compared to those from the second to fourth cycle, and similar behaviour for the EC in a range of 45–58 dS m^{-1} at the first cycle (Appendix 4.3). The evolution of Na^+ concentration and soluble salts in the leachates was congruent with the ESP and Ec_e values in the ameliorated soil. The soil salinity and sodicity were considerably reduced at the first lixiviation by over 90%, indicating that one leaching might be sufficient, at least under controlled conditions.

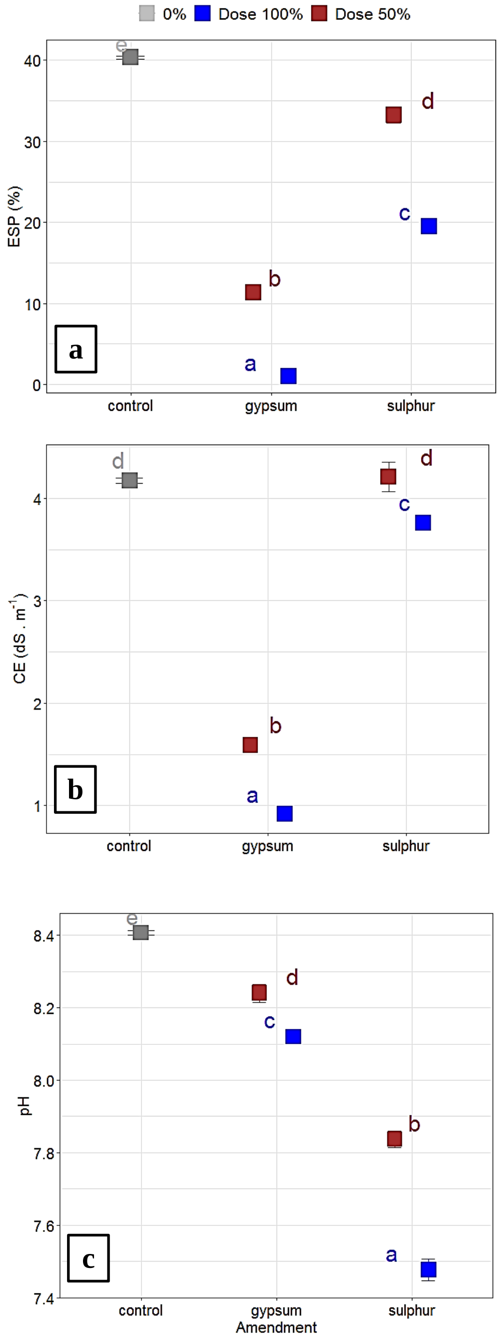


Figure 4.2 Effect of gypsum and sulphur addition on soil ESP (a), EC_e (b), and pH (c), after remediation. Means sharing a letter are not significantly different (Tukey, $p < 0.05$) and the bars indicate the standard error.

3.2. Organic amendments

The results after remediation showed that soil ESP, EC_e and pH differed significantly ($p < 0.05$) for the combined effect of organic amendment along with dose. Cattle manure at a dose of 2% performed the best in reducing the initial soil ESP (66.6) by 39%, followed by cattle manure at a dose of 1% (by 31.5%), and in turn by the rest of the treatments with a similar effect (Figure 4.3a). The treatments of cattle manure at doses of 1% and 2% were as effective as biochar and peat at a dose of 2% for lowering the initial EC_e (20.5 dS m^{-1}) by over 16 dS m^{-1}, while 1% biochar and 1% peat showed a lower effectiveness but higher than that of the only water (Figure 4.3b). The treatment of peat at a dose of 2% decreased the initial soil pH (8.6) to 7.76, followed by cattle manure at doses of 1% and 2 %, and 1% peat in equal magnitude, in contrast to biochar which maintained the pH around its initial value (Figure 4.3c). It should be noted that the percolation time of peat and biochar was approximately double that of cattle manure.

The superiority of cattle manure in decreasing the soil ESP and EC_e can be partly attributed to its TOC, Ca^{2+} and Mg^{2+} contents, which contribute to the improvement of soil structure and infiltration, thus the displacing of adsorbed Na^+ from the soil. The lower effectiveness of peat in reducing soil ESP was likely due to its swelling capacity (1.85 w/w of water/dry peat) which together with soil dispersion boosts the slowdown of the leaching process; in this sense, Shaygan et al. (2017) suggested that the swelling effect of bentonite along with water decreased the hydraulic conductivity, thus increased the sealing of the pore system and percolation in the reclaimed soil. Biochar also showed a limited effect on sodicity, probably due to its insufficient ability to influence soil structure, in concordance to Chaganti and Crohn (2015) who indicated that the mode of action of biochar is physiochemical while composts provide a comprehensive reclamation when biological and physiochemical factors act together. Water by itself was less effective in decreasing adsorbed Na^+ but lowered soil EC_e to 4.2 dS m^{-1}, coinciding with Mahmoodabadi et al. (2013) who found that EC_e decreased significantly even for the unamended soil possibly caused by solute leaching; moreover, Manzano Banda et al. (2014) stated that flushing water reduced salinity with and without the application of manure. In contrast to biochar, the peat significantly reduced soil pH, mainly due to its very low pH, causing an acidic counteracting effect, as Chaganti et al. (2015) found that composts significantly improved soil CEC and pH, but the biochar did not. Furthermore, Saifullah et al. (2018) affirmed that although many studies reported significant decreases in SAR and ESP of sodic and saline-sodic soils as well as improvement in plant growth due to the sorption of Na^+ salts by biochar, not necessarily represent a removal of Na^+ out of the soil.

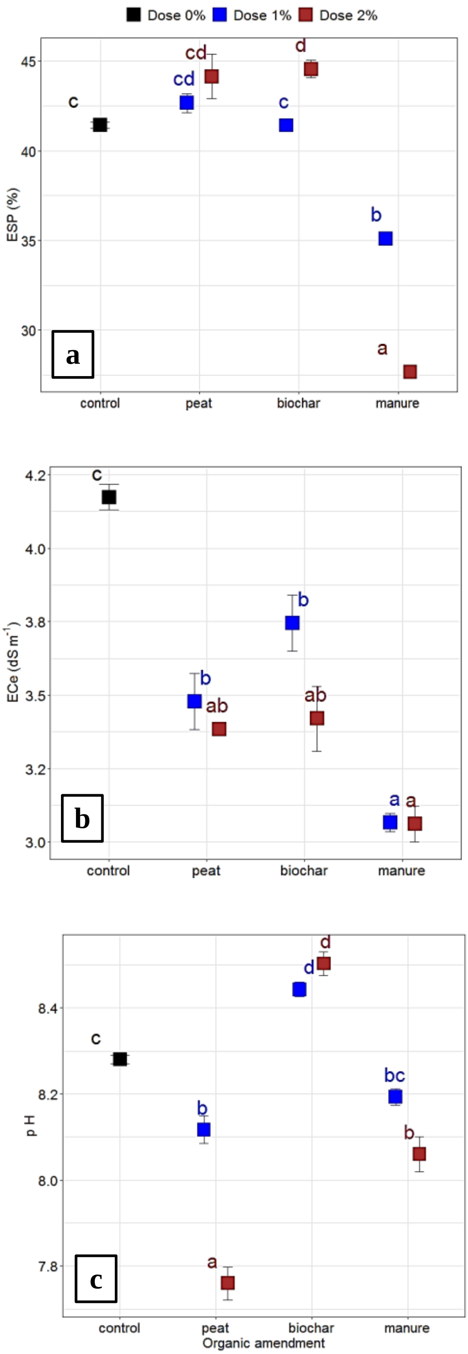


Figure 4.3 Soil ESP (a), EC_e (b), and pH (c) after remediation for the effect of the organic amendment. Means sharing a letter are not significantly different according to pairwise comparisons of LSM Tukey ($p < 0.05$).

Overall, these results suggest that cattle manure, biochar and peat enhanced the effect of leaching in remediating soil salinity and sodicity through the positive impact of their organic matter content on soil structure, infiltration, and Na^+ displacement, agreeing with Chaganti et al. (2015) who found that organic amendments significantly lowered the soil EC_e, ESP and SAR compared to the non-amended soils, and also improved soil structure, aggregate stability and saturated hydraulic conductivity, even more in compost treated soils; Lax et al. (1994), who reported that the physical properties of the salinized soil, such as structural stability, infiltration rate, water-holding capacity and washing capacity, were considerably improved by added organic matter from the solid waste application; and Abdel-Fattah (2012), who concluded that water hyacinth and rice straw compost singly or combined facilitated a pronounced decrease in soil EC, pH, SAR, and ESP compared to the control (Abdel-Fattah, 2012). Despite organic amendments were effective in reclaiming salinity, the soil ESP and pH threshold values from the USSL classification were not reached. Furthermore, subsequent assessments of potential amendments for remediation should consider an environmental evaluation besides cost analysis.

3.3. Combined amendments

Soil ESP, pH, EC_e and displaced Na^+ in the reclaimed soil, as, differed significantly ($p < 0{\cdot}05$) among the combinations. It should be mentioned that the treatment without amendments (only leaching) was not considered for the comparisons of means in Figure 4.4, but for those in Appendix 4.4a, since it received two cycles of leaching in 54 days due to its longer percolation time, and because of the marked differences between the output groupings of means with and without this treatment.

The soil ESP, EC_e and pH values of the only leaching treatment, decreased by 54%, 79% and 8%, respectively, over its soil-before value; moreover, the threshold values of EC_e (4 dS m^{-1}) and ESP (15%) from the USSL classification were reached with any treatment, except without amendment, however, that of soil pH (8.5) was only reached with chicken manure at any dose of gypsum (Figure 4.4, Appendix 4.4a). Cattle manure and chicken manure combined with any level of gypsum were more effective than sole gypsum treatments in lowering the initial soil ESP below 5%, and cattle manure and chicken manure at a dose of 100% gypsum were the most effective (Figure 4.4a). The soil-before EC_e was decreased by over 90% with any combination, even those at any dose of gypsum, and chicken manure at a dose of 100% gypsum was the most effective (Figure 4.4b). The treatments with combined chicken manure and gypsum were more effective than the rest of the combinations for reducing soil pH (Figure 4.4c). The displaced Na^+ values were relatively congruent with those of the ESP from reclaimed soil (Figure 4.5); however, it is only an alternative representation of Na^+ removal and balance, which did not confirm the treatments' effectiveness.

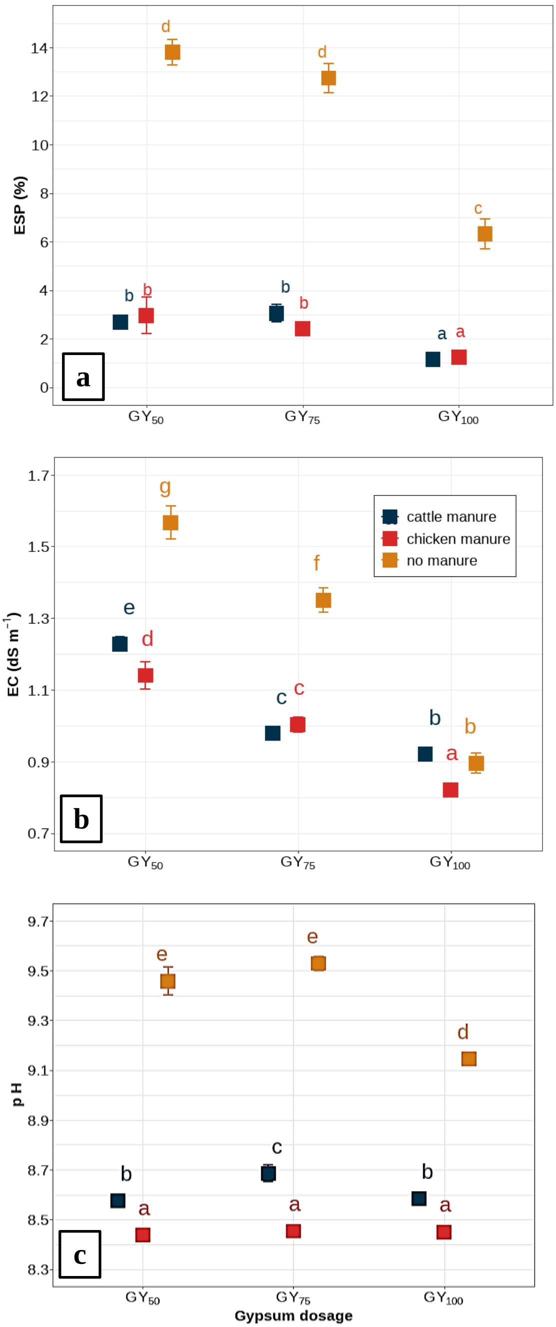


Figure 4.4 Combined effect of manures and gypsum levels on soil ESP (a), EC_e (b), and pH (c), after remediation. Means sharing a letter are not significantly different, according to the Scott–Knott test (p = 0.05). GY = gypsum.

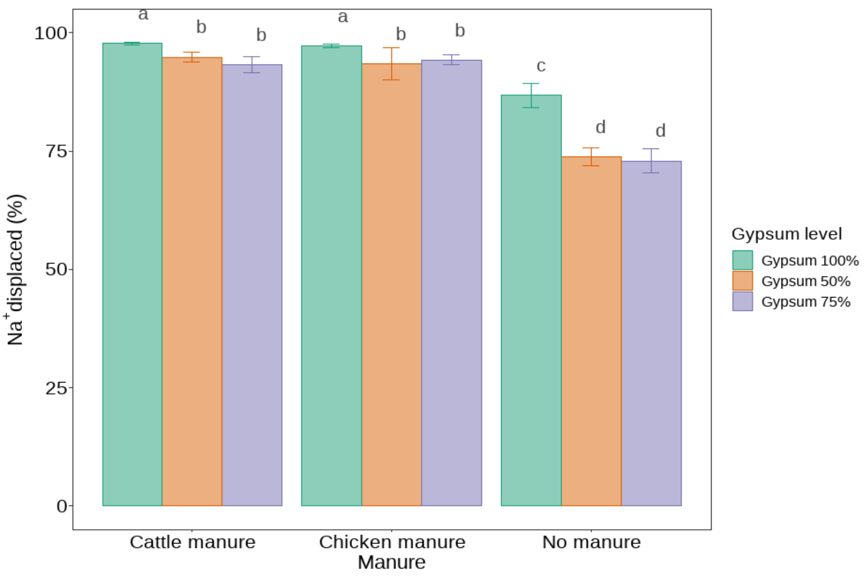


Figure 4.5 Combined effect of manures and gypsum levels on sodium displacement. Means sharing a letter are not significantly different according to the Scott–Knott test (p = 0.05).

These results agree with those from other studies on the effectiveness of organic amendments combined with gypsum, such as that of Chaganti et al. (2015) who reported that combined applications of gypsum and 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. (2012) found that gypsum application combined with partially burnt paddy husk and cow dung reduced the soil EC, SAR and pH more effectively, compared to applying gypsum alone; moreover, Abdel-Fattah (2012) observed that gypsum combined with water hyacinth compost or rice straw compost enhanced the soil amelioration process and caused a higher decrease in salinity and sodicity than gypsum alone, and in turn, than the control. In contrast, some investigations differed from these results, such as that by Hernández Araujo (2012) who found no differences among organic amendments (compost, vermicompost and *Lemna* spp) at 1.5 or 3% w/w, nor combined with gypsum; and that by Manzano Banda et al. (2014) who 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 sulphuric acid).

The effectiveness of cattle manure or chicken manure combined with any level of gypsum in reducing the soil ESP and soluble salts in the saline-alkali soil (Figure 4.4a,b) can be explained by the positive impact of organic matter from manures and

Ca^{2+} from gypsum on the soil structure, leading to an enhancement in soil aggregation, porosity, infiltration, and subsequent leaching efficiency; furthermore, although the addition of gypsum by itself improved those characteristics, the superiority of the treatments from combined amendments independent of gypsum doses, suggests that the indirect effect of organic amendments on soil physical properties, then facilitating the removal of Na^+ and salts was significant. In this regard, Ahmad et al. (2016) mentioned some factors that influence the leaching of salts and Na^+ from soil, 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. (2017) 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 (2015) 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 effectiveness of the treatments with sole gypsum compared to that with combined gypsum and manures for reducing soil salinity/sodicity (Figure 4.4) was probably due to the boosting effect from that combination besides the initial high exchangeable Na^+ of the soil and the Na^+: $Ca^{2+} + Mg^{2+}$ ratio of manures, leading to lower availability of Ca^{2+} and soil dispersion. However, the effect of sole gypsum 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 gypsum (~2–3 fold) in the presence of NaCl, meaning that relatively more Ca^{2+} could infiltrate the soluble form, agreeing with Gupta and Gupta (2019), 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 coincides with Sim et al. (2018), who found that NaCl largely increases the solubility of gypsum. In addition, Ahmad et al. (2016) 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: $GY_{100} > GY_{75} = GY_{50}$ > only water (Figure 4.4a), which coincides partially with that of Qadir et al. (1996), who also included phytoremediation by *L. fusca* (LF): GY_{100} > LF > GY_{50} > control.

The significant reduction in soil pH by combined treatments (Figure 4.4c), despite the previous high pH of the manures and soil can be due to the displacing of sodium salts, agreeing with Wong et al. (2009) who affirmed that the high initial pH of soil, most likely as a result of Na_2CO_3, 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. (2015) and Wong et al. (2009) 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 gypsum, the soil pH after remediation showed minimal variation compared to the initial pH (Figure 4.4c) likely because of the initial high ESP and soluble Na^+ leading to soil dispersion, which probably counteracted the Ca^{2+} contribution from gypsum. Because the three gypsum levels combined with manures showed relatively low mean differences with some significant differences among them for lowering the soil ESP and pH, manures with gypsum at doses of 50% and 75% can be considered as cost-efficient alternatives for further validations.

The percolation time (two cycles in 54 days) for the non-amendment treatment was considerably longer than that of the rest of the treatments (four cycles in a range of 10–35 days) as shown in Figure 4.6. This behaviour can be due to soil dispersion caused by the high exchangeable Na^+ in the soil before remediation, which can also explain the higher effectiveness in decreasing soil ESP and EC_e of sole gypsum at any level compared to that of the non-amendment treatment. Moreover, Shaygan et al. (2017) suggested that an increased percolation time and a greater rate of cation exchange were associated with a greater leaching efficiency.

Soluble salts expressed as EC (Appendix 4.4b) and SAR (Appendix 4.5) in the leachates decreased considerably for all treatments in the first leaching cycle; therefore, up to two leaching might be sufficient to reclaim this type of soil, at least under controlled conditions. This behaviour can be related to the increased leaching rate triggered by amendments and subsequent soil flocculation, which counteracted the soil dispersion caused by the high sodicity of the soil before remediation. These results agree with Abdel-Fattah (2012) who mentioned 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. (2016) and Hassan et al. (2011), who reported a higher removal of Na^+ in the first leaching cycle than that in the following leachates, coinciding with higher hydraulic conductivity; moreover, 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 influenced by the high initial EC_e of soils that keeps them flocculated to pass the solution (Ahmad et al., 2006).

It is important to highlight the fact that the original soil condition was altered before the column experiments for its homogenization as a controlled factor, and there was no measurement of soil-water properties as hydraulic conductivity or water retention, leading to a limitation in terms of interpretation and extrapolation of the findings to field conditions.

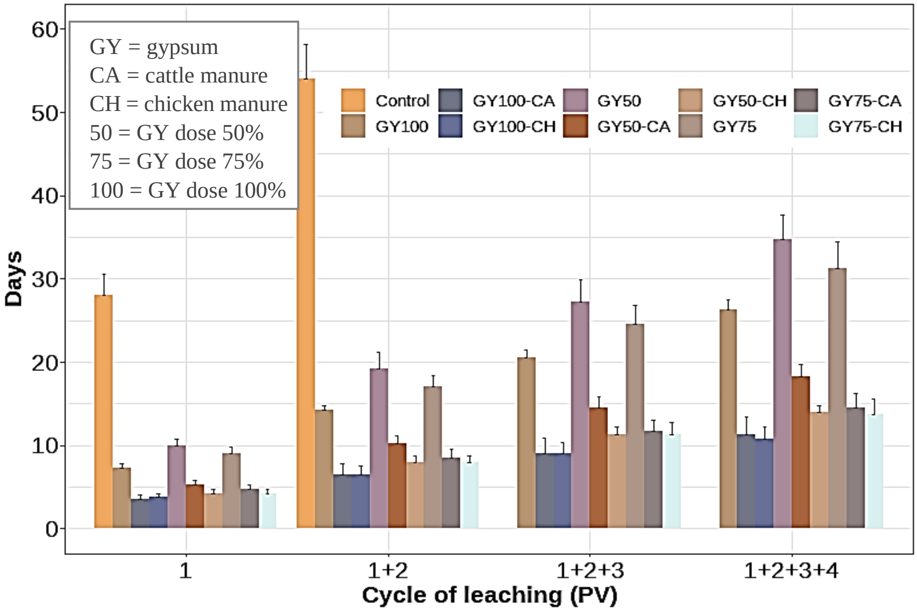


Figure 4.6 Percolation time in cumulate days in function to the applied leaching cycles (1^{st}, 2^{nd}, 3^{rd}, and 4^{th}). PV = pore volume

Further research could assess different soil textures, other gypsum levels, and lower rates of manures. Moreover, other studies could evaluate a two-step process of washing with gypsum followed by organic amendment similar to that of Sastre-Conde et al. (2015), the influence of mulch with gypsum as investigated by Zhao et al. (2020), and the inclusion of phytoremediation techniques as studied by Qadir et al. (1996).

The results from the field experiment showed that all treatments, except the control, were equally effective in decreasing the initial soil ESP; however, none of the treatments were effective in reducing the soil EC (Annex 7). These outcomes may be attributed to the water deficit caused by delayed rainfall in the early drought period and excessive evaporation during the remediation process. Therefore, further validation is needed, with the field experiment setup placed either at the beginning or middle of the rainy season.

4. Conclusions

Individual gypsum at a dose of 100% of the calculated requirement was the most effective in improving the soil ESP and EC_e, followed by gypsum at 50%; this can be attributed mainly to the calcium from gypsum which displaces the sodium and improves soil-water properties. Treatments with sulphur were less efficient than those with gypsum for improving soil sodicity, probably due to the short incubation time besides the low soil organic matter content.

Cattle manure at a dose of 2% organic matter was the best for decreasing soil ESP to 27.6%, and any treatment was more effective than that without amendment in lowering EC_e below 4 dS m^{-1}. Peat at a dose of 2% generated the highest reduction of soil pH (to 7.76). The superiority of cattle manure in reducing soil ESP and EC_e was mainly due to the improvement of the soil structure through its organic matter and divalent cations contribution, whereas peat and biochar were less effective probably due to their influence on soil clogging and slowdown of leaching.

The combined treatments of cattle manure or chicken manure with any level of gypsum were more effective than those of sole gypsum at any dose in reducing the initial soil ESP to below 5%, and any manure with 100% gypsum was most efficient. The soil before EC_e and ESP levels decreased to below 1.6 dS m^{-1} and 14%, respectively, with any combination of amendments or sole gypsum at any level, except only water. Any combination of manure with gypsum lowered the pH to below 8.7. The effectiveness of combining organic amendments with gypsum can be explained by their synergistic effect on Na^+ displacement resulting in the subsequent improvement of soil porosity, flocculation, and infiltration, leading to an enhancement in the leaching process. Manures with 50% and 75% gypsum levels could be an alternative to the 100% gypsum dose. Soluble salts and sodium were considerably lowered in all treatments during the first leaching cycle.

Individual gypsum or cattle manure with leaching can be used to remediate sodic and saline-sodic soils; furthermore, the addition of cattle manure or chicken manure might enhance the effectiveness of gypsum with leaching for that amelioration; however, further validations through field experiments including different soil types and doses are needed.

Chapter 5

General discussion, perspectives, and conclusion

1. General discussion

As a contribution to the management and rehabilitation of salt-affected soils in the High Valley of Cochabamba - Bolivia, this study addressed various problems related to soil salinity and sodicity through the objectives formulated from research questions (section 4 - Chapter 1). Some aspects that have been left outside the scope of the study were: the identification and level of influence of drivers of salinization, the description of salinization processes, dynamics as spatiotemporal analysis, mapping, and other restoration strategies such as flushing, phytoremediation and biosaline agriculture, all of which were excluded due to the availability of resources, time and scientific pertinence, but can be considered in subsequent research. Following this, a general discussion of the findings (Chapters 2, 3 and 4) from this study:

1.1. Characterization and classification of salt-affected soils

The characterization of eight soil profiles comprises the determination of chemical, physical, and morphological properties (sections 3.2 - 3.4, Chapter 2) as well as taxonomic classification (section 3.5, Chapter 2). High levels of sodicity and soil reaction were found along the horizons in the profiles' depth of Santa Ana (SP 1), Aramasi (SP 4), and San Benito (SP 3), besides a high soil salinity in their top horizons, which in turn were classified as Sodic Solonchak (Hypersalic, Siltic), Salic Solonetz (Hypernatric, Siltic, Protocalcic), and Salic Solonetz (Natric, Siltic), respectively.

The comparative analysis between the output categories and salinity/sodicity distributions from two salt-affected soil classification systems somehow demonstrates the potential impact of such differences on soil management and restoration, since the saline-sodic soil class from the USSL classification normally behaves as saline or sodic, nonetheless, such confusion can be overcome by the Alternative classification (Chhabra, 2004) which prioritizes the nature and ratios of soluble salt ions above the soil ESP, EC_e and pH. Saline-sodic and saline soils (USSL method) and saline soils (Alternative method) were dominant in the sampling (section 4.1 - Chapter 2). It should be remarked that any classification system has implicit limitations for the identification of soil categories because its specific indicators of salinity/sodicity and threshold values (Rengasamy, 2016; Chhabra, 2004) are site-specific and normally based on the degree of affection to the soil condition and/or crop growth, thus subject to variability in terms of soil types and crop characteristics, hence the importance of generating or adapting a tailored classification system for a given region.

As for the previous spatial predictions of salinity and sodicity in the High Valley by Weber (2018) and Araujo (2009), the spatial interpolation of soil ESP and EC was unsatisfactory due to the insufficient spatial correlation mainly caused by the limited number of observations about the surface of the study area and the imbalance caused by the excess non-salt-affected observations (section 4.2 – Chapter 2). Regarding the soil texture, most of the samples were classified as loam, silty-loam, clay-loam, and silty-clay-loam, according to the USDA system; additionally, it is important to highlight the low soil organic matter as total organic carbon (mean of 0.7% ± SD of 0.5%) for the whole sampling (section 4.3 – Chapter 2), considering the influence of organic matter on soil water properties and on the mobilization of Ca^{2+} from dissolved calcite, which in sum can potentially reduce the soil salinity and sodicity (Chaganti et al., 2015; Choudhary and Kharche, 2015).

The low representativeness of the soil information database led to its limited usefulness for the characterization, classification, and spatial prediction of salt-affected soils; in this regard, the survey was carried out according to methodological parameters (Weber, 2018) in terms of sampling size and sampling method, which was systematic-random for achieving a significant coverage of the area; however, the salt-affected soil samples were insufficient; therefore, complementary sampling and stratification can increase the representativeness of the soil database. Despite such limitations, the soil information represented a baseline for this study as well as an approximation for the current status of salt-affected soils in the High Valley.

1.2. *Prediction of salinity and sodicity*

The objective of generating predictive models lies in the need to reduce costs and time, rather than in forecasting values of interest; for instance, the determination of the ESP in soils is both time-consuming and costly (Keshavarzi et al., 2016). Like soil classification systems, predictive models are subject to local and specific characteristics; thus the accuracy of a given model is normally higher for the site in which it was developed because of the specific soil textures and other local factors. If models to predict soil salinity are developed in one specific area, they cannot be applied to another region because of differences in soil properties such as organic matter content and/or salt type (Das et al., 2023; Kahaer and Tashpolat, 2019). Therefore, models for predicting soil sodicity/salinity variables must be site-specific and subject to continuous improvement for local use. It is also important to note the link between the use of all the major soluble salt ions as explanatory variables in Chapter 3 and the Alternative classification (Chapter 2) which prioritizes the nature and proportion of these ions above/beside the conventional indicators (soil ESP, EC and pH) to properly classify salt-affected soils, thus we foresee their inclusion not only in conventional but also in complex predictive models.

The machine learning (ML) algorithms of support vector (SV) and random forests (RF) regressions performed the best in predicting the soil EC_e, as well as RF for estimating the soil ESP (section 3.1 – Chapter 3). The RF classification followed by SVM was superior in predicting salt-affected soil categories (section 3.2 – Chapter 3). As a result of the variable importance analysis through the RF algorithm, the most relevant explanatory variables were Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and HCO_3^-; however, this ranking relies on the heterogeneity of the samples and the sensitivity of the model. Additional explanatory variables (soil texture, pH and TOC) only improved the SV and PLS regression to predict ESP and the RF classification, which means that supplementary predictors, not only field-measured soil properties (Keshavarzi et al., 2016) but other easily obtained features – mentioned and cited in Chapter 3 – can significantly increase the accuracy of ML models.

According to the performance evaluation of multivariate regressions to predict soil ESP as a function of other chemical properties (EC, pH and SAR), the model to estimate soil ESP from EC and SAR, and that from pH, EC and SAR were acceptable and similar to that from only SAR, which in turn, agrees with Annex 4; moreover, the multivariate models to predict soil ESP and EC from easily obtained geomorphometric and remote sensing-based features showed a relatively low performance (section 3.3 – Chapter 3), mainly due to the insufficient observations and the distortion caused by excess non-salt-affected samples in the features that normally correlate well with salt-affected soil, such as salinity indices and some geomorphometric indices; in this sense, additional samples and features along with refinement and stratification, could improve the models' performances, also considering the methodology from some studies cited in Chapter 3. As a remark, the soil EC was considered as a response variable even though it is an easily measured property, because of its applicability in spatial predictions.

Based on these results, the RF and SVM algorithms might be appropriate to predict soil EC_e, ESP, and salt-affected soil categories from soluble salt ions, as well as the models to estimate the soil ESP from either SAR, EC + SAR or EC + SAR + pH, might contribute to the monitoring and management of salt-affected soils in the High Valley; however, additional samples and geo-environmental covariates, along with alternative modelling techniques and refinement can enhance their accuracy. In terms of limitations, although some ML models obtained good prediction effectiveness, overall models' performances need to be improved before using them to estimate sodicity/salinity variables in the study area.

1.3. Remediation of salt-affected soils

The previous soil-column experiment showed that gypsum outperformed sulphur in lowering soil ESP, either gypsum or sulphur or water alone was effective in decreasing soil EC_e; and also, that cattle manure or chicken manure was more effective than biochar and peat in improving soil sodicity, and any amendment except water alone was effective in improving soil salinity (sections 3.1, 3.2 – Chapter 4). The superiority of gypsum was mainly due to its Ca^{2+} content which displaces the exchangeable Na^+ and improves the soil-water properties, and the low effectiveness of sulphur was probably due to the insufficient time of incubation and organic matter needed for Ca^{2+} formation, while manures performed the best mainly due to their organic matter and divalent cations contribution, which improve the soil structure and infiltration, whereas the peat and biochar were less effective probably due to their influence in clogging soil pores. The second soil-column experiment aimed to evaluate the combined effect of manures and gypsum showed that cattle manure or chicken manure along with gypsum at any dose was more effective than gypsum alone at any level in reducing the initial soil ESP to below 5%, any combination of amendments or gypsum alone at any dose was efficient in lowering the soil EC_e to below 1.6 dS m^{-1}, and any combination of manure with gypsum lowered the pH to below 8.7 (section 3.3 – Chapter 4). The higher effectiveness of manures combined with gypsum in reclaiming soil sodicity/salinity can be explained by their synergistic effect on Na^+ displacement and improvement of soil structure, leading to an enhancement of the leaching process. Even though gypsum or manure alone can effectively improve soil salinity/sodicity, the addition of manure might enhance and hasten the effect of gypsum with leaching in ameliorating saline-sodic soils, agreeing with Chaganti et al. (2015), Prapagar et al. (2012) and Abdel-Fattah (2012), who confirm the superiority of the combined amendments over gypsum alone; however, additional experiments mainly under field conditions are needed to validate these results as well as to enrich the insights into amendment-based amelioration, before promoting results among the farmers.

Some reasons that amendment-based remediation techniques were prioritized above other restoration methods were: (1) Mineral/chemical amendments are widely used because of their direct effect on the displacement of adsorbed Na^+ through their Ca^{2+} contribution; (2) however, they are sometimes cost-intensive (Qadir et al., 2007), therefore organic amendments can be an alternative either for replacing or enhancing the effect of mineral amendments (Prapagar et al., 2012), through their indirect amelioration effect in improving the soil-water properties (Qadir et al., 2001); also although, (3) shoot-succulent halophytes can accumulate significant Na^+ quantities within their above-ground organs, and despite these can be insignificant compared to the ability of some plants to solubilize $CaCO_3$ then release Ca^{2+} ions to substitute Na^+ in calcareous sodic or saline-sodic soils through their root respiration and H^+ release (Qadir et al., 2007; Qadir et al., 2001b), (4) which is also water/irrigation dependent and thus infeasible in arid and semi-arid regions (Shahid, 2002); and then, (5) although mineral amendments being also water dependent, their amelioration effect is normally higher and accomplished in a shorter time than that of phytoremediation and even organic amendments; consequently (6) the study mainly addressed the combination between mineral and organic amendments for remediating salt-affected soils. Furthermore, the reason that experiments under controlled conditions were carried out instead of under field conditions was to obtain specific results and variability by controlling factors and to evaluate more treatments in a shorter time, which is unfeasible under field conditions.

In terms of limitations, despite these experiments under controlled conditions showing that organic and/or mineral amendment additions along with leaching were effective in remediating saline-sodic soils, the findings are still not suitable for diffusion among the farmers and decision-makers, as more assessments – mainly under field conditions – are needed. Moreover, it should be emphasized that the soil columns did not effectively mimic the natural condition of soils from the field, since the soil cores were altered and homogenized before the column experiments; therefore, these evaluations also aimed the balance between the benefit of testing in non-disturbed as a mimicry of the natural soil, and the need of altering and homogenizing the soil to control as much as possible the experimental factors. Paradoxically, the physical condition of the non-disturbed soil was relatively similar to that of the altered soil probably due to its highly sodic thus dispersed condition.

The soil hydraulic conductivity was not effectively measured, which is indispensable to discuss the behaviour of the lixiviation process and its implication in the leaching of salts and the amelioration effect in the soil; even so, the percolation time was measured (section 3.3 – Chapter 4), which is normally strongly and negatively correlated with hydraulic conductivity and infiltration. Further experiments should not only include the assessment of soil-water properties but also that of different soil textures as investigated by Ahmad et al. (2016); Hassan et al. (2011) and Kahlon et al. (2013).

Despite the biochar, peat and sulphur not being as effective as gypsum and manures, it is important to note the environmental aspects such as the origin and ecosystem services for these and other similar amendments, which must be addressed in further investigations and subsequent agricultural extension; as for the temperate peat bogs, Barkham (1993) highlighted the need for proper management of peat resource in a sustainable way, not only from the economic perspective but also from the ecosystem services, thus human well-being. In the context of the study, there are no specific regulations addressing the origin, processing and use of temperate/tropical peat and biochar for soil restoration purposes.

Finally, about the socio-economic aspect, these results might boost the rehabilitation of salt-affected soils in the High Valley and contribute to the enhancement of the soil/crop productivity, thus the farmer’s income. Eventually, farmers can also access alternative sources of income by cultivating value crops under biosaline agriculture.

2. Future perspectives

To improve the representativeness, significance and usefulness of the baseline soil information, also considering the large surface of the study area, complementary sampling should be added to the soil database and additional soil profiles should be assessed, using the same protocols for sampling and measurements as those used in this study. Moreover, a subsoil sampling can be considered because of the behaviour of soluble salts in function to soil-water dynamics within the soil depth. Alternative sampling strategies such as stratified, covariate space coverage sampling (Brus, 2022) and conditioned latin hypercube (Minasny and McBratney, 2006) can also improve the significance of the soil information database. Considering the heterogeneity of soils within the High Valley and compared to other regions, it is important to define a site-specific classification system based on the adaptation and validation of at least the USSL (Richards et al., 1954) and the Alternative (Chhabra, 2004) criteria, along with their threshold values. Furthermore, the assessment of the sources of salts, irrigation water resources, mineralogy of clays, spatiotemporal analysis, and environmental/social aspects, among other factors affecting the salinization processes, is essential for achieving comprehensive soil management.

As for the baseline soil information, additional observations might enhance the accuracy of prediction models, following the above recommendations about using similar protocols and alternative sampling methods. The use of easily obtained features as model covariates, such as those from remote sensing, geomorphometry, and physiography, among other geo-environmental characteristics and lab/field-measured properties, can significantly improve the performance of models in predicting soil salinity and sodicity, thus improving the classification and spatial prediction of salt-affected soils. Aiming to reduce the costs for the measurement of salinity/sodicity variables, it is also recommended to generate regression models to predict soil EC, pH and soluble ions measured in paste extract in function to similar variables but easily measured in different soil:water suspensions. It should be remarked that although the numerous models already obtained by various authors, it is critical to develop site-specifically tailored models, considering the heterogeneity of soil types and soluble/adsorbed ions complexes in the soil. Finally, alternative novel methods as machine learning and deep learning algorithms can be trained and validated to evaluate and compare their performances.

Regarding the amendment-based remediation, evaluations under field conditions are needed to accomplish results closer to real conditions than those under controlled conditions, then can be recommended to the farmers; in this context, it is important to validate the best-performed treatments from this study through on-field experiments such as that carried out by Quispe Zenteno et al. (2020) (Annex 7). However, additional experiments under controlled conditions are essential for assessing multiple factors such as various amendments, soil types and multiple doses (25%, 50%, 75%, 100% and 125%). It is also recommended to assess soil-column instead of pot experiments, because of its height, soil volume and subsoil layer, which mimic the natural conditions of soil in a better way than that of the pots.

It could be important to research alternative remediation strategies such as phytoremediation, leaching/irrigation techniques, and physical/mechanical methods, among others, taking into account the limitations such as inputs' costs, low availability of non-saline water, low farmers' income, heterogeneity of soils, water-soil dynamics and semiarid condition in the High Valley. Regarding the phytoremediation strategy, Mamani Flores et al. (2020) assessed the phytodesalination capacity of four halophytes and found that the native halophytes *Suaeda fruticosa* Moq and *Sesuvium portulacastrum* were more effective than the alien halophytes *Atriplex hortensis* and *Kochia scoparia* in removing Na^+ from soil (Annex 8). Other remediation techniques such as phytoremediation and organic matter addition can significantly improve soil health and thus the environmental conditions. Moreover, the origin of minerals and organic materials must be subjected to environmental evaluations before considering their use as potential amendments for salt-affected soil amelioration, either for research or promotion among the farmers.

In sum, considering the semiarid conditions in the High Valley, the use of mineral and/or organic amendments and phytoremediation based on calcite dissolution can be unfeasible mainly due to their water dependence, in contrast to the phytoremediation based on harvesting Na^+ from soil but inviable in terms of desalination capacity compared to the previously mentioned strategies (Qadir et al., 2007; Alemayehu and Haile, 2022); therefore, the biosaline agriculture (Negacz et al., 2021) as an adaptation strategy may be viable through the adaptive and subsequent agronomical evaluations of crops with low to high tolerance to salinity and sodicity, such as value halophytes (e.g. quinoa), forages, cover crops and vegetables among others.

Considering that soil salinity and sodicity are the main types of land degradation in the High Valley of Cochabamba, these findings are only the starting point to push forward policies, technical efforts and research. In this context, additional factors which drive salinization processes should be considered in further assessment, such as deforestation, residual waters, use of fertilizers, etc. Overall, these results represent the foundations as baseline information and tools to be considered by all the stakeholders for boosting the sustainable management of salt-affected soils in the High Valley. From the perspective of research, these results become a baseline for further improvement and validation. Relevant stakeholders are the University (FCAyP – UMSS) and the National Institute of Agricultural, Livestock and Forestry Research (INIAF – Bolivia). Within the agricultural sector, although the farmers are normally organized in associations, it is more feasible to coordinate with the municipalities for conducting activities on agricultural extension and research.

3. General conclusion

As the study aimed to contribute to sustainable management and effective rehabilitation of salt-affected soils in the High Valley of Cochabamba, the following general conclusions address the research questions and objectives.:

The baseline soil information and database, as a foundation for managing and monitoring salt-affected soils in the High Valley of Cochabamba, require improvement through additional sampling and assessment to enhance representativeness. Furthermore, the classification system should be tailored to the study area to enable precise identification and management of these soils.

The random forest and support vector machine algorithms, along with certain conventional multivariate models, may be suitable for estimating soil ESP, EC, and classifying salt-affected soils from soluble ions, other soil properties, and easily obtained features in the study area. Although these models meet the need for site-specific prediction tools, they require enhancement for greater accuracy through larger datasets and additional predictors.

Gypsum as a mineral amendment and cattle or chicken manure as an organic amendment were most effective in improving soil salinity and sodicity, particularly when combined. However, further assessment is needed under both controlled and field conditions, incorporating locally available amendments and considering socio-economic and environmental factors. Additionally, other amelioration strategies, such as phytoremediation and biosaline agriculture, may be evaluated given the semi-arid conditions of the valley.

The study results and some implications are summarized by objective in Table 5.1.

In summary, this study highlights the following key points:

Sustainable management and rehabilitation of salt-affected soils in the High Valley of Cochabamba rely on accurate classification, precise estimation, and effective amelioration of saline/sodic soils; consequently, this study contributes to these goals by providing: (1) comprehensive baseline soil information, (2) a foundation for tailored prediction and classification tools, and (3) insights into amendment-based remediation techniques—all of which require further refinement.

Table 5.1. Summary of the relevant findings of this study

Chapter	Objective	Results	Significance/perspectives
Chapter 2	Characterization of SAS samples and profiles	Database soil information Characterization of profiles (section 3)	Baseline for SAS management Further enhancement through additional samples
	Classification of SAS	Comparison between two systems (section 4)	
Chapter 3	Performance evaluation of ML-based models to predict salinity, sodicity and soil classes from soluble ions	EC_e: SV-R ≈ RF-R > PLS-R *ESP*: RF-R > SV-R ≈ PLS-R SAS classes: RF-C > SVM > PLS-DA	Prediction tools for SAS management and monitoring Further improvement of accuracy by adding observations and predictor variables
	Performance evaluation of models to predict soil ESP from soil properties and ESP/EC from other features	*ESP*: $f(SAR) \approx f(SAR+EC) \approx f(SAR+EC+pH)$ *ESP*, EC_e: f (other features - section 3.3)	
Chapter 4	Effectiveness evaluation of mineral amendments	*ESP*: $GY_{100}^{a} > GY_{50}^{b} > SU_{100}^{c} > SU_{50}^{d} > NA^{e}$ EC_e: $GY_{100}^{a} > GY_{50}^{b} > SU_{100}^{c} > SU_{50}^{d} \approx NA^{d}$	Insight into the most effective organic or/and mineral amendment(s) for ameliorating sodic-saline soils Further evaluation mainly under field conditions
	Effectiveness evaluation of organic amendments	*ESP*: $CA_2^{a} > CA_1^{b} > BI_1^{c} \approx NA^{c} \geq PE_1^{cd} \approx PE_2^{cd} \geq BI_2^{d}$ EC_e: $CA_2^{a} \approx CA_1^{a} \geq BI_2^{ab} \approx PE_2^{ab} \geq PE_1^{b} \approx BI_1^{b} > NA^{c}$	
	Effectiveness evaluation of combined amendments: gypsun and manure	*ESP*: $CA\text{-}GY_{100}^{a} \approx CH\text{-}GY_{100}^{a} > CA\text{-}GY_{75}^{b} \approx CH\text{-}GY_{75}^{b} \approx CA\text{-}GY_{50}^{b} \approx CH\text{-}GY_{50}^{b} > GY_{100}^{c} > GY_{75}^{d} \approx GY_{50}^{d}$ EC_e: $CH\text{-}GY_{100}^{a} > CA\text{-}GY_{100}^{b} \approx GY_{100}^{b} > CA\text{-}GY_{75}^{c} \approx CH\text{-}GY_{75}^{c} > CH\text{-}GY_{50}^{d} > CA\text{-}GY_{50}^{e} > GY_{75}^{f} > GY_{50}^{g}$	

SAS = salt-affected soils, ESP = exchangeable soil percentage, EC = electrical conductivity, SAR = sodium adsorption ratio
RF = random forests, SVM = support vector machines, PLS = partial least squares, DA = discriminant analysis, R = regression, C = classification
GY = gypsum, SU = sulphur, CA = cattle manure, CH = chicken manure, BI = biochar, PE = tropical peat, NA = no amendment, subscripts of 50, 75 and 100 mean the percentage dose of gypsum, subscripts of 1 and 2 mean the percentage dose of organic matter (w/w), and superscripts as letters represent the mean comparison at $p<0.05$ (not significantly different if sharing a letter)

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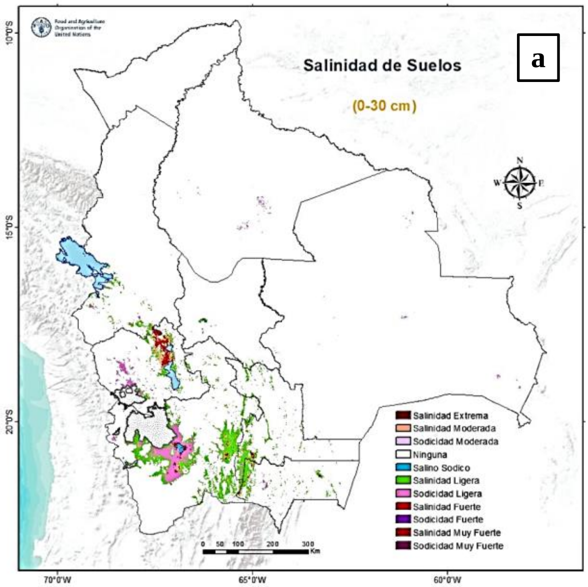
Appendices

Appendix 1.1



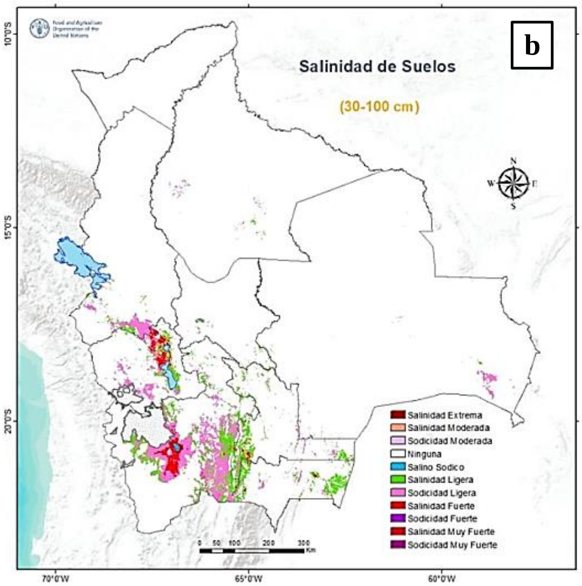


Figure A1.1 Spatial distribution of salt-affected soils in Bolivia (FAO/ 'Viceministerio de Tierras', 2020)

Appendix 1.2

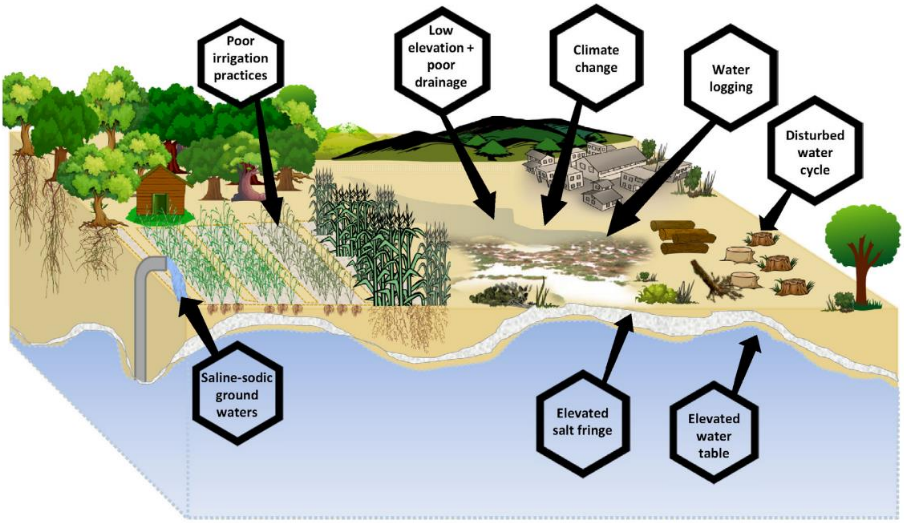


Figure A1.2a Some causes of salt accumulation in soils (Kumar et al., 2022).

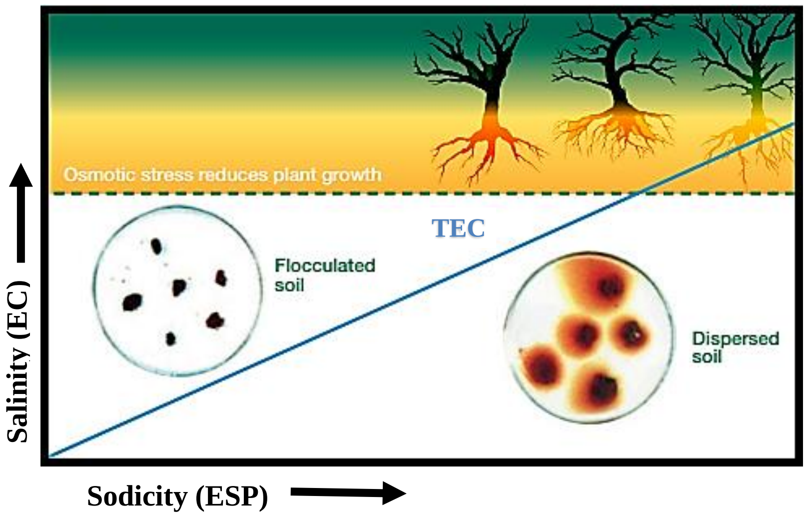


Figure A1.2b Empirical relationship between sodicity (ESP) and salinity (EC) (Rengasamy, 2016).

Appendix 1.3

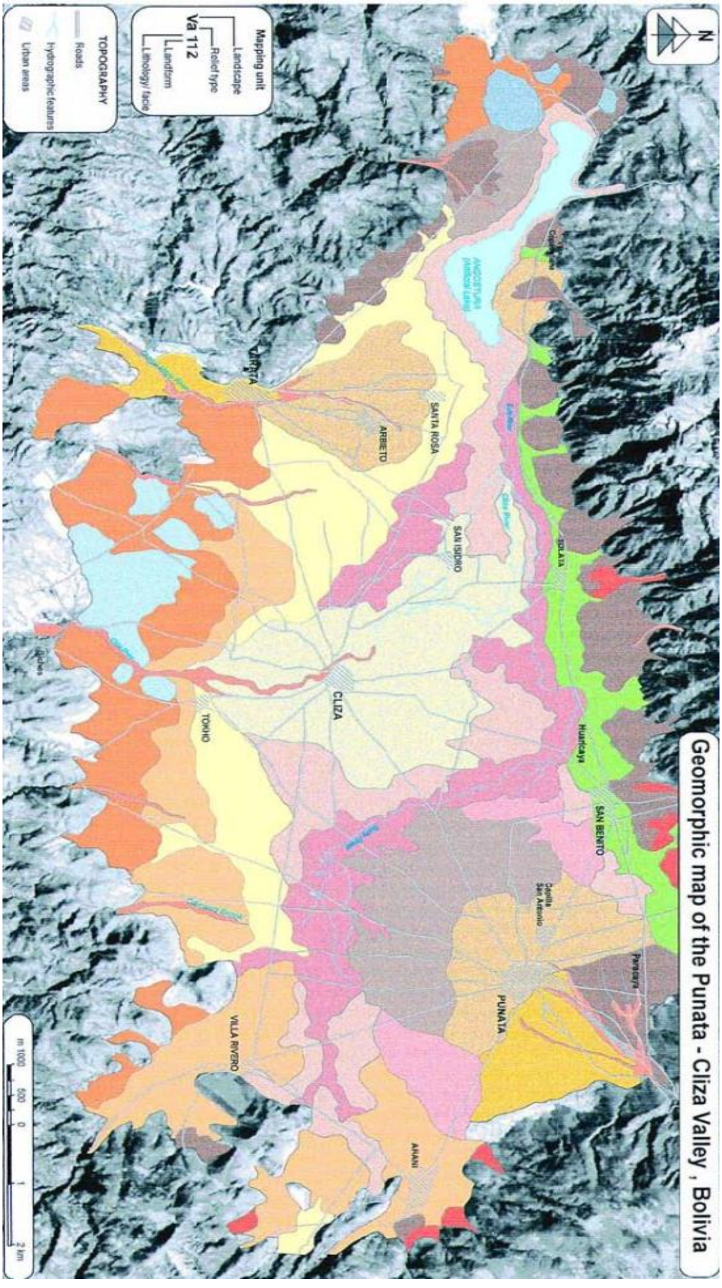


Figure A1.3 Geopedologic map - High Valley, Cochabamba, Bolivia (Metternicht, 1996)

GEOPEDOLOGIC LEGEND					
LANDSCAPE	RELIEF TYPE	FACIES	LANDFORM	CODE	SOILS
PIEDMONT	Dissected-depositional glacis	Alluvial	Proximal	Pi 111	*Association:* Typic Calciorthids, Typic Camborthids
			Central	Pi 112	*Consociation:* Typic Camborthids (ca)*, Ustochreptic Camborthids
			Distal	Pi 113	*Association:* Ustalfic Haplargids, Ustochreptic Camborthids
	Depositional glacis	Colluvio-alluvial	Distal	Pi 213	*Consociation:* Ustochreptic Camborthids, Typic Camborthids
	Active fans	Alluvial	Active channels	Pi 411	*Miscellaneous land type:* Mixed Alluvial
			Inactive channels	Pi 412	*Consociation:* Typic Torrifluvents, Typic Torriorthents
	Recent fans	Colluvio-alluvial		Pi 51	*Association:* Ustic Torriorthents, Typic Torrifluvents
	Old dissected fans	Glacio-alluvial	Proximal	Pi 661	*Association:* Typic Camborthids, Typic Haplargids
			Central	Pi 612	*Consociation:* Ustochreptic Camborthids (ca)*
			Distal	Pi 613	*Consociation:* Ustochreptic Camborthids
	Hills	Quartzitic sandstones		Pi 71	*Consociation:* Lithic Torriorthents
		Marls sandstones limestones		Pi 72	*Consociation:* Typic Calciorthids, Lithic Calciorthids
VALLEY	Lagunary depressions	Alluvio-lagunary	Higher lagunary flats	Va 111	*Association:* Fluventic Camborthids, Ustochreptic Camborthids
			Middle lagunary flats	Va 112	*Association:* Ustalfic Haplargids, Ustochreptic Camborthids
			Lower lagunary flats	Va 113	*Association:* Ustalfic Haplargids (saso)*, Ustochreptic Camborthids (sa)*
		Lagunary	Playas	Va 124	*Association:* Typic Salorthids, Natric Camborthids

* Phases: (ca) calcareous (saso) saline-alkaline (sa) saline

LEVEL	CATEGORY	GENERIC CONCEPT	SHORT DEFINITION
6	Order	Geostructure	Large continental portion characterized by a broad geologic structure (e.g., cordillera, geosynclinal basin)
5	Suborder	Morphogenetic environment	Broad type of biophysical medium originated and controlled by a style of internal and/or external geodynamics (e.g., structural, depositional, erosional)
4	Group	Landscape	Large portion of land characterized by a repetition of similar relief types or an association of dissimilar relief types (e.g., valley, piedmont, mountain)
3	Subgroup	Relief/molding	• Relief as determined by a given combination of topography and geologic structure (e.g., cuesta, horst) • Molding as determined by specific morphoclimatic conditions or morphogenetic processes (e.g., glacis, terrace, delta)
2	Family	Substratum	• Lithology of hard rocks (e.g., gneiss, sandstone) • Facies of soft cover formations (e.g., periglacial, lacustrine, alluvial)
1	Subfamily	Landform	Conspicuous basic geoform type, characterized by an unique combination of geometry, dynamics and history (e.g., levee, dune, backslope, flat)

Appendix 2.1

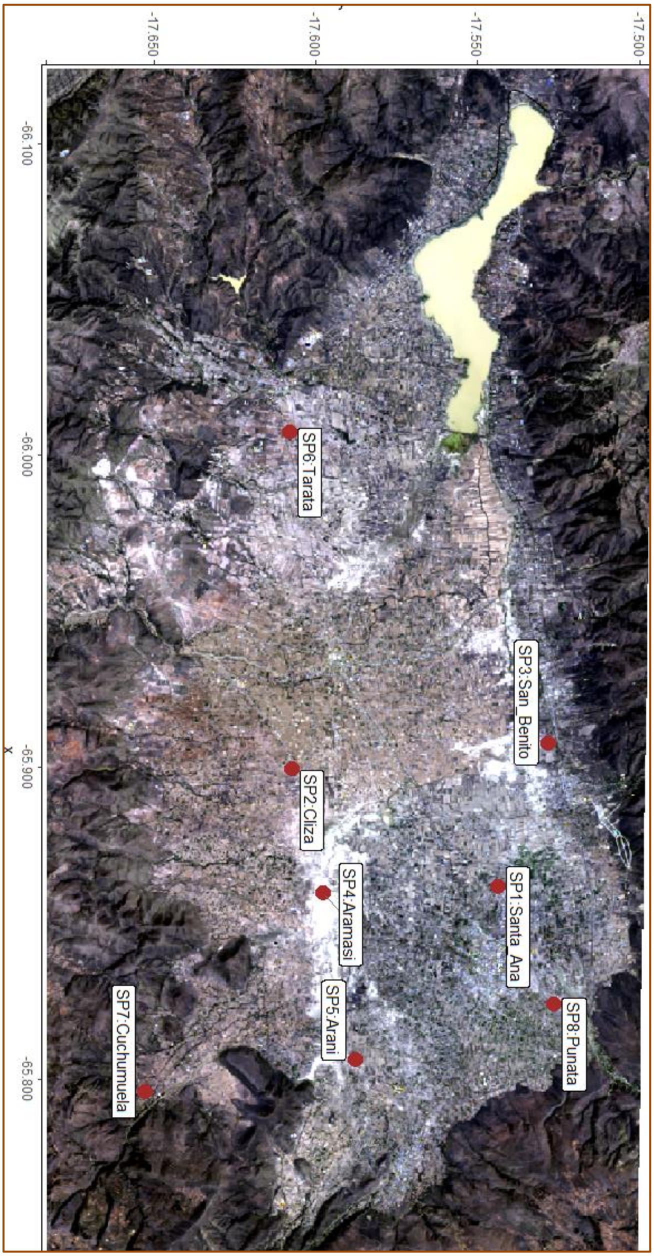


Figure A2.1 Spatial location of the soil profiles in the High Valley of Cochabamba.

Appendix 2.2

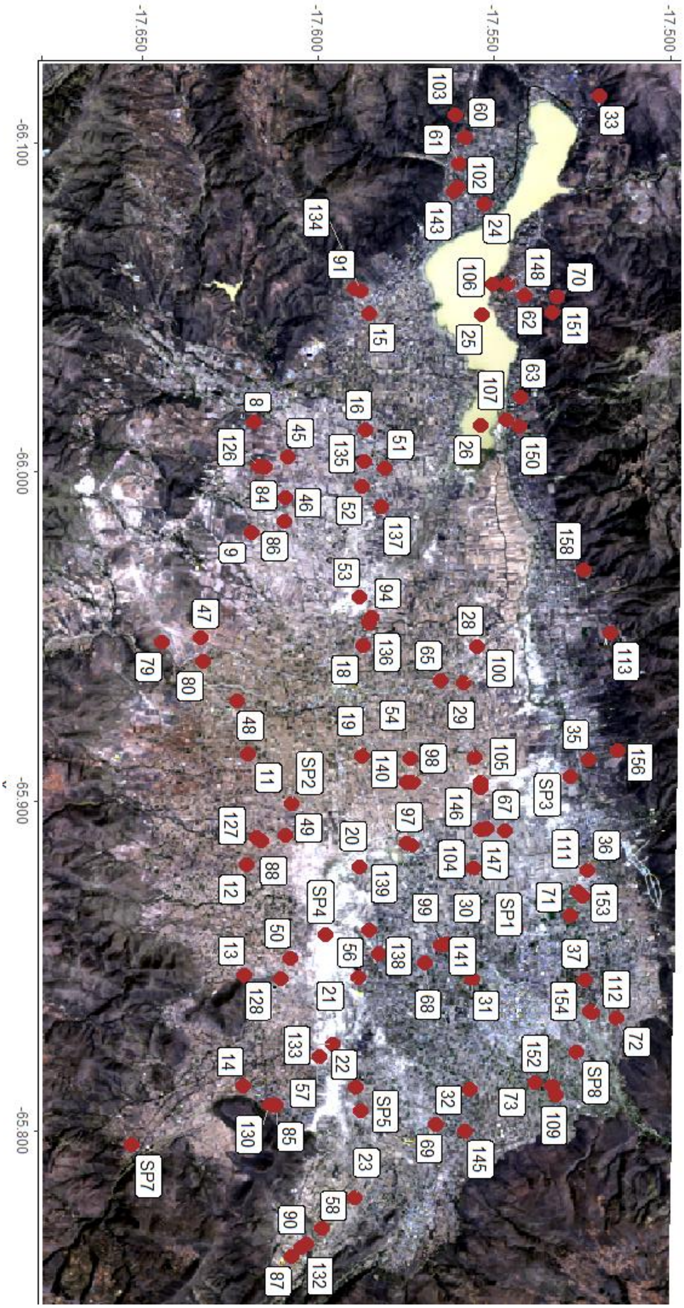


Figure A2.2 Spatial location of the soil samples in the High Valley of Cochabamba.

Appendix 2.3:

Table A2.3 Summary of the field form used for soil description (adapted from FAO, 2006)

Soil-formation factors	**Soil-surface characteristics**
Weather (present/trainer)	Rocks outcrops
Soil climate (temperature/mould)	Coarse surface fragments (cover, size)
Major Landform	Erosion (category, degree)
Position (undulating, flat)	Surface sealing (width, depth, distance)
Slope (form, gradient)	Surface cracks (width, depth, distance)
Land use / Vegetation / Crops	Salt (cover, thickness)
Human influence	

SOIL DESCRIPTION - HORIZONS	
Horizon boundary Depth HB (cm) Distinctness (cm) Topography	***Primary constituents*** Texture of the fine earth fraction Rock fragments: Abundance / Size / Shape
Soil colour (matrix) Munsell colour Chart	***Mottling*** Mottles: Colour (Munsell) / Abundance / Size /Contrast / Boundary
Carbonates, gypsum, salts Carbonates, Gypsum: Content / Form Salt content (EC,25 ºC)	***Field soil pH*** pH value
Redox Reducing conditions (Munsell colour)	***Odour*** Soil odour
Organic matter content Organic matter estimation (Munsell)	***Bulk density*** Bulk density (g/cm3)
Organization of constituents Structure: Grade / Type / Size Soil-water status Consistence: Dry / Moist / Stickiness / Plasticity	***Voids (porosity)*** Porosity Voids: Type, Abundance (dm^2) and Size (< > 2mm) / Very coarse (20–50mm)
Concentrations Coatings: Abundance / Nature / Form Compaction: Degree / Nature / Structure / Continuity	***Concentrations*** Mineral concentrations: Kind / Size / Shape / Nature / Hardness / Colour / Abundance
Biological activity Roots size (diameter <2mm, >2mm) Roots abundance Biological features: Kind / Abundance	***Human-made materials*** Artefacts - kinds Transported material

Appendix 2.4

Table A2.4a Soil chemical properties: salinity/sodicity parameters (ESP, EC and pH) and exchangeable cations for each horizon of the non-salt-affected soil profiles.

Soil profile	Horizon	Exchangeable cations ($mmol_c\ kg^{-1}$)				Soil salinity variables			
		Na^+	K^+	Ca^{2+}	Mg^{2+}	pH	EC $dS*m^{-1}$	ESP* %	Class USDA**
SP 6 Tarata	AP	0.00	0.01	0.30	0.02	7.46	1.24	1.2	Normal
	AB	0.00	0.01	0.28	0.02	7.33	1.92	0.5	Normal
	C1	0.00	0.01	0.35	0.02	7.50	0.79	0.2	Normal
	C2	0.00	0.00	0.26	0.02	7.50	0.72	0.2	Normal
	C3	0.00	0.00	0.25	0.02	7.49	0.75	0.4	Normal
SP 7 Cuchumuela	Ap	0.00	0.01	0.07	0.02	7.50	1.04	0.9	Normal
	Bt	0.01	0.02	0.12	0.05	7.67	0.78	2.7	Normal
	Bc	0.01	0.00	0.27	0.07	7.70	1.38	2.8	Normal
	Ck	0.01	0.04	0.32	0.06	7.74	1.83	2.3	Normal
SP 8 Punata	A	0.00	0.00	0.04	0.01	7.03	0.25	1.6	Normal
	C	0.00	0.00	0.02	0.01	6.92	0.36	5.4	Normal

Table A2.4b Soil chemical properties: soluble ions and sodium adsorption ratio for each horizon of the non-salt-affected soil profiles.

Soil profile	Horizon	Soluble Ions ($cmol_c\ L^{-1}$)								SAR
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	
SP 6 Tarata	AP	0.03	0.01	0.03	0.03	0.02	0.02	0.00	0.04	2.1
	AB	0.11	0.01	0.09	0.05	0.05	0.07	0.00	0.06	4.4
	C1	0.04	0.01	0.02	0.01	0.00	0.02	0.00	0.02	3.4
	C2	0.03	0.00	0.01	0.01	0.01	0.01	0.00	0.03	4.3
	C3	0.06	0.00	0.01	0.01	0.00	0.03	0.00	0.03	7.6
SP 7 Cuchumuela	Ap	0.01	0.01	0.11	0.03	0.05	0.08	0.00	0.03	0.5
	Bt	0.04	0.00	0.02	0.02	0.05	0.03	0.00	0.02	3.0
	Bc	0.05	0.01	0.01	0.03	0.03	0.02	0.00	0.02	3.9
	Ck	0.04	0.01	0.03	0.03	0.03	0.06	0.00	0.01	2.2
SP 8 Punata	A	0.04	0.01	0.02	0.01	0.03	0.03	0.00	0.02	3.2
	C	0.07	0.01	0.02	0.02	0.05	0.03	0.00	0.04	5.4

Appendix 2.4

Table A2.4c Soil chemical properties: available nutrients, organic carbon and CEC for each horizon of the non-salt-affected soil profiles.

Soil profile	Horizon	CEC	TOC %	Nutrient bioavailability ($g*kg^{-1}$)			
				P	K	Ca	Mg
SP 6 Tarata	AP	16.2	0.99	0.14	0.44	10.02	0.32
	AB	15.0	0.78	0.04	0.32	13.42	0.37
	C1	14.0	0.09	0.03	0.18	22.95	0.46
	C2	11.2	0.05	0.08	0.14	12.91	0.34
	C3	12.5	0.02	0.02	0.15	12.20	0.36
SP 7 Cuchumuela	Ap	12.5	1.13	0.01	0.27	1.60	0.22
	Bt	30.0	0.30	0.00	0.52	2.49	0.59
	Bc	40.0	0.13	0.16	1.21	6.37	0.85
	Ck	27.8	0.12	0.04	1.30	41.76	0.00
SP 8 Punata	A	9.00	0.93	0.01	0.09	0.89	0.17
	C	4.00	0.28	0.01	0.03	0.41	0.08

Table A2.4d Soil physical properties for each horizon of the non-salt-affected soil profiles.

Soil profile	Horizon	Colour	Depth cm	Soil fractions - texture			
				Clay %	Silt %	Sand %	Textural class
SP 6 Tarata	AP	10YR 6/4	0 -20	24.6	42.2	33.3	Lo
	AB	10YR 5/4	20 - 36	25.1	41.5	33.4	Lo
	C1	10YR 5/6	36 - 93	10.8	65.1	24.1	SiLo
	C2	10YR 6/6	93 - 110	19.7	54.8	25.5	SiLo
	C3	10YR 6/8	110 - 150+	19.5	49.5	31.0	Lo
SP 7 Cuchumuela	Ap	7.5YR 4/4	0 -18	26.7	32.8	40.5	Lo
	Bt	2.5YR 2.5/2	18 - 70	63.5	16.3	20.1	Cl
	Bc	7.5 YR 3/4	70 - 94	49.2	36.0	14.9	Cl
	Ck	10YR 5/6	94 – 130+	5.9	65.9	28.3	SiLo
SP 8 Punata	A	2.5Y 6/6	0 -20	18.3	50.4	31.3	SiLo
	C	2.5Y 6/2	20 - 30	10.4	16.9	72.7	SaLo

Appendix 2.5

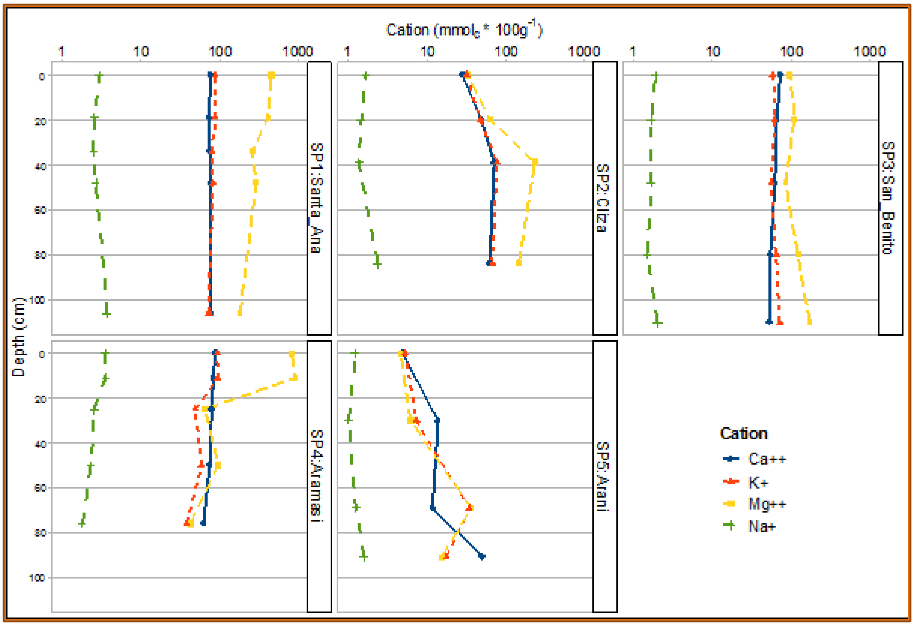


Figure A2.5a Distribution of soluble cations in the salt-affected soil profiles.

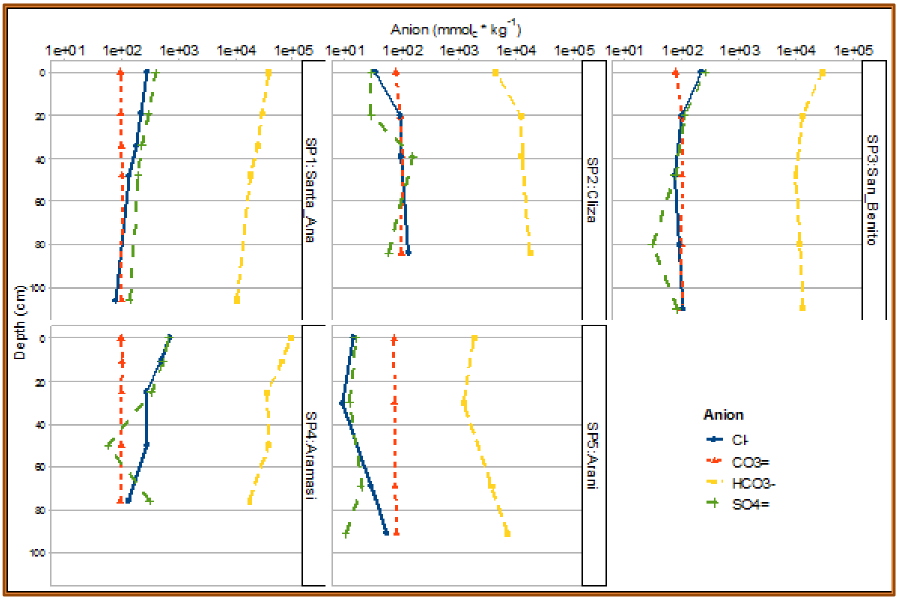


Figure A2.5b Distribution of soluble anions in the salt-affected soil profiles.

Appendix 2.6

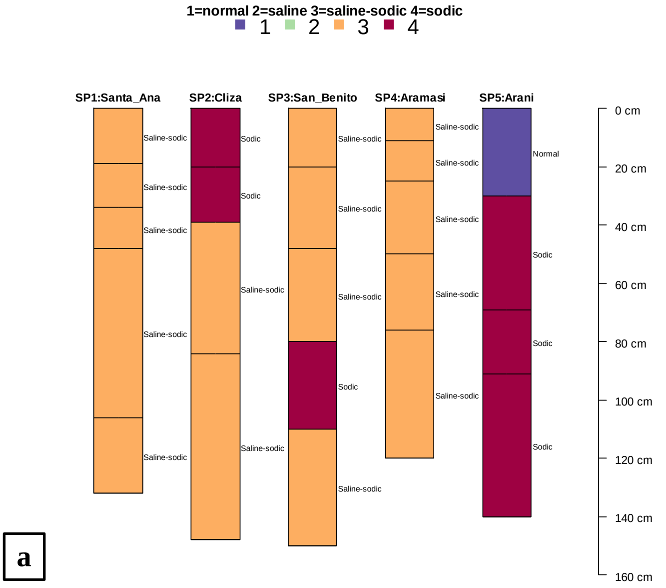


Figure A2.6a Illustration of the salt-affected soil profiles - classes (USSL classification) by horizon.

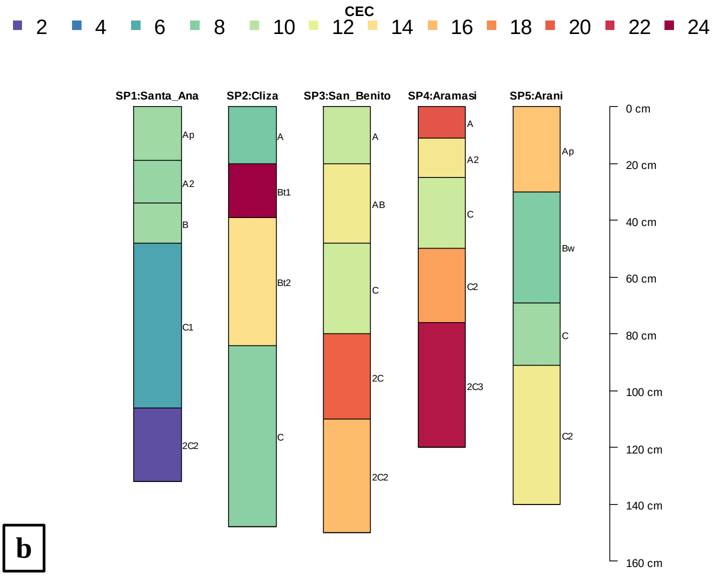


Figure A2.6b Illustration of the salt-affected soil profiles - cation exchange capacity by horizon.

Appendix 2.7

Table A2.7 Some descriptive statistics of top-soil properties used for classification.

Item	Mean	SD	CV	Min	Max	Median	Count
ESP	18.9	22.7	1.2	0.1	89.9	9.2	135.0
SAR	60.3	164.3	2.7	0.0	929.4	4.6	135.0
EC_e	8.8	13.6	1.6	0.3	78.9	4.2	135.0
pH_e	8.1	0.8	0.1	6.8	10.7	8.0	135.0
Ca^{2+}	4.0	5.6	1.4	0.1	38.2	2.1	135.0
Mg^{2+}	1.9	2.3	1.2	0.1	9.6	1.0	135.0
Na^{+}	54.3	130.5	2.4	0.0	869.7	6.2	135.0
K^{+}	0.6	0.6	1.1	0.0	3.9	0.4	135.0
Cl^{-}	29.3	66.6	2.3	0.0	377.0	5.0	135.0
SO_4^{2-}	18.9	39.5	2.1	1.2	231.3	3.8	135.0
HCO_3^{-}	5.9	8.1	1.4	0.0	60.0	3.0	135.0
CO_3^{2-}	12.7	48.6	3.8	0.0	400.0	0.0	135.0
Clay	24.0	10.6	0.4	5.9	65.4	21.8	135.0
Silt	46.5	10.7	0.2	16.3	74.9	46.7	135.0
Sand	29.5	13.9	0.5	1.6	72.7	28.9	135.0
TOC	0.7	0.5	0.7	0.0	3.0	0.7	135.0

SD = standard deviation; CV = coefficient of variation.

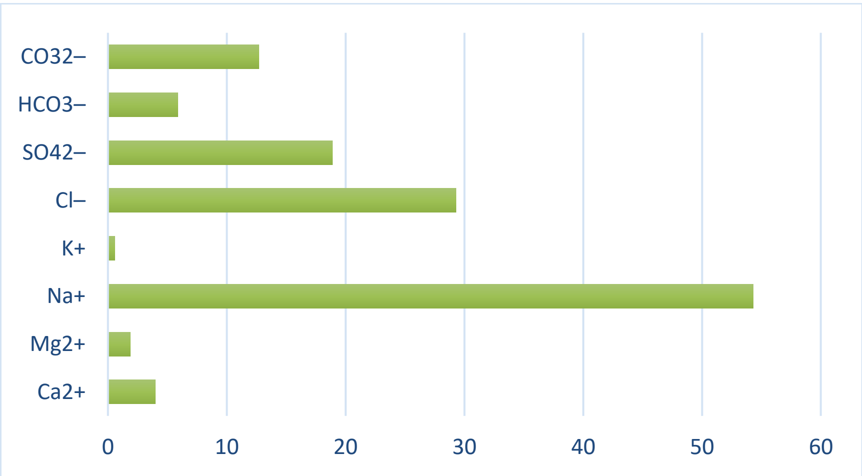


Figure A2.7 Average content of soluble ions for all the soil samples in $cmol_c\ L^{-1}$

Appendix 2.8

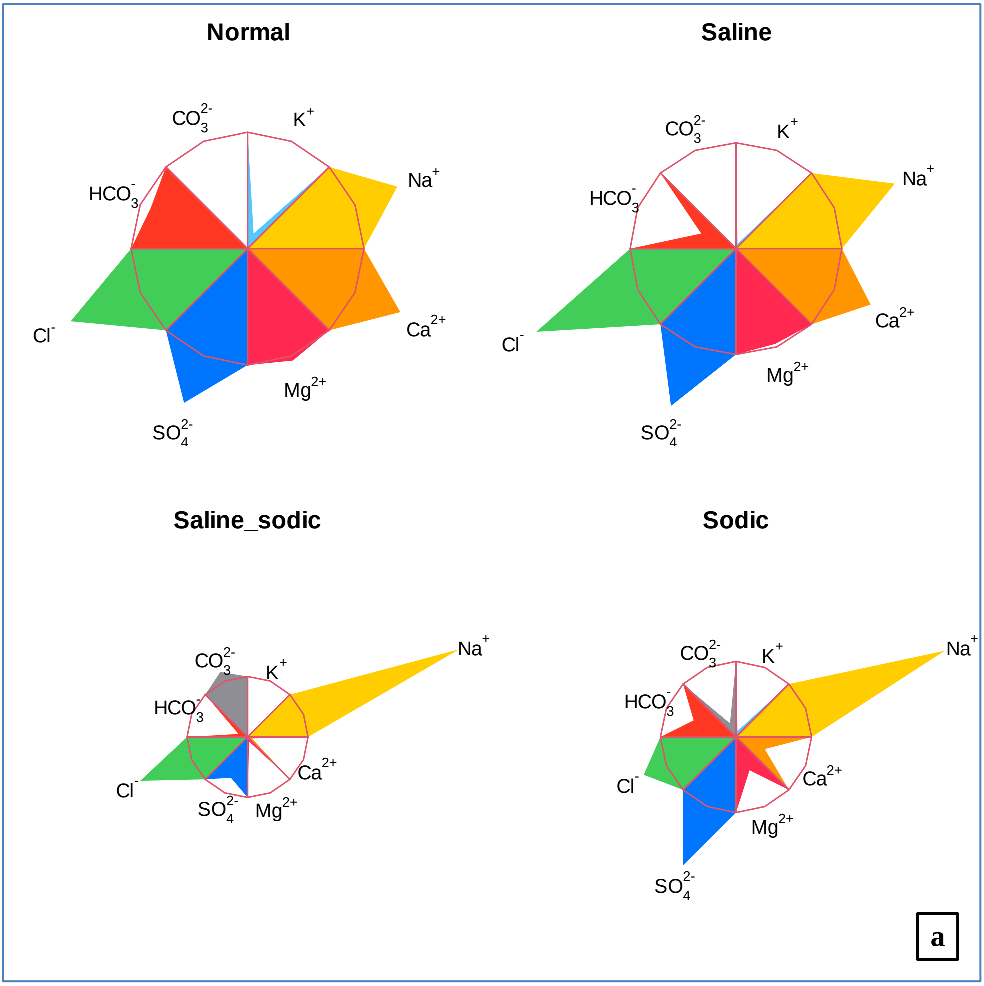


Figure A2.8a Maucha's diagram of average ionic concentrations for salt-affected soil classes (USSL classification)

Appendix 2.8

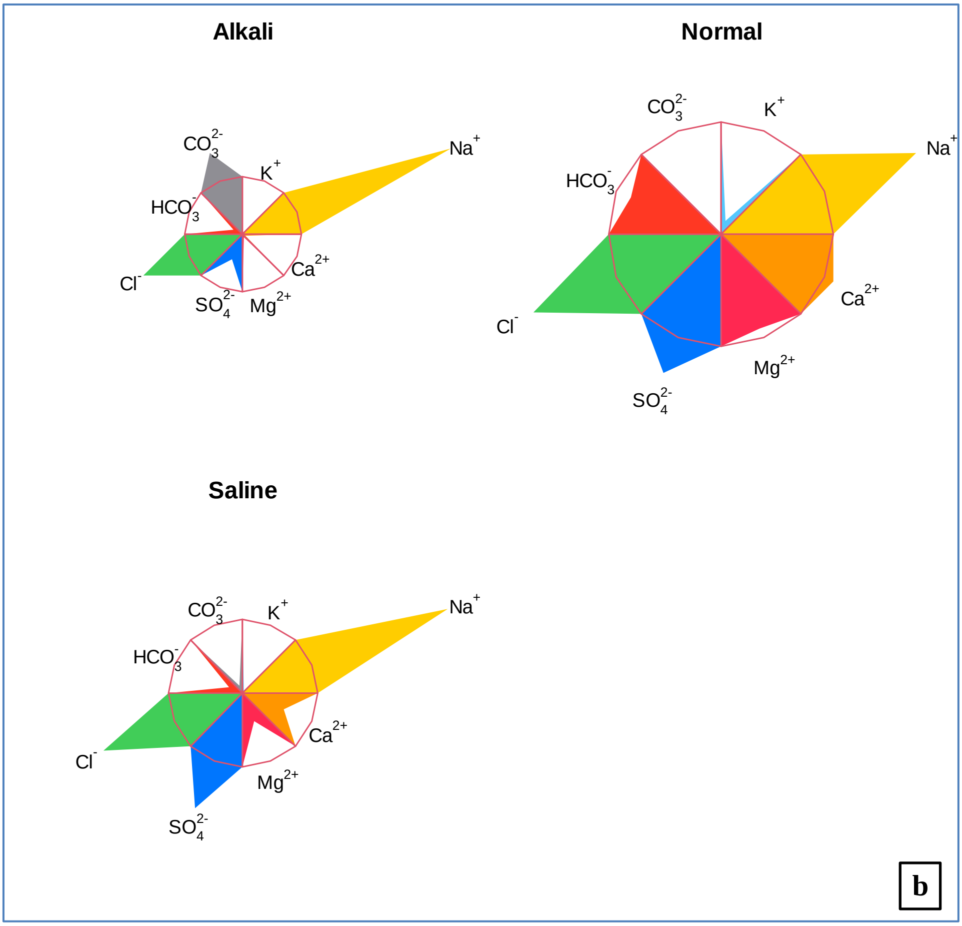


Figure A2.8b Maucha's diagram of average ionic concentrations for salt-affected soil classes (Alternative classification)

Appendix 2.9

Table A2.9 Salinity/sodicity parameters and salt-term classification of soil samples

ID	ESP	EC	pH_e	ECR	CROSS	USSL	Alternative*
1	1.4	3.9	7.5	5.2	0.6	Normal	Normal
2	0.1	3.7	7.7	1.3	1.7	Normal	Normal
3	15.1	3.5	7.8	40.4	1.8	Sodic	Normal
4	23.9	4.8	8.3	26.0	2.7	Saline-sodic	Alkali
5	4.8	4.6	7.8	7.8	0.8	Saline	Saline
6	3.7	3.7	7.9	5.5	2.3	Normal	Normal
7	2.1	3.6	7.6	3.4	2.1	Normal	Normal
8	30.2	3.8	7.7	71.3	2.0	Sodic	Normal
9	16.3	3.9	7.7	56.6	2.3	Sodic	Normal
10	19.1	3.9	7.3	52.7	1.7	Sodic	Normal
11	24.4	11.2	7.5	49.8	6.1	Saline-sodic	Saline
12	47.0	23.8	7.6	63.8	4.5	Saline-sodic	Saline
13	3.2	3.9	7.2	5.5	3.9	Normal	Normal
14	3.8	4.3	7.9	6.5	1.4	Saline	Saline
15	71.6	3.6	7.5	71.9	3.4	Sodic	Normal
16	15.1	4.3	7.3	16.8	3.9	Saline-sodic	Alkali
17	17.8	4.6	7.1	20.3	4.1	Saline-sodic	Saline
18	89.9	78.9	10.6	93.0	38.7	Saline-sodic	Alkali
19	10.0	4.9	9.0	11.3	2.2	Saline	Saline
20	22.1	3.4	8.1	75.2	1.7	Sodic	Normal
21	4.9	4.9	7.4	8.1	0.9	Saline	Saline
22	19.3	3.5	7.8	58.3	1.3	Sodic	Normal
23	0.1	6.3	7.8	7.1	0.3	Saline	Saline
24	3.0	3.6	7.4	4.0	1.5	Normal	Normal
25	18.2	9.4	7.5	36.6	3.1	Saline-sodic	Alkali
26	4.8	5.3	7.7	12.4	1.9	Saline	Saline
27	0.4	3.7	7.7	2.1	1.4	Normal	Normal
28	0.2	3.5	7.6	1.9	0.6	Normal	Normal
29	1.3	3.6	7.7	3.6	0.9	Normal	Normal
30	11.6	4.5	7.8	13.3	1.4	Saline	Saline
31	16.6	4.0	8.0	17.7	2.2	Saline-sodic	Alkali
32	27.6	8.4	7.9	42.2	5.9	Saline-sodic	Alkali
33	11.1	4.8	7.9	12.4	2.6	Saline	Saline
34	0.3	3.6	7.9	1.8	1.6	Normal	Normal

ID	ESP	EC	pH_e	ECR	CROSS	USSL	Alternative*
35	70.3	27.9	10.7	78.2	25.0	Saline-sodic	Alkali
36	0.4	4.2	8.1	2.1	0.9	Saline	Saline
37	23.8	5.6	8.1	25.6	3.0	Saline-sodic	Alkali
38	45.9	56.4	9.9	68.1	25.2	Saline-sodic	Alkali
39	2.1	4.3	8.0	3.7	2.2	Saline	Saline
40	1.1	3.7	7.0	3.6	0.7	Normal	Normal
41	2.8	3.5	7.0	4.5	2.7	Normal	Normal
42	15.0	3.7	6.8	46.2	2.5	Sodic	Normal
43	0.5	4.1	7.6	2.6	0.7	Saline	Saline
44	17.2	4.1	7.0	18.8	2.0	Saline-sodic	Saline
45	48.9	14.7	7.2	55.5	2.6	Saline-sodic	Saline
46	28.3	3.9	7.7	77.9	1.2	Sodic	Normal
47	15.2	5.1	8.2	17.6	3.2	Saline-sodic	Alkali
48	2.6	4.1	7.8	8.4	0.7	Saline	Saline
49	10.5	5.1	7.9	11.3	2.7	Saline	Alkali
50	0.9	3.6	8.4	3.7	1.1	Normal	Normal
51	2.1	3.8	8.1	4.8	0.4	Normal	Normal
52	0.6	5.5	8.0	1.3	1.2	Saline	Saline
53	1.1	4.0	8.3	2.1	0.9	Saline	Saline
54	0.2	3.7	7.5	1.5	1.4	Normal	Normal
55	0.8	5.0	7.3	4.6	1.4	Saline	Saline
56	17.4	3.8	8.0	40.6	1.4	Sodic	Normal
57	1.2	4.1	8.1	3.1	1.0	Saline	Saline
58	26.2	3.7	8.5	82.0	3.0	Sodic	Alkali
59	9.2	6.7	8.0	15.4	2.0	Saline	Saline
60	0.1	3.6	8.0	1.8	2.2	Normal	Normal
61	14.5	15.6	8.3	32.0	2.8	Saline	Saline
62	23.1	5.2	7.8	54.5	8.3	Saline-sodic	Alkali
63	27.6	5.8	8.6	30.1	6.6	Saline-sodic	Saline
64	2.6	4.5	8.1	5.6	1.4	Saline	Saline
65	4.6	4.0	8.3	8.8	2.5	Saline	Saline
66	2.0	3.5	8.4	3.5	0.7	Normal	Normal
67	1.5	4.5	7.7	6.4	1.5	Saline	Saline
68	7.1	8.7	7.5	7.8	0.6	Saline	Saline
69	70.3	78.9	7.8	80.0	6.3	Saline-sodic	Saline
70	25.0	3.8	8.1	76.6	2.4	Sodic	Normal
71	21.5	7.6	8.2	22.8	4.6	Saline-sodic	Saline

ID	ESP	EC	pH_e	ECR	CROSS	USSL	Alternative*
72	0.4	5.3	8.1	2.5	1.1	Saline	Saline
73	15.6	3.6	8.1	16.5	6.8	Sodic	Normal
74	18.7	3.6	8.4	53.5	2.5	Sodic	Alkali
75	2.0	4.5	8.0	4.5	0.8	Saline	Saline
76	0.2	3.9	8.4	2.3	0.7	Normal	Normal
77	7.4	4.3	8.3	10.3	2.8	Saline	Saline
78	50.4	31.6	9.3	64.5	20.6	Saline-sodic	Saline
79	1.2	3.8	8.2	3.7	0.5	Normal	Normal
80	25.8	3.5	7.8	62.8	1.1	Sodic	Normal
81	14.3	21.2	7.9	37.1	1.0	Saline	Saline
82	0.1	3.7	8.2	1.6	0.9	Normal	Normal
83	3.3	7.8	7.9	11.2	2.1	Saline	Saline
84	4.7	4.2	8.3	10.1	2.0	Saline	Saline
85	4.2	4.7	8.3	5.8	1.6	Saline	Saline
86	2.1	3.8	8.2	4.8	2.6	Normal	Normal
87	35.8	6.7	8.0	36.8	5.0	Saline-sodic	Alkali
88	0.4	4.2	7.8	2.2	1.1	Saline	Saline
89	3.3	4.1	8.0	5.5	2.4	Saline	Saline
90	1.2	5.3	8.3	6.6	0.8	Saline	Saline
91	3.9	4.6	8.1	5.1	1.6	Saline	Alkali
92	3.3	4.7	7.9	5.5	0.4	Saline	Saline
93	2.5	3.9	8.1	3.9	2.2	Normal	Normal
94	11.3	5.0	8.3	17.7	2.4	Saline	Alkali
95	0.3	3.6	8.2	1.6	2.1	Normal	Normal
96	1.4	3.8	8.0	6.5	1.5	Normal	Normal
97	3.3	5.8	8.0	6.2	1.1	Saline	Saline
98	37.2	4.0	8.5	87.4	5.5	Sodic	Alkali
99	20.8	6.2	7.8	22.3	1.1	Saline-sodic	Saline
100	0.3	4.3	8.2	4.3	0.7	Saline	Saline
101	0.1	3.7	8.0	1.6	1.0	Normal	Normal
102	5.1	1.6	7.3	12.4	1.8	Normal	Normal
103	15.1	1.2	7.5	16.7	2.5	Sodic	Normal
104	50.4	1.1	8.0	51.2	4.1	Sodic	Normal
105	16.2	2.0	7.6	16.1	9.3	Sodic	Normal
106	77.0	33.4	10.0	78.1	12.5	Saline-sodic	Alkali
107	72.2	5.8	10.0	74.7	15.1	Saline-sodic	Alkali
108	59.8	31.5	9.5	63.4	6.0	Saline-sodic	Alkali

ID	ESP	EC	pH_e	ECR	CROSS	USSL	Alternative*
109	71.2	53.9	10.1	84.1	45.0	Saline-sodic	Alkali
110	74.8	66.9	9.7	87.2	29.3	Saline-sodic	Alkali
111	28.2	3.0	7.9	30.2	7.8	Sodic	Normal
112	48.8	3.0	9.4	52.2	11.1	Sodic	Alkali
113	55.0	5.9	9.8	64.0	18.0	Saline-sodic	Saline
114	58.5	15.5	10.0	75.8	22.5	Saline-sodic	Alkali
115	1.0	1.7	7.5	6.0	0.5	Normal	Normal
116	2.3	0.7	7.7	7.6	1.3	Normal	Normal
117	2.7	0.7	7.7	7.9	1.7	Normal	Normal
118	2.8	0.5	7.7	2.8	2.2	Normal	Normal
119	1.6	0.3	7.0	3.9	1.8	Normal	Normal
120	5.4	0.6	6.9	5.4	2.5	Normal	Normal
121	50.8	3.1	9.6	55.1	18.5	Sodic	Alkali
122	46.9	8.2	9.9	53.0	22.7	Saline-sodic	Alkali
123	53.6	7.6	9.8	62.2	9.6	Saline-sodic	Saline
124	56.9	11.3	9.8	66.3	10.2	Saline-sodic	Saline
125	47.0	25.4	7.7	73.8	5.6	Saline-sodic	Saline
126	63.8	14.0	9.9	76.5	19.5	Saline-sodic	Alkali
127	64.3	23.0	10.0	74.4	21.6	Saline-sodic	Alkali
128	57.9	19.9	10.1	75.8	24.2	Saline-sodic	Alkali
129	44.2	29.7	9.8	71.9	26.1	Saline-sodic	Alkali
130	58.8	40.1	9.6	76.5	28.2	Saline-sodic	Alkali
131	0.5	1.7	7.3	2.3	0.6	Normal	Normal
132	0.4	0.4	7.5	1.3	2.0	Normal	Normal
133	0.2	0.4	7.5	1.0	2.8	Normal	Normal
134	1.2	1.1	7.5	3.3	1.3	Normal	Normal
135	0.2	0.5	7.5	0.9	1.8	Normal	Normal

Sodium adsorption ratio (SAR), exchangeable sodium percentage (ESP), exchangeable cation ratio (ECR), cations ratio of soil structural stability (CROSS). USSL= US salinity lab,
* Alternative = criterion by Chhabra (2004) and Szabolcs (1989), takes into account the soluble salt ions besides soil ESP, EC and pH.

Appendix 2.10

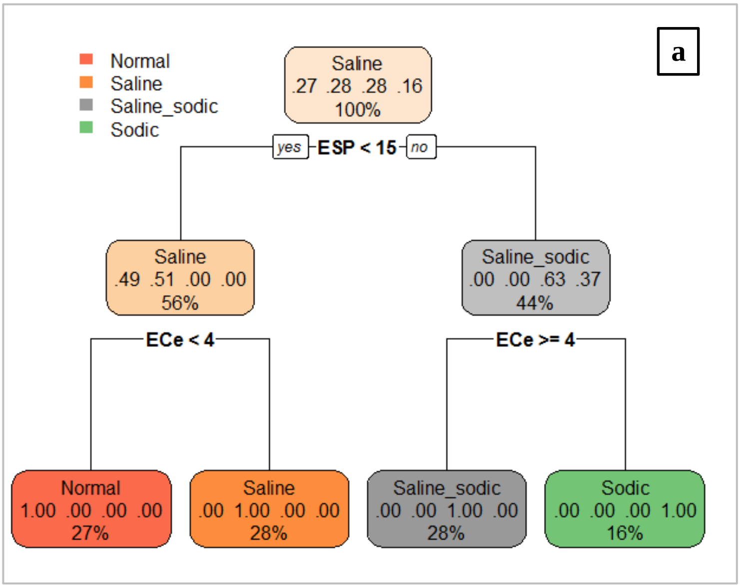


Figure A2.10a Referential classification pathway of the USSL classifications based on the decision tree algorithm.

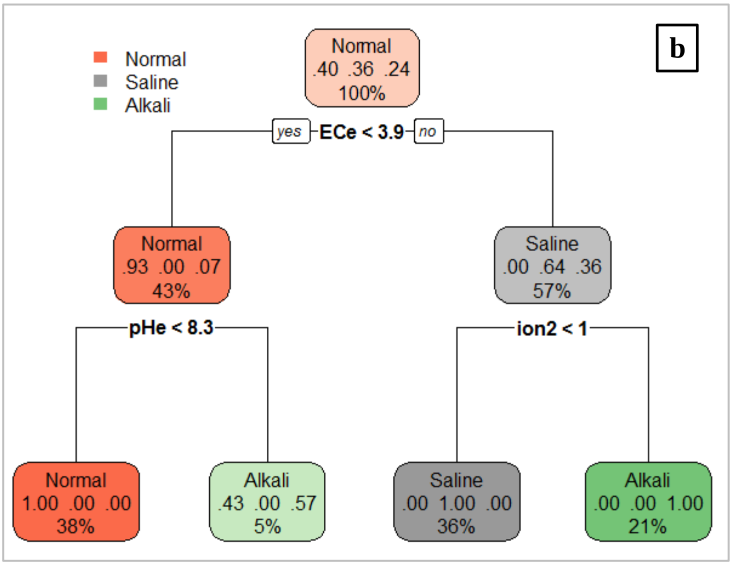


Figure A2.10b Referential classification pathway of the Alternative classifications based on the decision tree algorithm.

Appendix 2.11

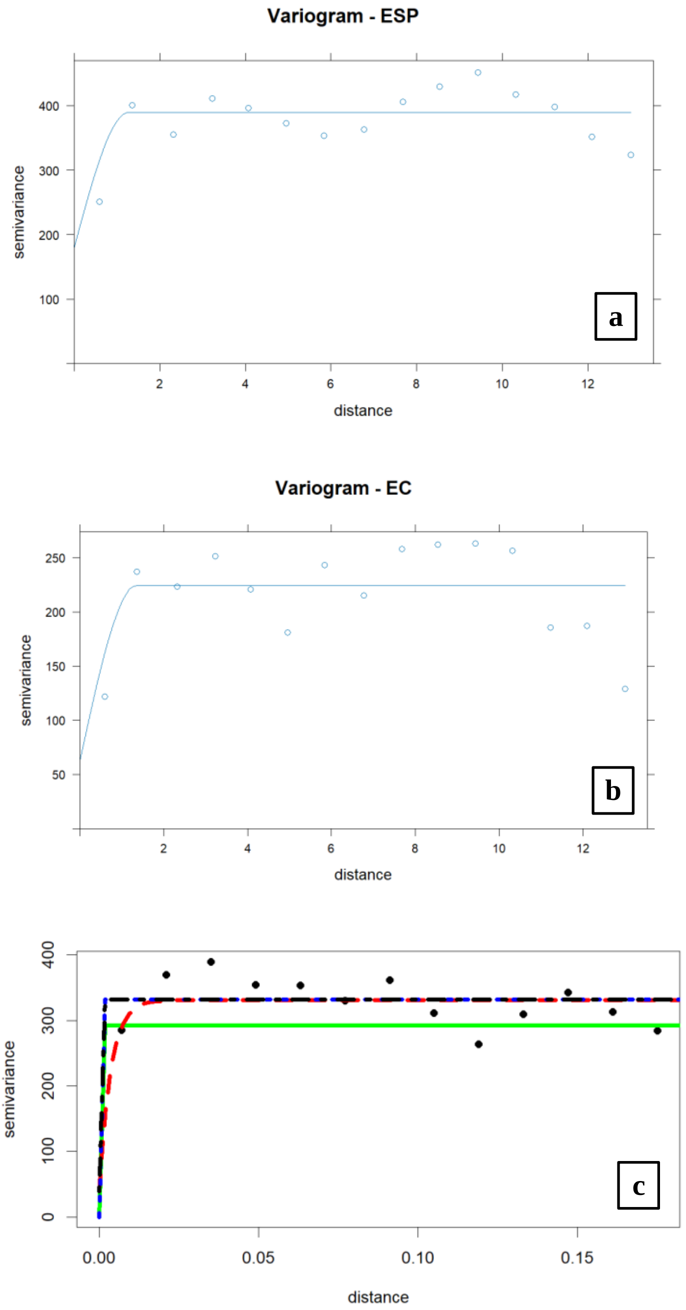


Figure A2.11 Variogram and model fitting for soil ESP (a), EC (b) and fitted covariance models on a variogram (c).

Appendix 2.12

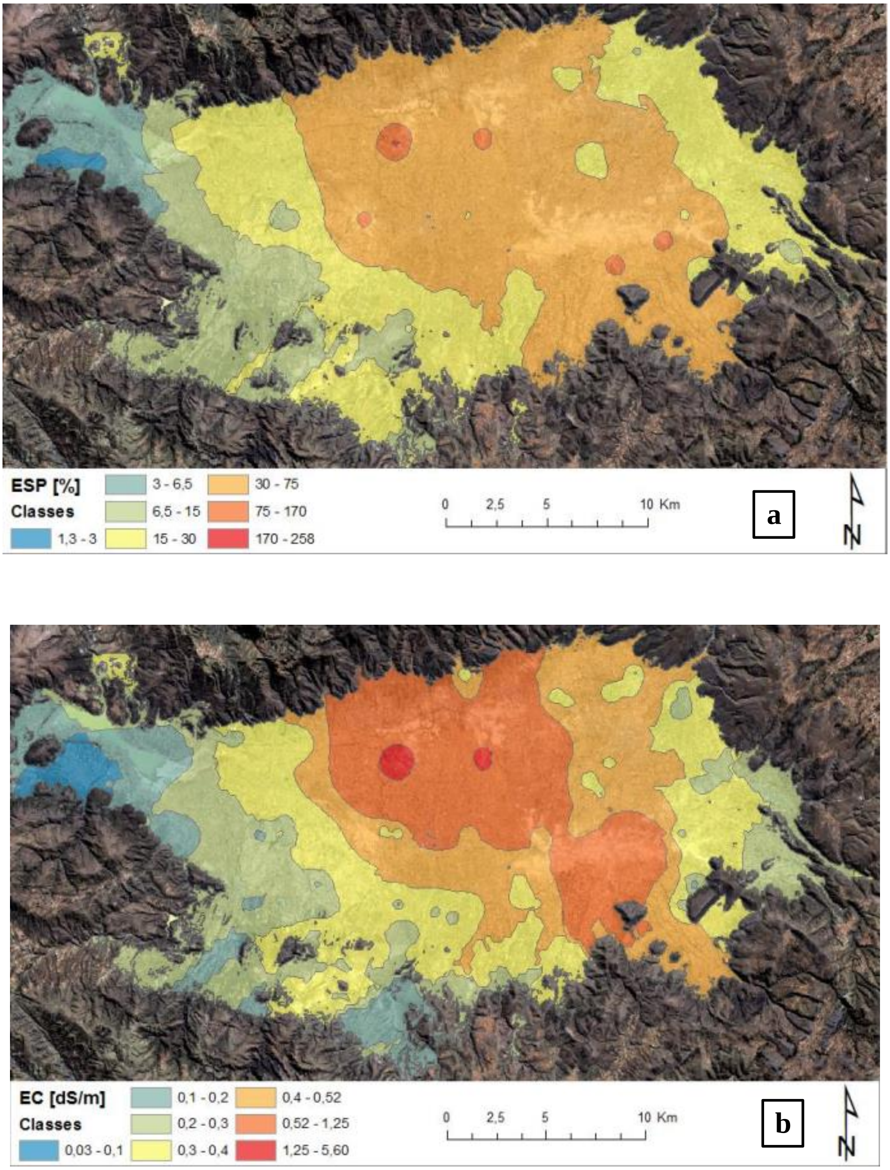


Figure A2.12 Maps showing the spatial distribution for soil ESP (a) and EC (b), by using the inverse distance weighted interpolation method (Weber, 2018).

Appendix 2.13

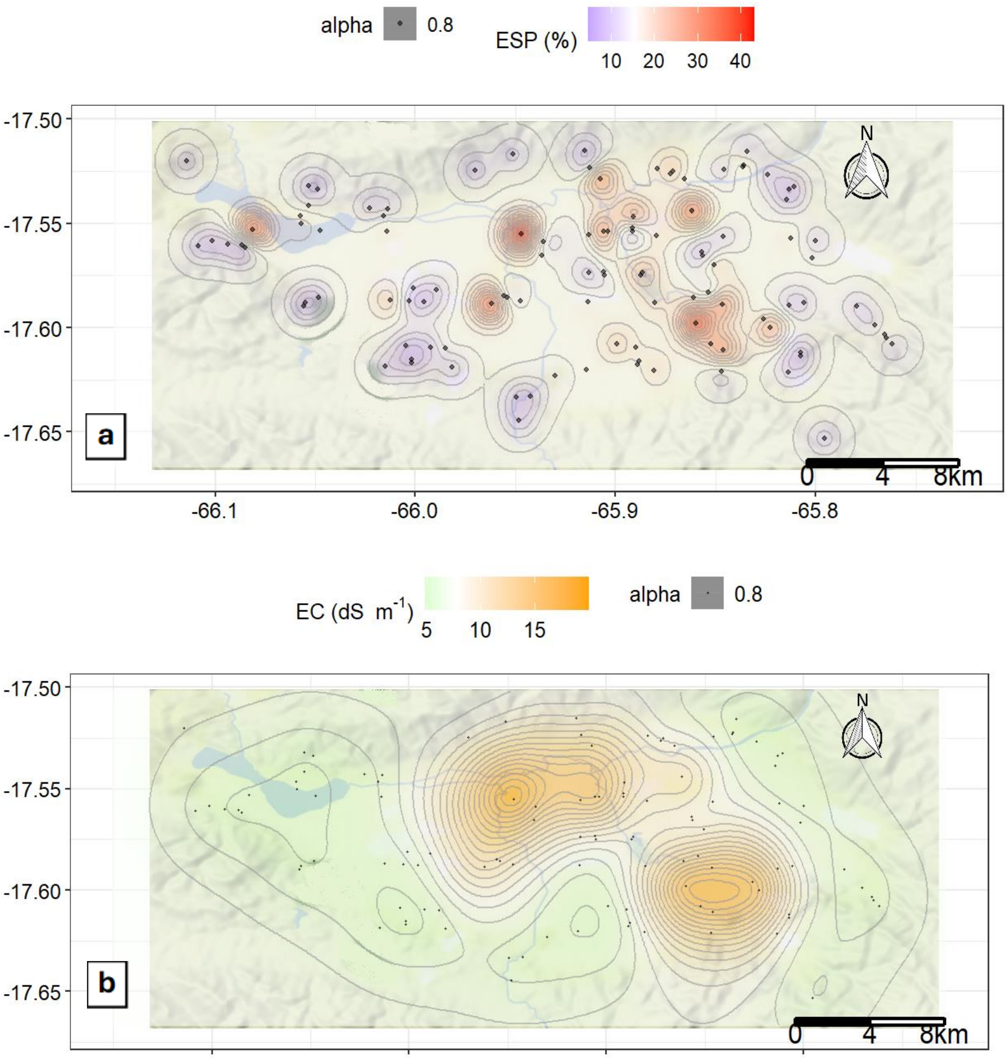


Figure A2.13 Spatial prediction for soil ESP (a) and EC (b), interpolated through ordinary kriging. Background image: terrain from Stadia-Map (2023)

Appendix 2.14

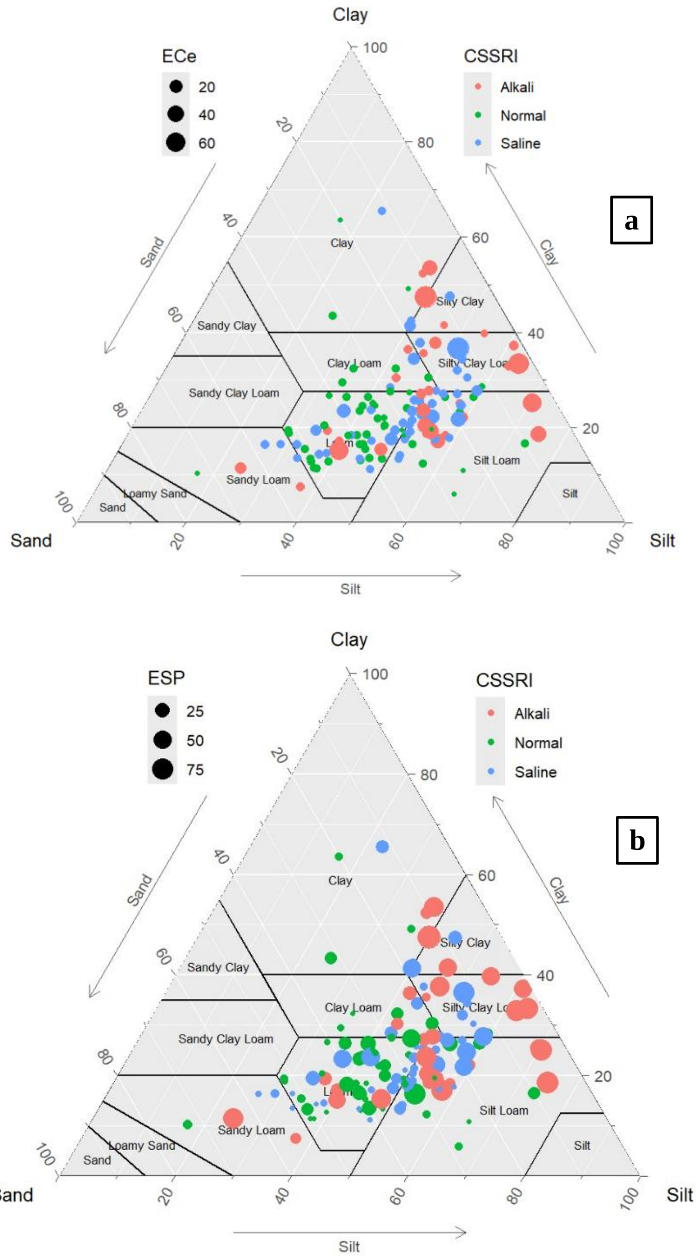


Figure A2.14 Textural classes by salt-affected soil (Alternative) classes for soil EC_e (a) and ESP (b) of the sampling, on the soil textural triangle (USDA system)

Appendix 3.1

Table A3.1a Descriptive statistics of explanatory (soluble salt ions) and response variables

Item	Mean	SD	CV	Min	Max	Median	Count
Ca^{2+}	3.7	4.5	1.2	0.1	26.2	2.2	125
Mg^{2+}	1.7	1.9	1.1	0.09	9.4	1.0	125
Na^{+}	27.4	54.9	2.0	0.02	326.1	5.6	125
K^{+}	0.5	0.5	1.0	0.02	2.2	0.4	125
Cl^{-}	17.4	35.3	2.0	0	205.0	5	125
SO_4^{2-}	14.2	29.6	2.1	1.2	153.4	3.7	125
HCO_3^{-}	5.4	6.6	1.2	0.5	34.0	3.0	125
CO_3^{2-}	6.3	22.2	3.5	0.0	134.0	0.0	125
ESP	16.3	20.4	1.2	0.1	77.0	4.9	125
EC_e	6.1	6.5	1.1	0.3	33.4	4.1	125

SD = standard deviation; CV = coefficient of variation.

Table A3.1b Setting of parameters for model training and cross-validation analysis.

Model	Algorithms	Parameters/Values
EC_e and ESP Regression	PLS-R	Number of components: 1 (EC_e), 3 (ESP)
	SV-R	CF grid: 0.01, 0.1, 0.25, 0.5, 1
	RF-R	NT of 3000, MTRY of 5 (EC_e), 2 (ESP)
Multiple classification	PLS-DA	Number of components: 2
	SVM-C	CF grid: 0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2
	RF-C	NT of 3000, NS of 10, MTRY of 2

R = regression; C = classification; NT = number of trees; NS = minimum node size; MTRY = number of randomly selected predictors; CF = capacity factor for SVM.

Table A3.1c Correlation matrix among sums of soluble and exchangeable cations, sodicity parameters, and EC_e.

	Sum-Sol Cations	Sum-Sol-Anions	Sum-Exc-Cations	SAR	ESR	ESP	EC_e
Sum-Sol Cations	1						
Sum-Sol-Anions	0.78	1					
Sum-Exc-Cations	0.32	0.42	1				
SAR	0.90	0.75	0.33	1			
ESR	0.57	0.77	0.45	0.61	1		
ESP	0.66	0.75	0.50	0.66	0.93	1	
EC_e	0.81	0.84	0.30	0.73	0.64	0.64	1

Sum-Sol = Sum of soluble; Sum-Exc = Sum of exchangeable; SAR = sodium adsorption ratio; ESR = exchangeable sodium ratio (ESP/100-ESP).

Appendix 3.2

Table A3.2 Vegetation indices derived from the satellite image bands, and their equations.

Index	Abbreviation	Equation*	Reference†
Normalized Vegetation Index	NDVI	$\frac{NIR - R}{NIR + R}$	1, 3, 4
Normalized Difference Infrared Index	NDII	$\frac{NIR - SWIR1}{NIR + SWIR1}$	2
Extended NDVI	ENDVI	$\frac{NIR + SWIR2 - R}{NIR + SWIR2 + R}$	1,3
Simple Ratio Vegetation Index	SRVI	$\frac{NIR}{R}$	3, 4
Canopy Response Salinity Index	CRSI	$\sqrt{\frac{(NIR * R) - (G * B)}{(NIR * R) + (G * B)}}$	1, 3, 4
Enhanced Vegetation Index	EVI	$2.5\ x\ \frac{NIR - R}{(NIR + 6R - 7.5B + 1)}$	1, 3, 4
Generalized Vegetation Index	GDVI	$\frac{NIR^2 - R^2}{NIR^2 + R^2}$	1, 3, 4
Combined Spectral Response Index	COSRI	$\frac{B + G}{R + NIR} * NDVI$	5
Soil Regulation Vegetation Index	SAVI	$\frac{(NIR - R)(1 + L)}{(NIR + R + L)}$	1, 3, 4
Clay Index	CLEX	$\frac{SWIR1}{SWIR2}$	2
Brightness index	BI	$\sqrt{R^2 + NIR^2}$	5

* B = B2 (blue), G = B3 (green), R = B4 (red), NIR = B5, SWIR1 = B6, SWIR2 = B7.

† 1) Li Yanan 2021, 2) Wang F. et al. 2019, 3) Aksoy et al. 2022, 4) Wang J. et al. 2021, 5) Moreira et al., 2015. These references are not necessarily the original sources for the above-listed indices.

Appendix 3.3

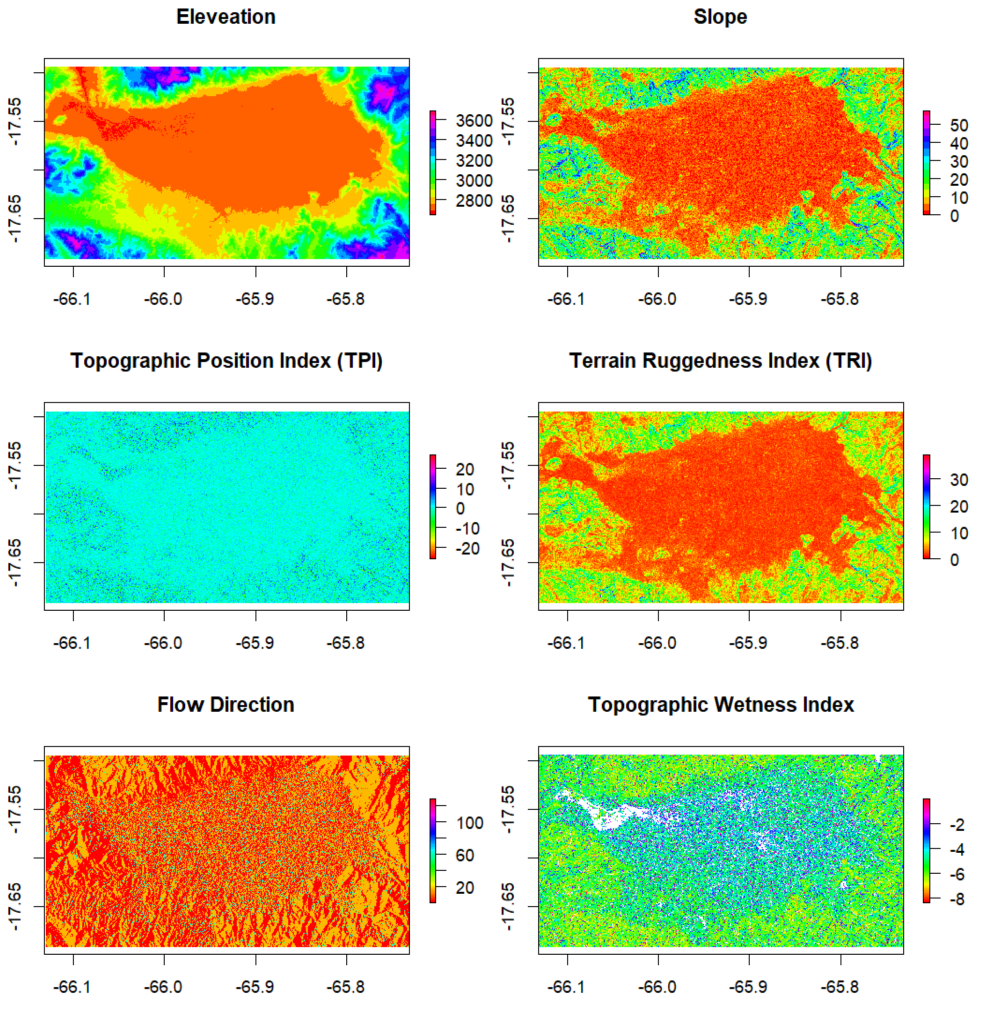


Figure A3.3 Geomorphometric (elevation derived) features - High Valley of Cochabamba (based on DEM)

Appendix 3.4

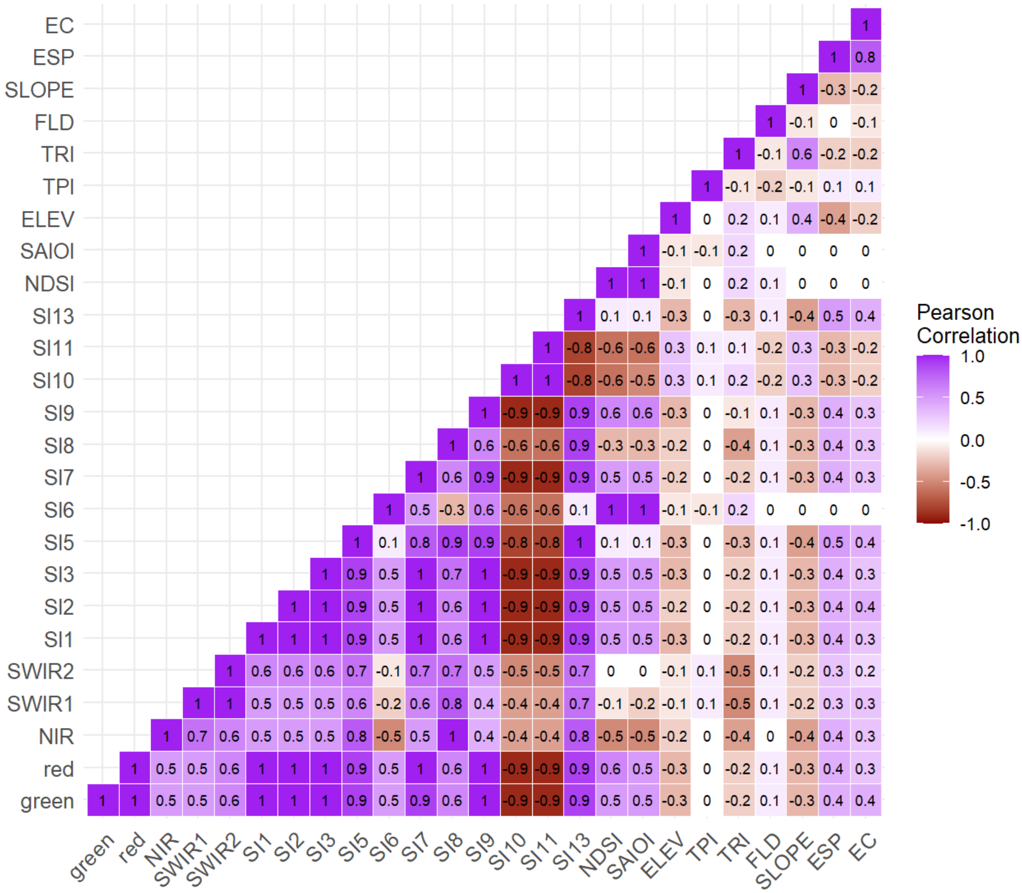


Figure A3.4 Correlation matrix for the geomorphometric features

Appendix 3.5

Table A3.5a Confusion matrixes of the predictions for the three ML classification algorithms.

Class	PLS-DA				SVM-C				RF-C			
	NO	**SA**	**SS**	**SO**	**NO**	**SA**	**SS**	**SO**	**NO**	**SA**	**SS**	**SO**
Normal	9	2	1	5	9	2	1	4	9	0	0	1
Saline	1	6	1	0	1	6	0	0	1	8	0	1
Saline–sodic	0	0	5	0	0	0	5	0	0	0	7	1
Sodic	0	0	0	0	0	0	1	1	0	0	0	2

NO = normal; SA = saline; SS = saline–sodic; SO = sodic.

Table A3.5b Sensitivity and specificity for the three classification models.

Class	Sensitivity			Specificity		
	PLS-DA	**SVM-C**	**RF-C**	**PLS-DA**	**SVM-C**	**RF-C**
Normal	0.90	0.90	0.90	0.60	0.65	0.95
Saline	0.75	0.75	1.00	0.91	0.95	0.90
Saline–sodic	0.71	0.71	1.00	1.00	1.00	0.96
Sodic	0.00	0.20	0.40	1.00	0.96	1.00

Appendix 3.6

Table A3.6 Factor analysis for the response and explanatory variables as geomorphometric features of multivariate regressions. Obtained through the R-base function *Factanal*.

```
## Loadings:
##       Factor1 Factor2 Factor3 Factor4 Factor5
## green  0.91    0.38                          
## red    0.87    0.42                          
## NIR    0.76   -0.60                          
## SI1    0.89    0.41                          
## SI2    0.87    0.40                          
## SI3    0.87    0.41                          
## SI5    0.97                                  
## SI7    0.81    0.41                    0.32  
## SI8    0.82   -0.41                          
## SI9    0.88    0.43                          
## SI10  -0.77   -0.42           -0.47          
## SI11  -0.77   -0.43           -0.46          
## SI13   0.97                                  
## SI6            0.95                          
## NDSI           0.98                          
## SAIOI          0.98                          
## SWIR1  0.46            0.80                  
## SWIR2  0.49            0.80                  
## ELEV  -0.31                                  
## TPI                                          
## TRI                   -0.47                  
## FLD                                          
## SLOPE -0.40                                  
## ESP    0.49                                  
## EC     0.36                                  
## 
##                Factor1 Factor2 Factor3 Factor4 Factor5
## SS loadings      10.87    4.95    2.08    0.82    0.50
## Proportion Var    0.43    0.20    0.08    0.03    0.02
## Cumulative Var    0.43    0.63    0.72    0.75    0.77
```

Appendix 3.7

Table A3.7a Coefficients and P(>|t|) values for the multivariate models to predict soil ESP from geomorphometric features as predictors.

	Estimate	Std. Error	t value	Pr(>|t|)
(Intercept)	-22412	10909	-2.055	0.04292
green	86008	43509	1.977	0.05123
red	94922	47034	2.018	0.04666
NIR	13184	5091	2.589	0.01127
SWIR2	-142.9	63.96	-2.234	0.02804
SI1	-32640	16668	-1.958	0.05341
SI3	-1717	343.1	-5.005	2.886e-06
SI6	895.3	541	1.655	0.1015
SI7	764.6	148.3	5.155	1.572e-06
SI8	-3338	1424	-2.344	0.02136
NDSI	15934	6085	2.618	0.01042
SAIOI	-16413	6612	-2.482	0.01497
ELEV	-0.2316	0.04804	-4.821	6.016e-06
FLD	0.07537	0.04541	1.66	0.1005

Table A3.7b Coefficients and P(>|t|) values for the multivariate models to predict soil EC from geomorphometric features as predictors.

	Estimate	Std. Error	t value	Pr(>|t|)
(Intercept)	-9548	4532	-2.107	0.03809
green	39621	20801	1.905	0.06019
red	33095	16575	1.997	0.04906
NIR	7281	4003	1.819	0.07248
SWIR1	183.2	69.51	2.636	0.009968
SWIR2	-185.7	70.08	-2.649	0.009611
SI1	-19084	8908	-2.142	0.03503
SI2	4241	1807	2.347	0.02123
SI3	-731.8	361.7	-2.023	0.04619
SI5	-2162	1117	-1.935	0.05629
SI6	341.2	256.5	1.33	0.187
SI8	-587.9	379.9	-1.547	0.1255
SI9	3479	1463	2.377	0.0197
SI10	-2066	747.2	-2.765	0.006976
SI11	2300	844	2.725	0.007803
ELEV	-0.0766	0.026	-2.946	0.004155

Appendix 4.1

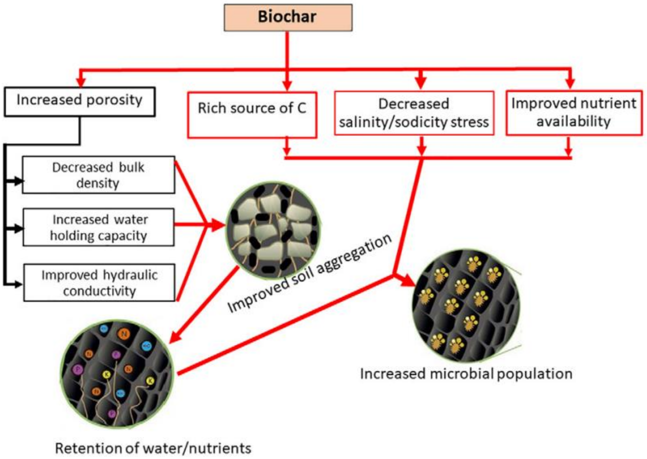


Figure A4.1 Possible mechanisms for the effects of biochar on physical/biological properties of salt-affected soils (Saifullah et al., 2017)

Table A4.1 Referential biochar properties from lab-test report (Eurofin – 2017, Germany)

Parameter	Lab	Accr.	Method	LOQ	Unit	ar	db
Biochar properties							
Bulk density	FR	JE02	DIN 51705		kg/m³	411	-
specific surface (BET)	SUIB/o		DIN 66137/DIN ISO 9277		m²/g	339,8813	-
true density	SUIB/o		DIN 66137/DIN ISO 9277		g/cm³	1,5665	-
water holding capacity (WHC)	SB99/o		DIN ISO 14238, A		% (w/w)	155	-
Moisture	FR	JE02	DIN 51718	0,1	% (w/w)	52,2	-
Ash content (550°C)	FR	JE02	DIN 51719 mod.	0,1	% (w/w)	1,9	3,9
Ash content (815°C)	FR	JE02	DIN 51719	0,1	% (w/w)	1,5	3,2
Volatile Compounds	FR	JE02	DIN 51720	0,2	% (w/w)	3,3	6,9
gross calorific value (Ho,V)	FR	JE02	DIN 51900	200	kJ/kg	16400	34300
net calorific value (Hup)	FR	JE02	DIN 51900	200	kJ/kg	14900	33900
Hydrogen	FR	JE02	DIN 51732	0,1	% (w/w)	0,9	1,8
Carbon	FR	JE02	DIN 51732	0,2	% (w/w)	43,9	91,9
Total nitrogen	FR	JE02	DIN 51732	0,05	% (w/w)	0,28	0,58
Oxygen	FR	JE02	DIN 51733, berechnet		% (w/w)	1,2	2,5
Total inorganic carbon (TIC)	FR	JE02	DIN 51726	0,1	% (w/w)	0,1	0,2
carbonate-CO2	FR	JE02	DIN 51726	0,4	% (w/w)	< 0,4	0,8
carbon (organic)	FR	JE02	berechnet		% (w/w)	43,8	91,7
H/C ratio (molar)	FR	JE02	berechnet			0,23	0,23
H/Corg ratio (molar)	FR	JE02	berechnet			0,23	0,23
O/C ratio (molar)	FR	JE02	berechnet			0,021	0,020
Sulphur (S), total	FR	JE02	DIN 51724-3	0,03	% (w/w)	< 0,03	0,03
pH in CaCl2	FR	JE02	DIN ISO 10390			8,2	-
Conductivity	FR		BGK III. C2	5	µS/cm	299	-
salt content	FR		BGK III. C2	0,005	g/kg	1,58	3,30
salt content	FR		BGK III. C2	0,005	g/l	0,649	1,36
thermogravimetry TGA 950°C by N-Atm.	FR		TGA 701 D4C			see annex	-

Appendix 4.2

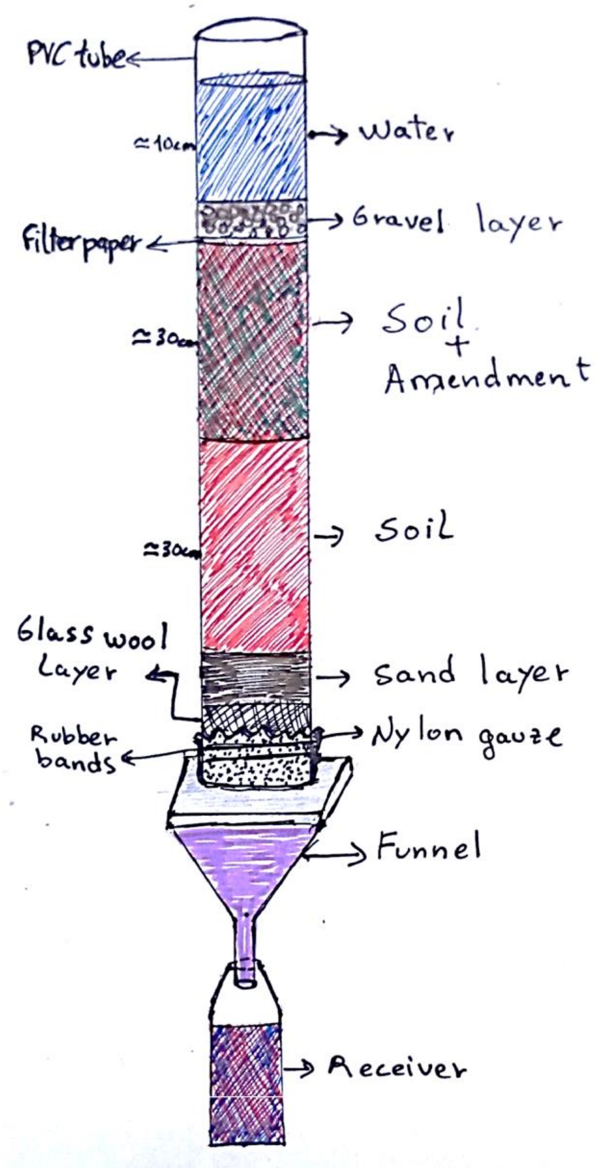


Figure A4.2 Illustration showing the structure and setup of a soil column.

Appendix 4.3

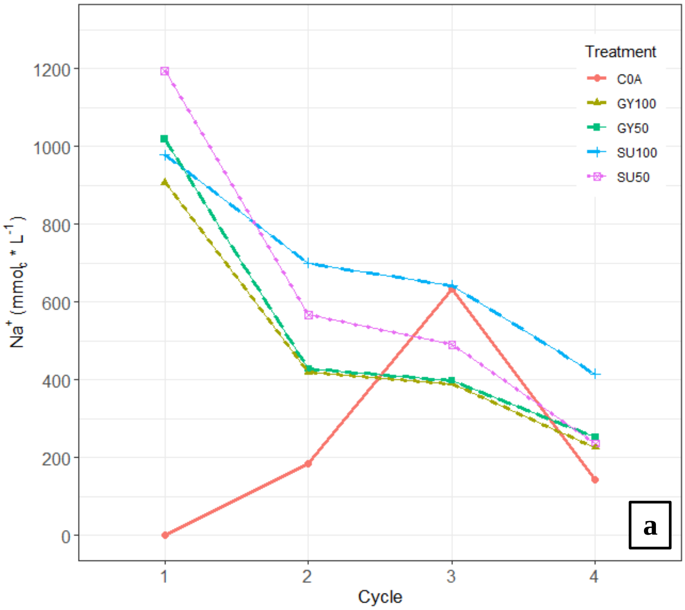


Figure A4.3a. Evolution of sodium concentration in the leachates.

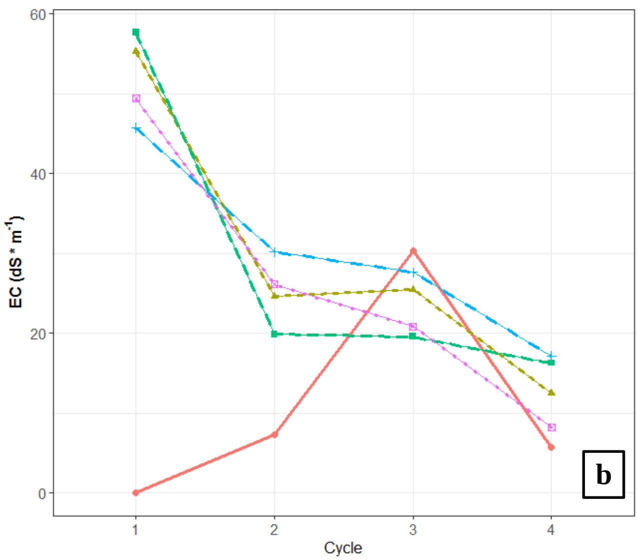


Figure A4.3b. Evolution of electrical conductivity in the leachates.

Appendix 4.4

Table A4.4a Effect of manures combined with gypsum levels on soil properties, compared to the control.

Treatment	ESP (%)	EC_e (dS m^{-1})	pH	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

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.

Table A4.4b Evolution of EC (dS m^{-1}) in the leachates at each leaching cycle.

Treatment	Cycle of Leaching			
	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 8.3).

Appendix 4.5

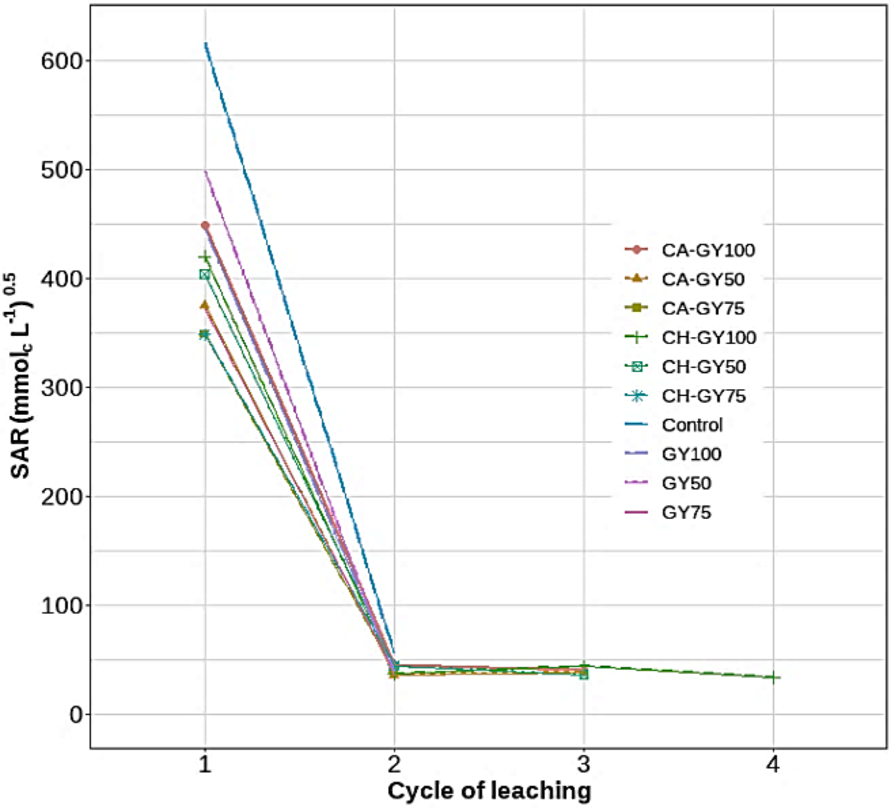


Figure A4.5 Evolution of sodium adsorption ratio (SAR) in the leachates at each leaching cycle. GY = gypsum, CA = cattle manure, CH = chicken manure.

Annexes

ANNEX 1

soil systems

MDPI

Article

Prediction of Soil Salinity/Sodicity and Salt-Affected Soil Classes from Soluble Salt Ions Using Machine Learning Algorithms

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Abstract: Salt-affected soils are related to salinity (high content of soluble salts) and/or sodicity (excess of sodium), which are major leading causes of agricultural land degradation. This study aimed to evaluate the performances of three machine learning (ML) algorithms in predicting the soil exchangeable sodium percentage (ESP), electrical conductivity (EC_e), and salt-affected soil classes, from soluble salt ions. The assessed ML models were Partial Least-Squares (PLS), Support Vector Machines (SVM), and Random Forests (RF). Soil samples were collected from the High Valley of Cochabamba (Bolivia). The explanatory variables were the major soluble ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}). The variables to be explained comprised soil EC_e and ESP, and a categorical variable classified through the US Salinity Lab criteria. According to the model validation, the SVM and RF regressions performed the best for estimating the soil EC_e, as well as the RF model for the soil ESP. The RF algorithm was superior for predicting the salt-affected soil categories. Soluble Na^+ was the most relevant variable for all the predictions, followed by Ca^{2+}, Mg^{2+}, Cl^-, and HCO_3^-. The RF and SVM models can be used to predict soil EC_e and ESP, as well as the salt-affected soil classes, from soluble ions. Additional explanatory features and soil samples might improve the ML models' performance. The obtained models may contribute to the monitoring and management of salt-affected soils in the study area.

Keywords: machine learning; electrical conductivity; exchangeable sodium percentage; salt-affected soil classification

Citation: Andrade Foronda, D.; Colinet, G. Prediction of Soil Salinity/Sodicity and Salt-Affected Soil Classes from Soluble Salt Ions Using Machine Learning Algorithms. *Soil Syst.* **2023**, *7*, 47. https://doi.org/10.3390/soilsystems7020047

Academic Editors: Thomas Baumgartl and Mandana Shaygan

Received: 23 March 2023
Revised: 28 April 2023
Accepted: 5 May 2023
Published: 10 May 2023

1. Introduction

Salt-affected soils are mainly related to arid and semiarid regions and basically comprise saline and/or sodic soils. Saline soils have a significant amount of soluble salts which consist of major ions like sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), chloride (Cl^-), carbonate (CO_3^{2-}), and sulfate (SO_4^{2-}). Sodic soils have an excess of exchangeable Na^+ in the cation exchange complex, as well as in the soil solution. Soluble salts and Na^+ normally originate either from natural processes such as weathering (primary salinity/sodicity) or are induced by human activities such as the inappropriate management of land and water resources (secondary salinity/sodicity). Soil salinity negatively affects root growth and crop yield through the osmotic effect caused by the high concentration of soluble salts, and soil sodicity causes adverse effects, such as an increase in soil pH, loss of soil physical structure (clay dispersion, swelling, and plugging of soil pores), and the deterioration of soil–water relations (decrease in infiltration, hydraulic conductivity, retention and drainage), leading to soil erosion, crusting, compaction, runoff, waterlogging, nutrient imbalances, and specific ion effects on plants [1–7].

Salinity levels can be expressed as total soluble salts (TSS) or as soil electrical conductivity (EC) of saturated extract or soil–water suspensions. Sodicity levels are usually determined as the exchangeable sodium percentage (ESP) through the amount of exchangeable Na^+ as a proportion of either the cation exchange capacity (CEC) or the sum of exchangeable cations [4,8], as well as by the sodium adsorption ratio (SAR) calculated from the soluble Na^+ relative to the soluble Ca^{2+} + Mg^{2+} concentrations in a soil solution using the formula proposed by Richards et al. [9]. The widely used salt-affected soil classification from the US Salinity Lab (USSL)—based on the threshold values of a soil EC_e of 4 dS m^{-1}, ESP of 15%, and pH of 8.5—generates four classes, namely, normal, saline, saline–sodic, and sodic soil. The Australian classification is analogous to the USSL criteria with the exception that it considers a soil ESP threshold value of 6% and takes into account the pH levels [10]. Furthermore, neutral and alkali salts determine the distinction between sodicity and alkalinity, so alkali soils normally have an excess of exchangeable Na^+ and carbonates besides a pH above 8 [11]. Concerning that fact, Chhabra et al. [12] proposed an alternative classification including the ion ratios of $(2CO_3{}^{2-} + HCO_3{}^{-})/(Cl^{-} + 2SO_4{}^{2-})$ and $Na^+/(Cl^- + 2SO_4{}^{2-})$ expressed in mol m^{-3}, besides soil EC_e and ESP, for facilitating the specific management and reclamation of salt-affected soils.

Data mining can be described as the capacity of identifying patterns from data to establish relationships and models through data analysis, and machine learning (ML) is a process of learning from a system's experience for self-improving based on resultant information. Moreover, supervised learning models the relationships and dependencies between the target prediction output and the input data/features to predict the output values for new data. Partial Least-Squares (PLS)—Discriminant Analysis (DA) is a 'supervised' version of principal component analysis (PCA) which achieves dimensionality reduction with complete cognizance of the classes, arriving at a linear transformation that converts the data to a lower dimensional space with as small an error as possible [13]. In addition, PLS regression combines features from PCA and multiple regression, allowing the reduction of the dimensionality while focusing on covariance. Support Vector Machines (SVM) seek to design a decision surface and separate the margin between the different levels, finding this hyperplane using support vectors and margins. Then, the SVM with linear kernel function fits an optimal hyperplane between the classes, making linear and separable small samples [14], while support vector regression fits a line as the hyperplane with the maximum number of points. Breiman and Cutler's Random Forests (RF) algorithm is a tree-based ensemble which generates trees built on resampled subsets of data, with each tree depending on an ensemble of random variables. RF classification combines the trees by unweighted voting and chooses the most voted class over all the tree ensembles at training time if the response is categorical, or combines the resulting trees by unweighted averaging if the response is continuous [15,16].

ML methods have been used to classify soils based on various features such as chemical, physical, and biological variables, as well as on specific criteria. Within the framework of ML algorithms, many methods have been progressively developed to automate the soil classification process, such as Decision Trees, k-Nearest Networks, Artificial Neural Networks, and SVM [17]; in that context, some investigations on various soil type classifications using ML methods were carried out [18–21]. The review on ML and soil sciences by Padarian et al. [22] shows that the modelling of continuous and categorical soil properties is based on their relationships with environmental covariates and is mainly focused on mapping. Some key findings in the compilation by Motia and Reddy [23] were that: the implementation of soil classification uses more ML methods than soil regression; the assessment of soil salinity still shows a low contribution from ML; SVM and RF techniques are widely used in ML predictions of soil parameters and classifications; and the $RMSE$ and R^2 are the top metrics used for the performance evaluation of ML prediction models in soil analysis.

Apart from simple/multivariate regression-based models, most of the studies based on ML methods in predicting and mapping salinity use variables from remote sensing (spectral bands and derived indices) [24–29], and combined with other environmental covariates (elevation, geology, hydrology, morphometry, and climate) [30–34]. Field-measured data (physical and chemical soil–water properties), which are used to a lesser extent, may improve the prediction performances for soil salinity, even more if alternative salt-term parameters are considered. Moreover, the determination of the content of exchangeable cations—and thus the soil ESP—is usually less cost-effective and more time-consuming than that of soluble ion concentrations, which are often used for estimating salinity/sodicity indirectly. Therefore, this study aimed to evaluate and compare the prediction performances of three ML regression and classification algorithms (PLS, SVM, and RF) for estimating the soil EC_e and ESP, and classifying salt-affected soils from soluble salt ions. Then, the results may contribute alternative covariates for modelling as well as to the characterization and management of salt-affected soils in the study area.

2. Materials and Methods

2.1. Study Area and Data

The observations (135 soil samples) were collected at a depth of ~25 cm from the agricultural lands of the High Valley of Cochabamba-Bolivia (Figure 1), under the framework of the survey by Weber [35]. The area is located between the latitude boundaries of −17°29′47.7″ to −17°39′48.6″ and longitude of −66°5′16.8″ to −65°45′13.0″, at an elevation of ~2750 m. The climate of the valley is semiarid with a mean annual temperature and rainfall of 15–16 °C and 450–550 mm, respectively. Regarding the geomorphic characterization of this area [36] (Metternicht and Zinck, 2010), most of the salt-affected soils are in the landscape of a valley with a relief type consisting of lagunary depressions, aluvio-lagunary/lagunary facies, a landform consisting of lagunary flats, and soil associations consisting of Ustalfic Haplargids/Ustochreptic Camborthids and Typic Salorthids/Natric Camborthids. The soil textural classes consisting of loam, silty loam, and silty clay loam were predominant among the samples.

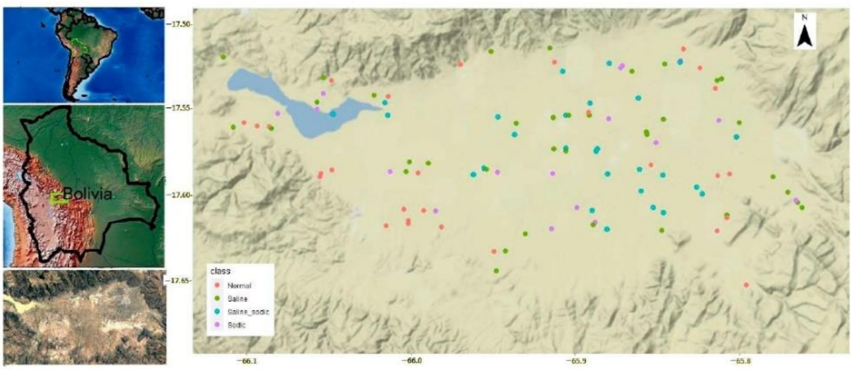


Figure 1. Soil sampling points and their salt-affected classes (USSL criteria) in the High Valley of Cochabamba, Bolivia.

2.2. Variables

As the explanatory variables, concentrations of soluble cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (HCO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}) were determined from a paste extract, following the standard procedures of Richards et al. [9] at the Soil-Water Lab, Faculty of Agricultural and Livestock Sciences, *Universidad Mayor de San Simón* (Bolivia).

The continuous variables to be predicted were the soil EC_e and the soil ESP calculated using the formula (Equation (1)) [4,8] with the exchangeable cation values obtained through a derived ISO 22171 at a pH of 7 and atomic adsorption spectroscopy at the *Station Provin-*

ciale d'analyses agricoles Lab (Belgium), taking into account the assessment by So et al. [37] for overcoming their overestimation as total extractable cations. The categorical variable to be explained comprises four categories classified using the USSL criteria [9], namely: normal (ESP < 15%, EC_e < 4 dSm^{-1}, pH < 8.5), saline (ESP < 15%, EC_e > 4 dSm^{-1}, pH < 8.5), saline–sodic (ESP > 15%, EC_e > 4 dSm^{-1}, pH <> 8.5), and sodic (ESP > 15%, EC_e < 4 dSm^{-1}, pH > 8.5). For practical purposes, the alkali soil was classified as sodic.

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

where cations are expressed as a concentration in $cmol_c\ kg^{-1}$.

2.3. Data Preparation and Model Implementation

The flow process of the modelling is described in Figure 2. Extreme values in the dataset were checked by applying a threshold value using the *Mahalanobis* distance from the PCA, and then 10 observations were discarded. In overcoming the possibility of hidden dependencies of the cross-validation (CV) and for testing purposes, the models were evaluated through an internal validation by partitioning the dataset into two sets, calibration (75%) and validation (25%), for both regression and classification models. The data were scaled into each calibration process. A subsequent performance evaluation showed that a min–max normalization was not needed.

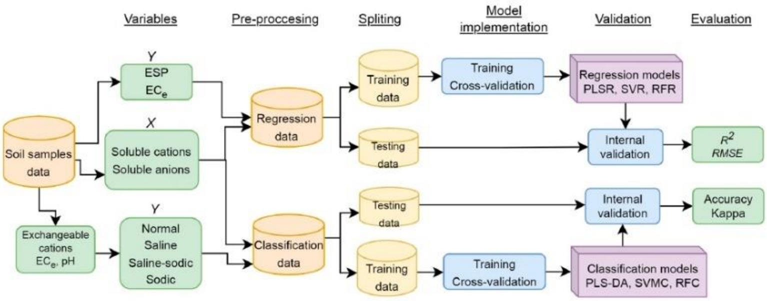


Figure 2. Flow chart of the methodological path of this study.

Three supervised ML algorithms were used: Partial Least-Squares (PLS) and Support Vector Machines (SVM) with linear kernel function as discriminating methods, and Random Forests (RF) as a tree-based method, for the respective regression (PLS-R, SV-R, RF-R) and classification (PLS-DA, SVM-C, RF-C) algorithms. A multivariate linear regression (ML-R) model was added for comparison purposes. The models were trained with tenfold groups, and CV was repeated five times. The specific tuning of the parameters for the training and CV of regression and classification models is shown in Table A1.

2.4. Model Performance Evaluation

The prediction was performed for the three regression/classification methods by using the obtained models from the training process on the testing datasets; then, the performances were compared. The metrics to evaluate the effectiveness of the regression techniques were the determination coefficient R^2 (Equation (2)) and the root mean square error *RMSE* (Equation (3)) as the standard deviation of the error. For classification models, the metrics were the overall accuracy (Equation (4)) as the correct classification of the data obtained by executing the model, and Cohen's kappa statistics (Equation (5)) like the strength of the agreement as the extent to which the data are correct representations of the variables measured [38]. Additionally, the measures of sensitivity and specificity, as the proportions of true positives and true negatives correctly predicted, respectively, were calculated for classification.

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (p_i - o_i)^2}{\sum_{i=1}^{n} \left(\bar{o} - o_i\right)^2} \tag{2}$$

$$RMSE = \left[n^{-1}\sum_{i=1}^{n} (p_i - o_i)^2\right]^{1/2} \tag{3}$$

where n is the number of observations, p_i is the predicted values, o_i is the observed data, and $\bar{o}$ is the mean for o_i.

$$\text{Accuracy} = \sum_{i=1}^{n} \frac{True\ classification}{Total\ cases} \tag{4}$$

$$Kappa = \frac{P_o - P_e}{1 - P_e} \tag{5}$$

where n is the number of classes, P_o is the total agreement probability, and P_e is the agreement probability due to chance.

2.5. Other Assessments

The relative importance of the variables was assessed through the RF measures of Mean Decrease Accuracy/Gini for classification and the percent increase in MSE and increase in node purity for regressions. For overcoming the imbalance caused by the sodic category, a resampling technique was applied. The stability of the models was assessed in function to three different data partitions as an indicator of the change in the level of performance; then, the dataset was split for obtaining a validation dataset proportion over (30%) and below (20%) the referential of 25%. Finally, the models were assessed with additional explanatory variables, namely, soil pH and EC_e determined from the same solution in which the soluble ions were measured, total organic carbon (TOC), and soil texture (clay, silt, and sand).

2.6. Software

Statistical analysis and ML modelling/evaluation were performed by using the R software (v.4.1.3) [39] and RStudio (v.1.31093) [40]. The regression and classification models (PLS, SVM, RF) were trained and evaluated through the package *caret* (classification and regression training) [41], and complementary packages for data preparation, analysis and visualization such as *randomForest* [42] and *FactomineR*, among others, were used.

3. Results and Discussion

3.1. Statistical Overview

Some descriptive statistics of the dataset are shown in Table A2. The distribution of samples according to the salt-affected soil classes was relatively balanced, except for the sodic soil category (Figure 3a). Among the explanatory variables, soluble Ca^{2+} with Mg^{2+} (r of 0.87) and Na^{+} with the anions were relatively highly correlated, as well as the soil EC_e and ESP with Na^{+} and soluble anions (Figure A1). Despite these relatively high relationships, it should be considered that ML algorithms deal with multicollinearity through regularizations and by focusing the prediction and accuracy instead of the influence among variables; moreover, all soluble salt ions are part of the dominant composition and balance in the soil solution of each site-specific sample. Correlations between the contents of cations in the soil sorption complex and those in the soil–water solution are relatively low (Table A3) in contrast to the findings of Porębska and Ostrowska [43]. According to the PCA, around 98% of the variance was explained by seven out of eight components. The components are not so good for discriminating the clusters (Figure 3b); consequently, for a complete separation of the soil categories, the PLS-DA, SVM, and RF classification algorithms were performed.

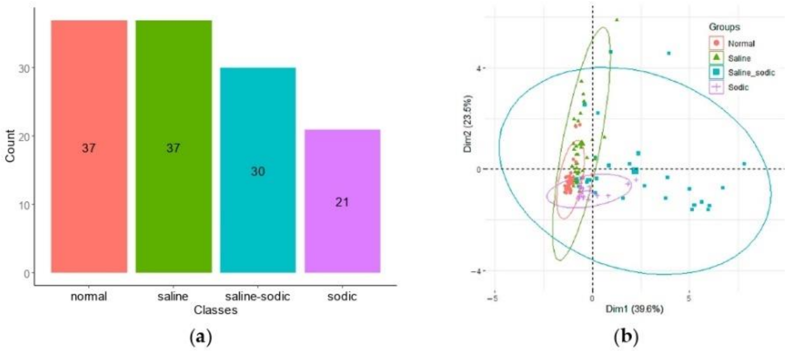


Figure 3. Distribution of the observations according to the salt-affected categories (**a**). PCA plot of observations grouped by soil categories (**b**).

3.2. Evaluation of the Regression Models

Among the assessed ML regression models for predicting soil EC_e, the SV-R and RF-R algorithms performed the best with relatively similar values of R^2 and *RMSE*, followed by ML-R and PLS-R models, which, in contrast, showed good cross-validation performances (Table 1). The overall high proportions of soil EC_e variance explained by the soluble ions agree with the fact that the soluble major ions complex is normally a good predictor for the soil EC and vice versa, and also coincide with the high correlations between soil EC_e and soluble ions as total dissolved salts [44,45]. Furthermore, the low performance of the PLS-R model agrees with the fact that it is better in cases where the number of explanatory variables is high or where multicollinearity is an issue. As a partially related study, Wang et al. [46] found that RF regression performed comprehensively better than SVM among other ML models in predicting salinity from field-measured spectral and salinity parameter data.

Table 1. Prediction performances of the regression models for estimating soil EC_e and ESP.

Method	EC_e		ESP	
	RMSE	R^2	*RMSE*	R^2
PLS-R	2.9 (3.3)	0.82 (0.72)	19.0 (13.6)	0.41 (0.63)
SV-R	1.9 (3.5)	0.92 (0.74)	18.4 (14.0)	0.40 (0.65)
RF-R	2.1 (3.7)	0.91 (0.66)	12.6 (12.4)	0.71 (0.60)
ML-R	2.4 (2.8)	0.88 (0.81)	19.1 (13.6)	0.40 (0.54)

RMSE stands for root mean square error. Values in parentheses mean the CV performances.

For estimating the soil ESP, the RF-R obtained the best prediction performance (R^2 of 0.71 and *RMSE* of 12.6), followed by the rest of the models with similar results; even so, they obtained relatively good cross-validation performances (Table 1). The relatively high performance of the RF-R model for predicting soil ESP is partly related to the relationships between SAR and ESP or exchangeable sodium ratio (ESR) (Table A3), and has some correspondence to the results obtained to predict ESP from SAR by using simple regression [47–50], and there is also correspondence with those to estimate the ESR from SAR [51,52].

Through the variable importance analysis by using the RF-R algorithm, two measures were obtained: percent increase in mean square error (MSE) as the prediction error of each variable if omitted from the analysis, and the increase in node purity as how much the model error increases when a particular variable is randomly permuted or shuffled. According to these metrics, Na^+ is the most important variable for predicting both soil ESP and EC_e, besides Cl^- and HCO_3^- which are indispensable for estimating soil EC_e, as well as Ca^{2+} for ESP (Figure 4a,b). In addition, despite the relatively low importance of K^+ in predicting soil ESP (Figure 4b), it might be important to keep this cation for modelling because it influences soil dispersion, as demonstrated through the exchangeable cation ratio (ECR) [53] and the cation ratio of soil structural stability (CROSS) [54] as alternative indicators for soil ESP and SAR, respectively.

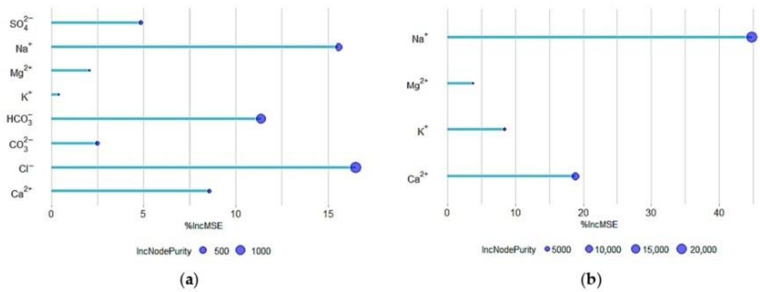


Figure 4. Variable importance as the percent increase in mean square error (%IncMSE) and the increase in node purity (IncNodePurity) from the RF model for the soil EC_e (**a**) and ESP (**b**).

3.3. Evaluation of the Classification Models

According to the internal validation, the RF-C model obtained the best performance with the highest prediction accuracy (87%) indicating a good classification with a significant strength of agreement beyond chance (kappa of 82%), followed by the SVM-C and PLS-DA models, both with a regular classification and moderate agreement. Additionally, according to the CV analysis, the RF-C and SVM-C algorithms performed better than the PLS-DA model with relatively similar results (Table 2).

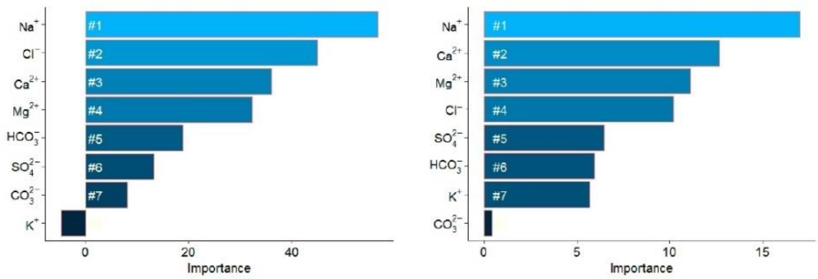
Table 2. Accuracy and kappa values of the model training and model testing.

Method	Calibration/CV *		Validation	
	Accuracy	Kappa	Accuracy	Kappa
PLS-DA	0.55	0.37	0.67	0.52
SVM-C	0.63	0.49	0.70	0.58
RF-C	0.61	0.47	0.87	0.82

* CV stands for cross-validation.

The overall Out of Bag (OOB) error of the RF bootstrapping was 37.9%, and the error classes were 0.29, 0.38, 0.26, and 0.68 for normal, saline, saline–sodic, and sodic soil, respectively. The misclassifications of sodic soil were mainly due to its imbalance in contrast to the other categories. The soil pH used to classify the soil may decrease the quality of the classification models because it is not directly related to the soluble/exchangeable cations, as the soil EC_e and ESP are. Based on the predictions in the confusion matrixes (Table A4), the measures of sensitivity and specificity were calculated. Overall, the sensitivity as the true positive rate was regular to good for predicting the normal, saline, and saline–sodic classes but poor for the sodic class; in addition, the RF-C model generated higher values of sensitivity than those of the SVM-C and PLS-DA (Table A5).

According to the estimation of the variables' relative importance using the Mean Decrease Accuracy and Mean Decrease Gini calculations, the soluble Na^+ was the most relevant parameter for classifying the salt-affected soils, followed by Ca^{2+}, Mg^{2+}, and Cl^- (Figure 5a,b). These rankings coincide with the variable selection through RF backward elimination and become important for eventually discarding the less important variables if and when the performance of the model is improved. The importance estimations have some correspondence with the ratio of soluble Na^+ to the base cations expressed by the SAR and also with the relevance of neutral salts over alkali salts for these soils.



(**a**) (**b**)

Figure 5. RF relative importance estimation of the explanatory variables according to the measures of *MeanDecreaseAccuracy* (**a**) and *MeanDecreaseGini* (**b**).

3.4. Resampling

For overcoming the imbalance generated by the minority class (sodic), the models were trained a second time by applying the resampling method 'Synthetic Minority Over-Sampling Technique' through the Smote function [55]; then, the results from the performance validation showed a slight improvement for the SVM-C model, but a significant decrease for the RF-C model in accuracy and kappa values (Table 3), compared to those without resampling (Table 2).

Table 3. Accuracy and kappa values of the model training and testing with the Smote function.

Method	Calibration/CV *		Validation	
	Accuracy	Kappa	Accuracy	Kappa
PLS-DA	0.55	0.39	0.60	0.48
SVM-C	0.61	0.46	0.73	0.62
RF C	0.60	0.45	0.77	0.68

* CV stands for cross-validation.

3.5. Stability Analysis

The stability was evaluated by performing a new validation of the regression and classification models based on three different partitions (percent calibration datasets of 70, 75, and 80). The RF regression models for predicting soil EC_e and ESP obtained lower differences between performances of the three calibration data amounts than those of SV-R and PLS-R, whereas, for the classification, the PLS-DA followed by the SVM-C technique were more stable than the RF-C model in predicting soil categories (Table 4).

Table 4. Stability assessment for the performance validations of the models.

Model and Metrics	Method	Percent of Calibration Dataset 70%	75%	80%	Difference *
EC_e Regression $RMSE/R^2$	PLS-R	3.5/0.68	2.9/0.82	2.3/0.92	1.2/0.24
	SV-R	3.4/0.71	2.0/0.92	1.9/0.95	1.5/0.24
	RF-R	2.9/0.79	2.1/0.91	3.0/0.88	1.7/0.15
ESP Regression $RMSE/R^2$	PLS-R	15.1/0.52	18.9/0.41	14.9/0.57	7.8/0.27
	SV-R	15.5/0.54	18.4/0.40	15.5/0.58	5.8/0.32
	RF-R	12.6/0.65	12.6/0.71	11.1/0.78	1.5/0.13
Classification Accuracy/Kappa	PLS-DA	0.65/0.51	0.67/0.52	0.71/0.57	0.06/0.06
	SVM-C	0.70/0.58	0.70/0.58	0.79/0.69	0.09/0.11
	RF-C	0.78/0.70	0.87/0.82	0.79/0.71	0.17/0.23

* Difference = sum of absolute differences among the metric values of the three partitions.

3.6. Additional Variables

By adding the soil pH, EC_e, TOC, clay, silt, and sand to the matrix of predictor variables, only the performances of PLS and SVM regressions to predict soil ESP showed a significant improvement (Table 5) compared to those in Table 1. These results partly contrast with those of Keshavarzi et al. [56] who obtained R^2/*MSE* values of 0.84/5.36 and 0.90/5.09 for the AI-based models Multi-Layer Perceptron and Adaptive Neuro-Fuzzy Inference System, respectively, for predicting ESP from EC_e, pH, and clay. Although the RF classification model obtained a slight increase in effectiveness (Table 5), should be noted the redundancy caused by the soil EC_e and pH as explanatory variables and as classifiers of the explained categories at the same time; however, their further inclusion might be pertinent if more easily obtained parameters are used, such as EC and pH measured in soil–water suspensions.

Table 5. Obtained model performances by adding features to the matrix of explanatory variables.

Method	Regression—EC_e		Regression—ESP		Classification	
	RMSE	R^2	*RMSE*	R^2	Accuracy	Kappa
PLS	7.6	0.89	12.5	0.62	0.61	0.45
SVM	4.4	0.96	12.1	0.63	0.61	0.47
RF	12.1	0.55	12.7	0.62	0.90	0.87

3.7. Some Remarks

Overall, RF and SVM regression models performed the best for predicting soil EC_e from soluble ions, as well as the RF model for estimating the soil ESP from soluble cations; and the RF followed by the SVM classification algorithm outperformed the PLS-DA in predicting salt-affected soil classes from soluble salt ions. Considering that it is important to apply tailored reclamation techniques based on modelling and predictive tools calibrated and validated for site-specific salt-affected soils [57], the obtained models become important tools for the monitoring and management of salt-affected soils for the study area, and also as source of alternative covariates for further modelling.

As tentative limitations, all the models still need an optimization of their prediction effectiveness; therefore, additional observations might be included in the dataset for improving the performance and stability of the classification/regression models, as well as for overcoming class imbalances and reinforcing the selection of variables. Additionally, the input of additional features such as remote sensing data and field-measured soil properties can also be useful for improving the modelling and predictions. Further classification modelling could consider alternative classification systems such as that of Chhabra et al. [12] which generates only three soil classes (normal, saline, and alkali).

4. Conclusions

The performances of ML classification and regression algorithms (PLS, SVM, and RF) in predicting soil EC_e, ESP, and salt-affected soil classes were evaluated and compared. Among the assessed ML regressions, SVM and RF obtained the best performances for predicting the soil EC_e, whereas the RF model was superior for estimating the soil ESP. The RF classification algorithm showed the best prediction accuracy (87%) with a kappa value of 82%, followed by SVM and PLS-DA. Soluble Na^+ was the most important explanatory variable for all the prediction models, followed by Ca^{2+}, Mg^{2+}, Cl^-, and $HCO_3{}^-$ which were important for classification, as well as for regression. The sodic class was poorly predicted, and the applied resampling for overcoming its imbalance did not significantly improve the classification performances. The stability analysis showed that the amount of training data generated less impact on the RF regression models, whereas the SVM and PLS-DA were more stable than RF for classification. Additional explanatory variables somewhat improved the PLS and SVM regressions to predict ESP and the RF classification effectiveness. It can be concluded that the RF or SVM and the RF regression can be suitable to estimate the soil EC_e and ESP, respectively. In addition, the RF and SVM classification models can be appropriate in predicting salt-affected soil classes from soluble salt ions. Additional samples and explanatory features can be included in the dataset for improving the prediction performances. The assessed models might contribute significantly to the monitoring, mapping, and management of salt-affected soils in the study area.

Author Contributions: Conceptualization, D.A.F.; methodology, D.A.F.; validation, D.A.F.; formal analysis, D.A.F. and G.C.; investigation, D.A.F.; writing—original draft preparation, D.A.F.; writing—review and editing, D.A.F. and G.C. All authors have read and agreed to the published version of the manuscript.

Funding: Funded by the 'Académie de recherche et d'enseignement supérieur'—ARES (Belgium) and provided by the 'Universidad Mayor de San Simón'—UMSS (Bolivia). Code: AI-11420/UMSR1.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are available on request from the corresponding author.

Acknowledgments: The team from Soil-Water-Plant Exchanges—TERRA—GABT (University of Liège) and the team from the Soil-Water Lab and CISTEL (UMSS).

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

Appendix A

Table A1. The setting of parameters for model training and cross-validation analysis.

Model	Algorithms	Parameters/Values
EC_e and ESP Regression	PLS-R	Number of components: 1 (EC_e), 3 (ESP)
	SV-R	CF grid: 0.01, 0.1, 0.25, 0.5, 1
	RF-R	NT of 3000, MTRY of 5 (EC_e), 2 (ESP)
Multiple classification	PLS-DA	Number of components: 2
	SVM-C	CF grid: 0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2
	RF-C	NT of 3000, NS of 10, MTRY of 2

R = regression; C = classification; NT = number of trees; NS = minimum node size; MTRY = number of randomly selected predictors; CF = capacity factor for SVM.

Table A2. Descriptive statistics of explanatory variables (soluble salt ions), ESP and EC_e.

Item	Mean	SD	CV	Min	Max	Median	Count
Ca^{2+}	3.7	4.5	1.2	0.1	26.2	2.2	125
Mg^{2+}	1.7	1.9	1.1	0.09	9.4	1.0	125
Na^+	27.4	54.9	2.0	0.02	326.1	5.6	125
K^+	0.5	0.5	1.0	0.02	2.2	0.4	125
Cl^-	17.4	35.3	2.0	0	205.0	5	125
SO_4^{2-}	14.2	29.6	2.1	1.2	153.4	3.7	125
HCO_3^-	5.4	6.6	1.2	0.5	34.0	3.0	125
CO_3^{2-}	6.3	22.2	3.5	0.0	134.0	0.0	125
ESP	16.3	20.4	1.2	0.1	77.0	4.9	125
EC_e	6.1	6.5	1.1	0.3	33.4	4.1	125

SD = standard deviation; CV = coefficient of variation.

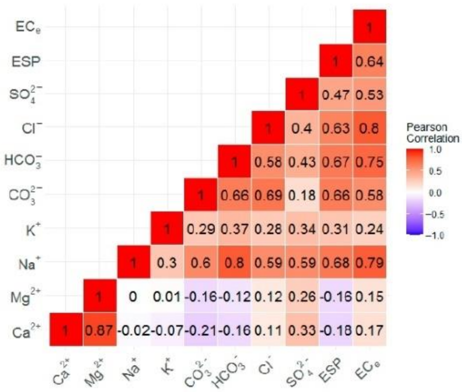


Figure A1. Correlation matrix among the explanatory variables, ESP and EC_e.

Table A3. Correlation matrix among sums of soluble and exchangeable cations, sodicity parameters, and EC_e.

	Sum-Sol Cations	Sum-Sol-Anions	Sum-Exc-Cations	SAR	ESR	ESP	EC_e
Sum-Sol Cations	1						
Sum-Sol-Anions	0.78	1					
Sum-Exc-Cations	0.32	0.42	1				
SAR	0.90	0.75	0.33	1			
ESR	0.57	0.77	0.45	0.61	1		
ESP	0.66	0.75	0.50	0.66	0.93	1	
EC_e	0.81	0.84	0.30	0.73	0.64	0.64	1

Sum-Sol = Sum of soluble; Sum-Exc = Sum of exchangeable; SAR = sodium adsorption ratio; ESR = exchangeable sodium ratio (ESP/100-ESP).

Table A4. Confusion matrixes of the predictions for the three ML classification algorithms.

Class	PLS-DA				SVM-C				RF-C			
	NO	SA	SS	SO	NO	SA	SS	SO	NO	SA	SS	SO
Normal	9	2	1	5	9	2	1	4	9	0	0	1
Saline	1	6	1	0	1	6	0	0	1	8	0	1
Saline–sodic	0	0	5	0	0	0	5	0	0	0	7	1
Sodic	0	0	0	0	0	0	1	1	0	0	0	2

NO = normal; SA = saline; SS = saline–sodic; SO = sodic.

Table A5. Sensitivity and specificity for the three classification models.

Class	Sensitivity			Specificity		
	PLS-DA	SVM-C	RF-C	PLS-DA	SVM-C	RF-C
Normal	0.90	0.90	0.90	0.60	0.65	0.95
Saline	0.75	0.75	1.00	0.91	0.95	0.90
Saline–sodic	0.71	0.71	1.00	1.00	1.00	0.96
Sodic	0.00	0.20	0.40	1.00	0.96	1.00

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ANNEX 2

agriculture

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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

Citation: Andrade Foronda, D.; Colinet, G. Combined Application of Organic Amendments and Gypsum to Reclaim Saline–Alkali Soil. *Agriculture* **2022**, *12*, 1049. https://doi.org/10.3390/agriculture12071049

Academic Editor: Xiaohua Long

Received: 18 May 2022
Accepted: 13 July 2022
Published: 18 July 2022

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 Ca^{2+} and precipitates as $CaCO_3$; 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], saline–alkali 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 $(2CO_3^{2-} + HCO_3^-)/(Cl^- + 2SO_4^{2-})$ 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 ($CaSO_4 \cdot 2H_2O$) application counters reduced hydraulic conductivity in Na^+-dominated soils through Na^+–Ca^{2+} 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 Na_2CO_3, the addition of gypsum provides a source of Ca^{2+} which precipitates as $CaCO_3$ and $Ca(HCO_3)_2$, 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 Ø 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).

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

Property	Value	Property	Value
Bulk density (g cm^{-3})	1.3	EC_e (dS m^{-1})	24.1
Clay (%)	17.8	pH	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		

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; $CaCO_3$ (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^+, Ca^{2+} and Mg^{2+} 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
pH	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 $CaCl_2$) 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).

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

where cations are expressed as a concentration in $cmol_c$ kg^{-1}.

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

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).

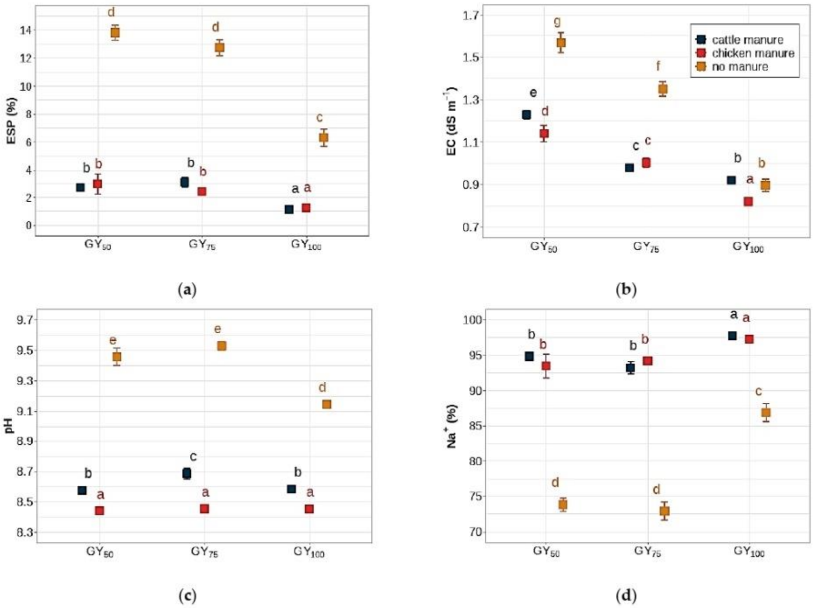

Figure 1. Soil ESP (**a**), EC_e (**b**), pH (**c**) and displaced Na^+ (**d**) for the interactions between manures/no manure and gypsum levels. Means sharing a letter are not significantly different, according to the Scott–Knott test (p = 0.05). The bars indicate the standard error.

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-GY_{100} and CH-GY_{100} 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-GY_{100} 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 Ca^{2+} 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 Ca^{2+} 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 Na_2CO_3, 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 Ca^{2+} 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.

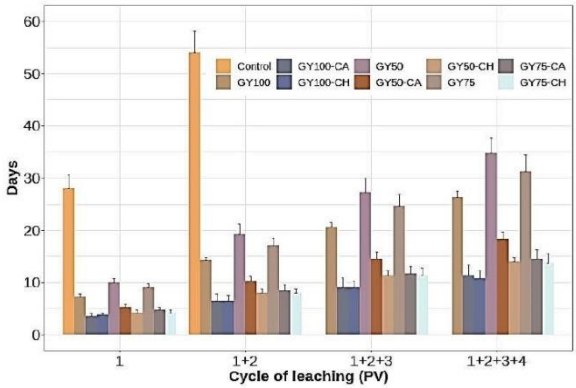

Figure 2. Percolation time in accumulated days according to the applied cycles of leaching as pore volumes. Cycles of leaching: 1 = first, 2 = second, 3 = third, and 4 = fourth.

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 Ca^{2+} 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 EC_e 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.

Author Contributions: Conceptualization, D.A.F. and G.C.; methodology, D.A.F.; validation, D.A.F.; formal analysis, D.A.F.; investigation, D.A.F.; resources, D.A.F.; writing—original draft preparation, D.A.F.; writing—review and editing, D.A.F. and G.C.; supervision, D.A.F. and G.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the 'Académie de recherche et d'enseignement supérieur—ARES' (Belgium) coded as AI-11420, and provided by the 'Universidad Mayor de San Simón—UMSS' (Bolivia).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are available on request from the corresponding author.

Acknowledgments: Ruben Saire Quispe, the team of the Soil-Water Lab (UMSS), the team of CISTEL (UMSS), and the team of Soil-Water-Plant Exchanges—TERRA—GABT (University of Liège).

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

Appendix A

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

Treatment	ESP (%)	EC_e ($dS\ m^{-1}$)	pH	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

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].

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

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

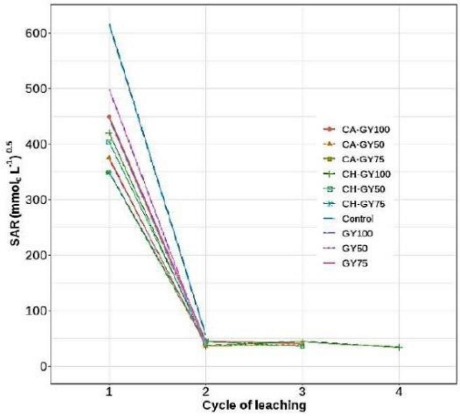

Figure A1. Evolution of sodium adsorption ratio (SAR) in the leachates at each cycle of leaching.

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ANNEX 3

environmental sciences proceedings

MDPI

Proceeding Paper

Reclamation of a Saline-Sodic Soil with Organic Amendments and Leaching †

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† Presented at the 2nd International Laayoune Forum on Biosaline Agriculture, 14–16 June 2022; Available online: https://lafoba2.sciforum.net/.

Abstract: Excessive amounts of Na^+ and soluble salts are characteristics of saline-sodic soils. Loss of soil structure and osmotic stress in plants are negative effects of salinity-sodicity. This study evaluated the effect of cattle manure, biochar and tropical peat at 1 and 2% (*w*/*w*) with leaching, on the exchangeable sodium percentage (ESP), electrical conductivity (EC_e) and pH of a saline-sodic soil from the High Valley of Cochabamba (Bolivia). The soil was placed in simulated soil columns and two lixiviations were applied. The initial values of soil were as follows: ESP of 66.6%, EC_e of 20.5 dS m^{-1}, and pH of 8.55. Results after leaching differed significantly (p = 0.05) among the interactions. Cattle manure at 2% was the most effective in reducing soil ESP to 27.6%, followed by the rest of the treatments. The three amendments at any level were efficient in lowering EC_e below 4 dS m^{-1}. Peat at 2% decreased the soil pH to 7.76. The superiority of cattle manure can be explained by the improvement of soil aggregation and leaching efficiency, through its OM and Ca^{2+} + Mg^{2+} contribution. Overall, cattle manure was superior in reclaiming the soil salinity-sodicity, and only the EC_e threshold value from the US Salinity Lab classification was reached by any amendment, indicating that cattle manure, biochar or tropical peat with leaching, can be used to reclaim some saline-sodic soils.

Keywords: saline-sodic soil; soil remediation; manure; biochar; peat

Citation: Andrade Foronda, D. Reclamation of a Saline-Sodic Soil with Organic Amendments and Leaching. *Environ. Sci. Proc.* **2022**, *16*, 56. https://doi.org/10.3390/environsciproc2022016056

Academic Editor: Abdelaziz Hirich

Published: 16 June 2022

1. Introduction

As a category of salt-affected soils, saline-sodic soils are characterized by an excessive amount of soluble salts, and sodium (Na^+) in the soil solution and cation exchange complex. Loss of soil structure and osmotic stress in plants are some of the negative effects of salinity-sodicity. Soil salinity can be measured through electrical conductivity (EC), and sodicity by the exchangeable sodium percentage (ESP) or the sodium adsorption ratio (SAR). Saline-sodic soils can be classified using the threshold values from the US Salinity Lab (USSL) classification [1], as follows: ESP > 15%, EC_e > 4 dS m^{-1} and pH < 8.5. Saline-sodic soils can be reclaimed by leaching with non-saline water and adding chemical/organic amendments.

The addition of organic amendments in sodic soils binds the small soil particles together into large water-stable aggregates, increases porosity and thus improves the soil physical properties [2]. Using organic amendments instead of inorganic amendments can reduce input cost savings as a sustainable and efficient management method to reclaim salt-affected soils [3], besides the beneficial impacts on nutritional and biological soil properties.

A soil-column experiment was carried out to evaluate the reclamation effect of cattle manure, biochar and tropical peat at two rates with leaching, on the ESP, EC_e and pH of a saline-sodic soil.

2. Materials and Methods

The soil (Table 1) was collected from the High Valley of Cochabamba (Bolivia) at a depth of 25 cm. It should be noted that the soil pH is slightly higher than the threshold value of the USSL classification. The organic amendments (Table 2) used to reclaim the soil were: cattle manure (CM) collected locally, tropical peat (PE) as tree fern fiber from the tropical area, and biochar (BI) branded by Greenpoch SA (Belgium).

Table 1. Chemical and physical parameters of the saline-sodic soil, before reclamation.

Property	Value	Property	Value	Property	Value
TOC (%)	0.3	EC_e (dS m^{-1})	20.5	K^+ ($mmol_c$ L^{-1})	1.5
Clay (%)	18.2	ESP (%)	66.6	HCO_3^- ($mmol_c$ L^{-1})	40.3
Silt (%)	52.1	Na^+ ($mmol_c$ L^{-1})	339.2	CO_3^{2-} ($mmol_c$ L^{-1})	20.0
CEC (cmol kg^{-1})	5.0	Ca^{2+} ($mmol_c$ L^{-1})	0.5	Cl^- ($mmol_c$ L^{-1})	185.0
pH	8.55	Mg^{2+} ($mmol_c$ L^{-1})	0.7	SO_4^{2-} ($mmol_c$ L^{-1})	71.1

TOC: total organic carbon, CEC: cation exchange capacity, EC_e: electrical conductivity (paste extract).

Table 2. Some chemical properties and TOC of the organic amendments.

Property	Cattle Manure	Biochar	Tropical Peat
Na^+ (mmol kg^{-1})	1.4	0.1	0.0
Ca^{2+} (mmol kg^{-1})	46.7	5.1	15.5
Mg^{2+} (mmol kg^{-1})	77.4	4.0	30.9
EC (d Sm^{-1})	3.7	0.3	0.7
pH	8.5	9.7	3.6
TOC (%)	23.7	33.0	22.5

Following the protocol of [4], simulated soil columns were assembled with PVC tubes (Ø of 15 cm), and each was filled with 6.7 kg of soil sieved at 4 mm, and then the upper layer was mixed with the respective amendment. The dose of amendments was calculated on a dry weight basis to reach 1 and 2% of organic matter (OM). To simulate the water from the rain, distilled water was used for the leaching process. The volume of water was calculated as a pore volume (PV) using the formula provided by Kahlon et al. [5] and Ahmad et al. [4]. After an initial soil saturation with 3/4 PV, two lixiviations were applied, each with one PV for two to four weeks. Response parameters were soil ESP, EC_e, and pH. The ESP was calculated using Equation 3 in Qadir et al. [6]. The design was completely randomized and the treatments were: CM-1%, CM-2%, BI-1%, BI-2%, PE-1%, PE-2% and control (only leaching). The results were evaluated using LSM-Tukey adjustment.

3. Results and Discussion

The results after leaching showed that soil ESP, EC_e and pH, differed significantly ($p < 0.05$) among the interactions. CM-2% was the best treatment for reducing the initial soil ESP by 39%, followed by CM-1% (by 31.5%), and lastly the rest of the treatments with a similar effect (Figure 1a). CM-1% and CM-2% were as effective as BI-2% and PE-2% for lowering EC_e by over 16 dS m^{-1} concerning the initial soil, while BI-1% and PE-1% showed a lower efficiency but higher than that of the control (Figure 1b). PE-2% decreased the initial pH to 7.76, followed by CM-1%, CM-2% and PE-1% in equal magnitude; in contrast, BI maintained a pH around the initial value (Figure 1c). Although organic amendments were effective in reclaiming this saline-sodic soil, the ESP and pH threshold values from the USSL classification were not reached. It should be pointed out that the percolation time of PE and BI was double that of CM.

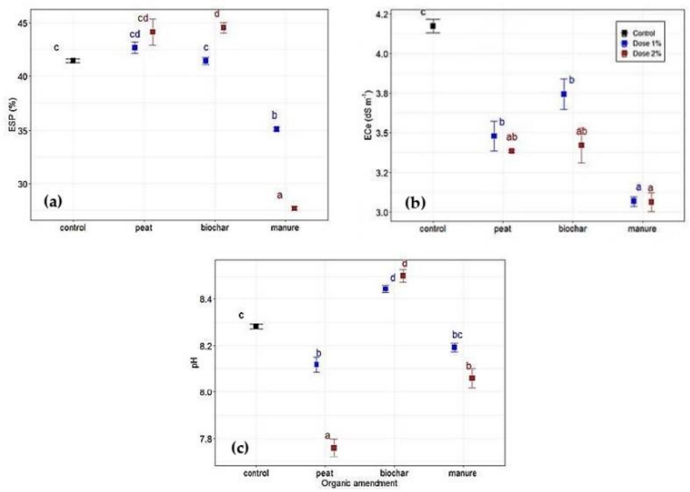

Figure 1. Soil ESP (**a**), EC_e (**b**) and pH (**c**), for the interactions between organic amendments and doses. Means sharing a letter are not significantly different according to pairwise comparisons of LSM with Tukey adjustment ($p < 0.05$). The bars indicate the standard error.

The superiority of CM in decreasing ESP and EC_e can be partly attributed to its initial amounts of TOC, Ca^{2+} and Mg^{2+}, contributing to the improvement of soil structure and infiltration, thus displacing Na^+ from the soil. The lower effectiveness of PE in reducing ESP was likely due to its swelling capacity which interacted with soil dispersion leading to a slowdown of the leaching process. In this regard, [7] reported that reclaimed soil with bentonite showed a lower decrease in salinity and sodicity levels and a higher percolation time due to the swelling capacity. The BI also showed a weak effect on sodicity potentially due to its insufficient ability to influence soil structure, and since, as [8] indicated, the mode of action of BI is physiochemical while composts provide a comprehensive reclamation when biological and physiochemical factors act together. In contrast to BI, the PE significantly reduced the soil pH due to its very low pH, causing an acidic counteracting effect, as [3] found that composts significantly improved soil CEC and pH values but the BI did not.

Water by itself was less effective in decreasing Na^+, but lowered EC_e to 4.2 dS m^{-1}, coinciding with [9], which found that EC decreased significantly even for the unamended soil possibly caused by solute leaching; moreover, [10] stated that flushing water reduced salinity with and without the application of manure.

Overall, the results suggest that CM, BI and PE enhanced the reclamation effect of leaching in remediating soil salinity and/or sodicity, through the positive impact of their OM on soil structure and infiltration, thus improving Na^+ displacement, agreeing with the following findings: organic amendments significantly lowered the level of soil EC_e, ESP and SAR compared to the control soils, improved soil structure, aggregate stability and saturated hydraulic conductivity, even more in compost treated soils [3]. The physical properties of the salinized soil, such as structural stability, infiltration rate, water-holding capacity and washing capacity were considerably improved by OM from the solid waste application [11]. Water hyacinth and rice straw compost singly or combined showed a pronounced decrease in EC, pH, SAR, and ESP compared with control [12].

4. Conclusions

Cattle manure at 2% was the best treatment for decreasing soil ESP to 27.6%, and any treatment was more effective than control in lowering EC_e below 4 dS m^{-1}. Peat at 2% showed a higher reduction in the soil pH (to 7.76). The superiority of cattle manure in reducing ESP and EC_e may be due to the improvement of the soil structure and infiltration through its OM and divalent cations contribution, whereas peat and biochar were less effective possibly due to the swelling capacity and insufficient rate, respectively, which in addition to the soil dispersion led to a slowdown of leaching. Overall, cattle manure with leaching was more efficient in ameliorating soil salinity-sodicity, and any amendment was effective in lowering salts. However, the ESP and pH threshold values from the USSL classification were not reached. This study suggests that some saline-sodic soils can be reclaimed by adding cattle manure, biochar or tropical peat, with leaching.

Funding: This research was funded by the 'Académie de recherche et d'enseignement supérieur-ARES' AI-11420 (Belgium), and provided by the 'Universidad Mayor de San Simón-UMSS' (Bolivia).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The Soil-Water Lab (UMSS) and Jose Luis Mamani.

Conflicts of Interest: The author declares no conflict of interest.

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ANNEX 4

Summary of the article: Estimation of exchangeable sodium percentage from sodium adsorption ratio for salt-affected soils from the high valley of Cochabamba.

Andrade Foronda, D.; Rodríguez G., E.; Colinet, G. (2020). Estimación del Porcentaje de Sodio Intercambiable en Función de la Relación de Adsorción de Sodio para Suelos Afectados por Sales. *Rev. Agric*. 62**,** 31–36.

This study aimed to generate and evaluate simple regression models to estimate soil exchangeable percentage (ESP) from sodium adsorption ratio (SAR) and SAR from electrical conductivity (EC) based on a soil sampling from the High Valley of Cochabamba.

Materials and methods

The soil samples were collected at a depth of ~25 cm from the High Valley of Cochabamba - Bolivia. Some soil properties of the soil observations are listed in Table A4.1. Lab measurements, determination and calculations of continuous variables were done following the standard procedures of Richards et al. (1954).

Table A4.1 Descriptive statistics of some soil properties for calibration (a) and validation (b) dataset.

Property	Calibration				Validation			
	Mean	Min	Max	SD	Mean	Min	Max	SD
EC_e ($dS.m^{-1}$)	2.22	0.17	20.60	3.31	2.88	0.34	31.50	7.19
pH	7.93	6.84	8.97	0.39	7.72	6.92	9.82	0.69
Sand (%)	30.81	4.60	57.46	13.02	28.99	8.75	72.71	14.53
Silt (%)	46.31	23.00	73.46	9.74	44.07	16.33	65.86	13.56
Clay (%)	22.88	7.48	65.40	9.69	26.94	5.88	63.54	15.48
OM (%)	1.78	0.50	6.00	1.06	0.85	0.05	2.48	0.80
SAR	7.22	0.01	58.40	10.90	17.94	0.50	75.90	22.88
ESP (%)	8.60	0.00	60.97	11.50	13.22	0.20	61.70	19.99

SD means standard deviation.

The linear models to predict ESP from SAR and SAR from EC were generated through the following linear regression mathematical formula:

$$Y = b0 + b1 * x$$

Where Y is the dependent variable, $b0$ *and* $b1$ are the linear regression beta coefficients for the intercept and slope, respectively, and x is the independent variable.

The metrics used to assess the performance of simple regression models were the coefficient of determination - R^2 (Eq. 5), the root mean square error – *RMSE* (Eq. 6) and the residual standard error – *RSE* (Eq. 8) Additionally, a paired sample T-test was used to assess the differences between the predicted and measured values. Statistical analysis was performed by using the R software v.3.1.9 (R Core Team, 2013).

Results and discussion

The correlation coefficient between soil exchangeable percentage (ESP) and sodium adsorption ratio (SAR) was high (0.92) and between SAR and electrical conductivity (EC) was moderately high (0.65). The linear regression to predict soil ESP from SAR ($ESP = 0.9725 * SAR + 1.5765$) showed a better association (R^2 of 0.85, *RSE* of 4.5) between the variable to be predicted and the predictor, than that (R^2 of 0.41, *RSE* of 8.4) to predict SAR from EC ($SAR = 2.129 * EC + 2.499$), as shown in Figure A4.1.

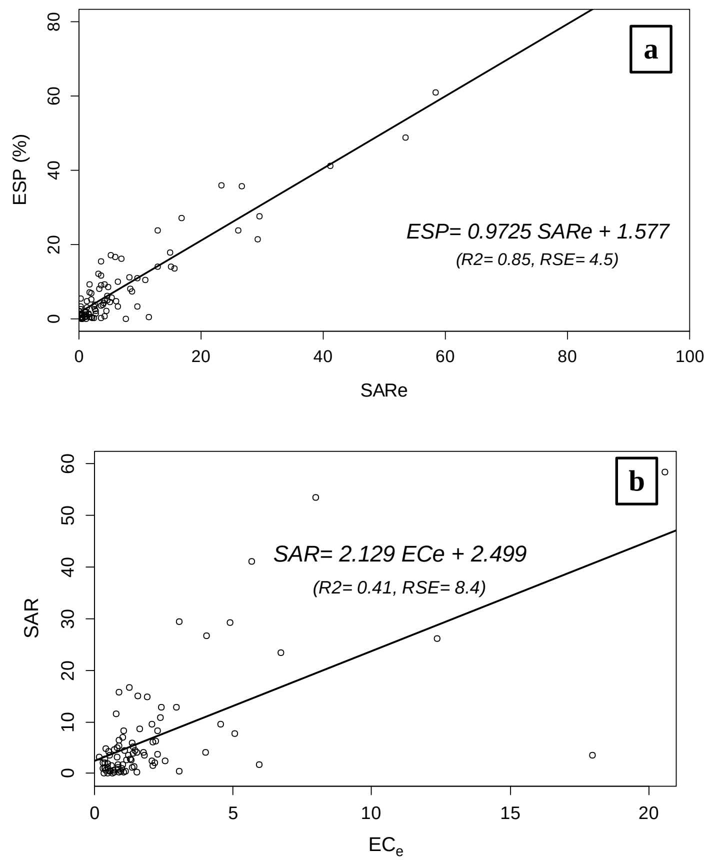

Figure A4.1 Fitted linear regression models to predict ESP from SAR (a) and SAR from EC (b).

The paired sample T-test (Table A4.2) for the obtained model ($ESP = 0.9725 * SAR + 1.5765$) showed that the predicted ESP values are not different from those of the measured ESP from the testing dataset. This result is consistent with the findings of Seilsepour et al. (2009); Elbashier et al. (2016a); Zare et al. (2014); and Chi et al. (2011), and the estimated ESP through the widely used USSL model ($ESP = 0.01475 * RAS - 0.0126$) was not significantly different from the measured values, thus more efficient than the obtained model. According to the approach of Bland and Altman (1999), the differences between the estimated and measured soil ESP values have a normal distribution since 95% of the predicted values fall between 5.81% ± 1.96 SD of the measured values. Besides the addition of salt-affected soil samples to the dataset, logarithmic or square-root regressions can be fitted to probably outperform the linear model as evaluated by Chi et al. (2011). The T-test also shows that the difference between the predicted SAR from EC values ($SAR = 2.129 * EC + 2.499$) and measured SAR values in the validation dataset was significantly different in contrast to that obtained by the model ($SAR = 0.464 * EC + 7.077$) of Seilsepour and Rashidi (2008) which was assessed in a similar soil texture to that of this study (Table A4.2).

Table A4.2 Paired sample T-test between the predicted and measured values for the generated and reference models to predict ESP from SAR and SAR from EC_e.

Model	Average difference*	SD of the difference*	P value	95% CI of the difference
$ESP = 0.9725 * SAR + 1.5765$ [1]	5.81	12.40	0.063	-0.35, 11.98
ESP from SAR (USSL)[2]	2.91	11.18	0.285	-2.65, 8.47
$SAR = 2.129 * EC + 2.499$ [1]	9.30	16.78	0.03	-17.64, -0.95
$SAR = 0.464 * EC + 7.077$ (SR)[3]	-0.11	1.26	0.747	-0.80, 0.59

(1) Generated models, (2) ESP/(100 − ESP) = 0.01475*SAR − 0.0126 (Richards et al., 1954),
(3) Seilsepour and Rashidi (2008)
* Expressed in percentage for soil ESP and dS m^{-1} for EC.

Conclusion

The simple regression to predict soil ESP from SAR $ESP = 0.9725 * SAR + 1.5765$ was more efficient than that estimating SAR from EC; however, the model from the USSL still outperformed such obtained model in forecasting the ESP. Further validation is needed with additional samples to increase the accuracy of the model, then can be used for predicting ESP in the High Valley.

ANNEX 5

Summary of the article:

Gypsum and sulphur to reclaim saline-sodic soil: pot experiment.

Andrade Foronda, D.; De Froidmont, C.; Colinet, G. (2020). Yeso Agrícola y Azufre para la Remediación de un Suelo Salino-Sódico del Valle Alto de Cochabamba. *Rev. Agric*. 62**,** 65–72.

This experiment aimed to assess the effect of gypsum and sulphur at two doses in reclaiming sodicity and salinity of a saline-sodic soil from the High Valley of Cochabamba, and to identify the most effective amendment(s) and dose(s), and to identify the most effective amendment(s) and dose(s).

Materials and methods

The soil was collected in the High Valley of Cochabamba (17º 32'38.6" S, 65º51'41.9" W) at a depth of 20 - 25 cm. The experiment was carried out in a greenhouse at the Faculty of Agricultural Sciences (UMSS - Bolivia). The soil properties were bulk density of 1.4 g cm^{-3}, cation exchange capacity of 5.1 $cmol_c$ kg^{-1}, electrical conductivity (EC) of 22.7 dS m^{-1}, exchangeable soil percentage (ESP) of 69.7% pH of 9.6, 19.3% clay, 54.9% silt and 25.8% sand. The irrigation water had an EC of 2.3 dS m^{-1}, pH of 8.1 and Na^+ concentration of 25 mg L^{-1}. The purity of gypsum (GY) was 91.7% (18.5% Ca^{2+}), and the purity of sulphur (SU) was 97.5%. The gypsum requirement (GR) to lower the ESP to at least 15% was calculated through the equation used by Hoffman and Shannon (2007) and Lebron et al. (2002), and the sulphur requirement was determined as the GR multiplied by a factor of 5.38 (Richards et al., 1954). The soil was dried, homogenized and 4mm sieved, and then mixed with GY or SU at a dose of 50% or 100% of the calculated GR and requirement. Each pot of 2.5 L volume was adapted to collect the leachate (Figure A2.1) and then filled with two kilograms of soil/mix over a layer of two cm gravel. The volume of leaching water was calculated through the pore volume. (PV) formula proposed by Kahlon et al. (2013) and Ahmad et al. (2016). An initial water volume of 490 ml (3/4 PV) was added to saturate the soil, and then five lixiviations – each of 660 ml as one PV – were applied until a relatively constant EC was reached in the leachates. After reclamation, soil samples were collected from each pot and then analysed. The pH was determined through the 1N KCl method and the EC was measured in the soil: water (1:5) suspension and converted to EC of paste extract (EC_e) using a conversion factor (Sonmez et al., 2008). Exchangeable cations were measured through the Metson method at pH 7 and atomic adsorption spectroscopy (AAS). Soil ESP and SAR were calculated by using the formulas proposed by Hazelton & Murphy (2007) and Richards et al. (1954), respectively. The experimental design was completely randomized with five replications. The treatments were: GY-50%, GY-100%, SU-50%, SU-100%, and no amendment. Mean comparisons among treatments were performed by using the LSD–Tukey adjustment ($p < 0.05$).

A5.1 Figure Adapted pot for leachate collection.

Results and discussion

There were no significant differences in the combination between the amendment and dose levels. Gypsum was more effective than sulphur and only water in reducing the initial soil ESP (69.7%) by over 30% (Figure A5.2a). The initial soil EC_e (22.7 dS m^{-1}) decreased by over 50% either with gypsum or sulphur or without amendment (Figure A5.2b). Gypsum and sulphur reduced soil pH by equal magnitude (Figure A5.2c).

Gypsum was superior in improving soil salinity/sodicity, agreeing with the results obtained by Qadir et al. (1996), Ahmad et al. (2016) and Tavares et al. (2012); however, Manzano Banda et al. (2014) found that only leaching was as effective as either gypsum, sulphur or manure in ameliorating saline-sodic soil. The lower effectiveness of sulphur was likely due to the insufficient incubation time and low soil organic matter content since sulphur needs to be oxidized by microbiological activity and oxygen to form sulphuric acid, which in turn dissolves the calcite in the soil generating the Ca^{2+} needed to remove the exchangeable Na^+; in this regard, Hanson et al. (2006) stated that the effect of sulphur is slower in comparison to the direct application of sulphuric acid, therefore, it is presumed that a longer incubation time was needed for the sulphur treatments. Moreover, the reduction in soil ESP by gypsum was proportional to that of pH in concordance with the conclusions of Gupta et al. (1981) and Abrol et al. (1980). The efficiency of any treatment to lower EC can be explained by the effect of sole water on the leaching of soluble salts including Na^+ which precipitates forming Na_2SO_4 as mentioned by Legros (2007) and Abdel-Fattah (2012). Because the interaction between the type of amendment and dose was not significant, it was likely that a dose of 50% of either gypsum or sulphur was sufficient to improve the soil sodicity. Further evaluations are needed, including intermediate doses – besides 50 and 100% – of 25%, 75% and 125% as well as different soil types.

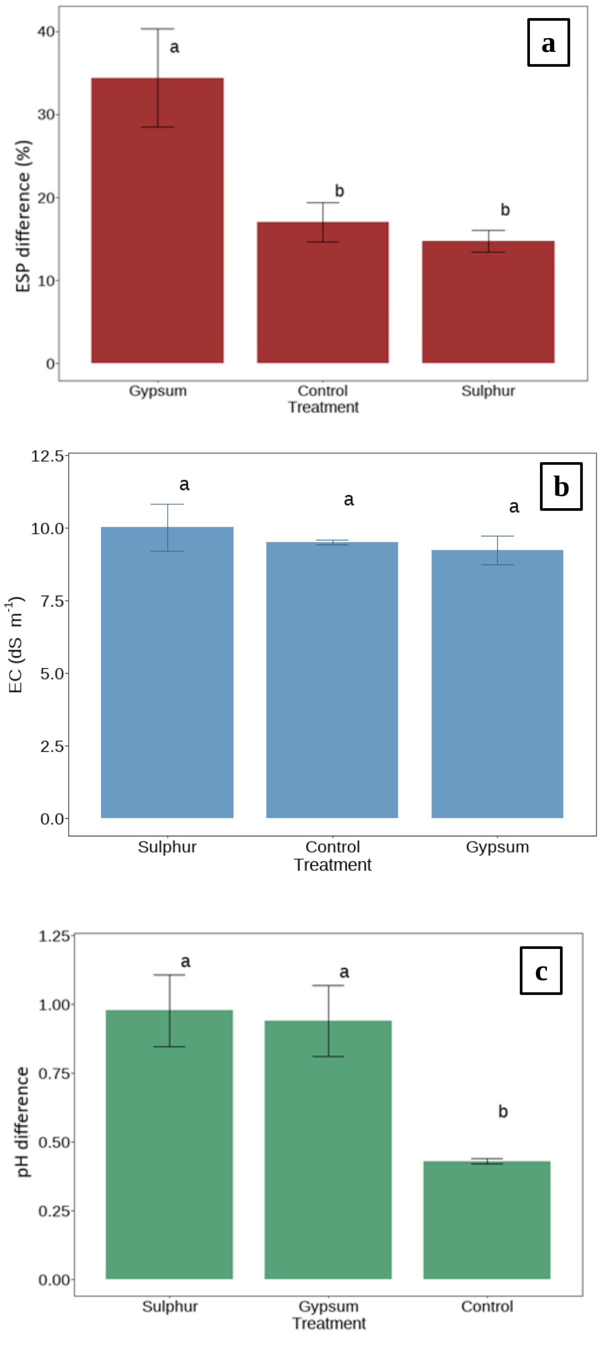

Figure A5.2 Effect of gypsum and sulphur addition on soil ESP (a), ECe (b), and pH (c). The soil ESP and pH differences represent the subtractions between before and after remediation. Means sharing a letter are not significantly different. Tukey test ($p < 0.05$).

The cumulative Na^+ in the leachates (Figure A5.3) of gypsum treatments showed higher values than those of sulphur, in concordance to the soil ESP values after reclamation. In terms of salinity, leaching alone was as effective as gypsum or sulphur in lowering soil EC, agreeing with Manzano Banda et al. (2014) and Hernández Araujo (2012), who found that reduction in soil salinity and sodicity was largely due to the only-water additions in contrast to the amendment application. Moreover, the findings of Zambrana Yañez et al. (2020) - summarized in Annex 9 - show the effect of gypsum addition under non-leaching conditions. Overall, gypsum was more effective than sulphur in reclaiming the soil sodicity however, none of the amendments reached the soil ESP threshold value of 15% (USSL classification) probably due to the high initial ESP and clogging of soil pores and the insufficient incubation time and soil conditions for Sulphur.

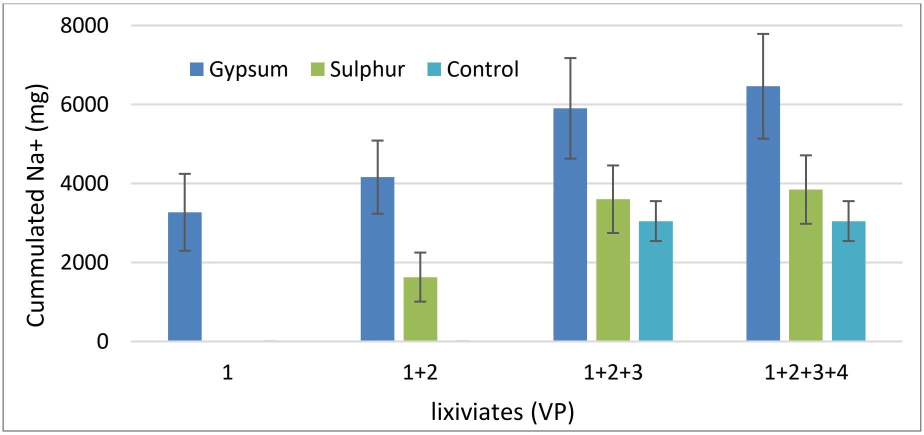

Figure A5.3 Cumulative sodium (mg) in the leachates

Conclusions

Gypsum and sulphur with leaching somehow improved the saline-sodic condition of the soil, however, without reaching the soil EC, pH and ESP threshold values of the USSL classification. Gypsum was more effective than sulphur in reducing soil ESP, mainly due to its readily available calcium content which facilitates the displacement of sodium and subsequent improvement of soil structure, in contrast to the sulphur which needed additional time for incubation and later calcium formation. The decrease in EC_e with water alone was considerable (over 50%) to the same extent as the treatments with amendments. The dose of 50%, either for gypsum or sulphur, showed a similar effect as that of 100% in improving soil sodicity. Up to three lixiviations were sufficient for improving soil salinity and sodicity. Gypsum with leaching might be an alternative to remediate sodic and saline-sodic soils, however, further evaluations are needed considering intermediate doses such as 25% and 75% as well as different soil types, and a longer incubation period for sulphur addition.

ANNEX 6

Summary of the article:
Organic amendments to reclaim a saline-sodic soil: pot experiment.

Castellón, D. ; Andrade Foronda, D. (2020). Enmiendas Orgánicas para la Remediación de Suelos Salino-Sódicos del Valle Alto de Cochabamba. *Rev. Agric*.62**,** 57–64. (Coauthor)

This pot experiment aimed to evaluate the effect of four organic amendments (cattle manure and chicken manure, biochar and peat) at two doses (1 and 2% of organic matter w/w) in ameliorating a saline-sodic soil from the High Valley of Cochabamba, and to identify the most effective amendment(s) and dose(s).

Materials and methods

The experiment was carried out in a greenhouse at the Centre for Vegetable Seeds Production - ‘Instituto Nacional de Investigación Agropecuaria’ (17°26'25.72" S, 66°20'44.0" W). The soil was collected from the High Valley of Cochabamba (17°32'38.6" S, 65°51'41. 9" W) at a depth of ~25 cm and its properties were: silt-loam texture, bulk density of 1.4 g cm^{-3}, organic matter content of 1.2%, electrical conductivity (EC_e) of 16.2 dS m^{-1}, exchangeable sodium percentage (ESP) of 68.1% and pH of 9.66. The exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ contents were 80.2, 6.2, 5.6 and 196.0 $mg100g^{-1}$, respectively. The organic amendments – whose properties are shown in Table A6.1 – used for this study, were Biochar, tropical peat, cattle manure and chicken manure.

Table A6.1 Chemical properties of organic amendments.

Parameter	**Peat**	**Biochar**	**Cattle manure**	**Chicken manure**
EC ($dS.m^{-1}$)	0.72	1.03	3.75	5..48
Organic matter (%)	22	13	47	34
pH	3.6	9.74	8.5	8.0
Ca^{2+} (%)	0.62	1.25	1.87	14.37
Mg^{2+} (%)	0.75	0.75	1.88	3.38
K^+ (%)	0.0	0.0	1.25	0.4
Na^+ (%)	0.0	0.0	0.01	0.69
N (%)	13	4.6	12	17.66
P (%)	0.0	0.09	0.67	2.61

EC = electrical conductivity

The soil was homogenized, dried and 2 mm sieved, and organic amendments were dried, and 4 mm sieved, and then added to the soil (1300 g) at doses of 12 g and 24 g calculated as 1% and 2% of organic matter content on a dry soil basis, respectively. A leachate collector was connected to the bottom of each pot of ~1L volume. The soil along with amendment was placed over a one cm layer of gravel. The properties of leaching water were pH of 7.12, EC of 0.23 dS m^{-1}, Ca^{2+} of 0.75 meq L^{-1}, Mg^{2+} of 0.75 meq L^{-1} and Na^{+} of 1.24 meq L^{-1}; and its volume was calculated using the pore volume (PV) formula proposed by Ahmad et al. (2016). To saturate the soil, ¾ PV was added and then five PV (each of 390 ml) were applied to each pot until a relatively constant EC in the leachates was reached. The leachates were collected after each lixiviation and soil samples were collected after the fifth addition of water. Soil EC was measured in a 1:5 (soil: water) suspension and was converted to EC of paste extract through a factor (Sonmez et al., 2008). Exchangeable cations were determined through a modified Metson method at a pH of 7. Soluble Ca^{2+} and Mg^{2+} were determined through titration and Na^{+} was measured by using the Laqua Twin® Na-11 device. The soil ESP was calculated according to the formula proposed by Hazelton and Murphy (2007) and the SAR by applying the formula of Richards et al. (1954). The experimental design was completely randomized with two factors (amendment and dose). Tukey's ($p < 0.05$) was used for mean comparisons among treatments.

Results and discussion

The effect of amendment *x* dosage on soil ESP was significant ($p < 0.05$), but not for soil EC_e and pH. Any amendment at any dose decreased the soil ESP by over 28% concerning the initial value (68.1%) followed by peat at a dose of 1% (Figure A6.1a); these results agree with those of Chaganti and Crohn (2015) and Chaganti (2014) who evaluated the effectiveness of composts and biochar in improving sodicity; however, it is important to remark the statement of Saifullah et al. (2018) who affirmed that removal of Na^{+} out of the soil can be insufficient despite many studies reported significant improvements in soil salinity/sodicity as well in plant growth because is mostly due to the sorption of Na^{+} salts by biochar. The soil ECe was reduced by over 60% through any amendment (Figure A6.1b). Soil pH was slightly reduced by any amendment except biochar which increased the pH (Figure A6.1c) probably due to its initial pH (9.74) coinciding with García (2013). The effectiveness of organic amendments in reducing soil ESP and ECe, also agrees with the results of Sastre-Conde et al. (2015), Guo et al. (2019), and David and Dimitrios (2002). The low effectiveness of peat was probably due to its high swelling capacity (1.85 g water/gpeat) which can lead to the clogging of the pores system.

Conclusions

Manures, biochar and peat were effective in reducing soil ESP and EC_e, however without reaching the threshold values of the USSL classification, which can be explained by the insufficient Ca^{2+} for displacing exchangeable Na^{+} and then improving the soil structure, and due to the specific characteristics of the organic amendments. Further investigation is needed to validate the effectiveness of locally available amendments in different types of soil and various doses.

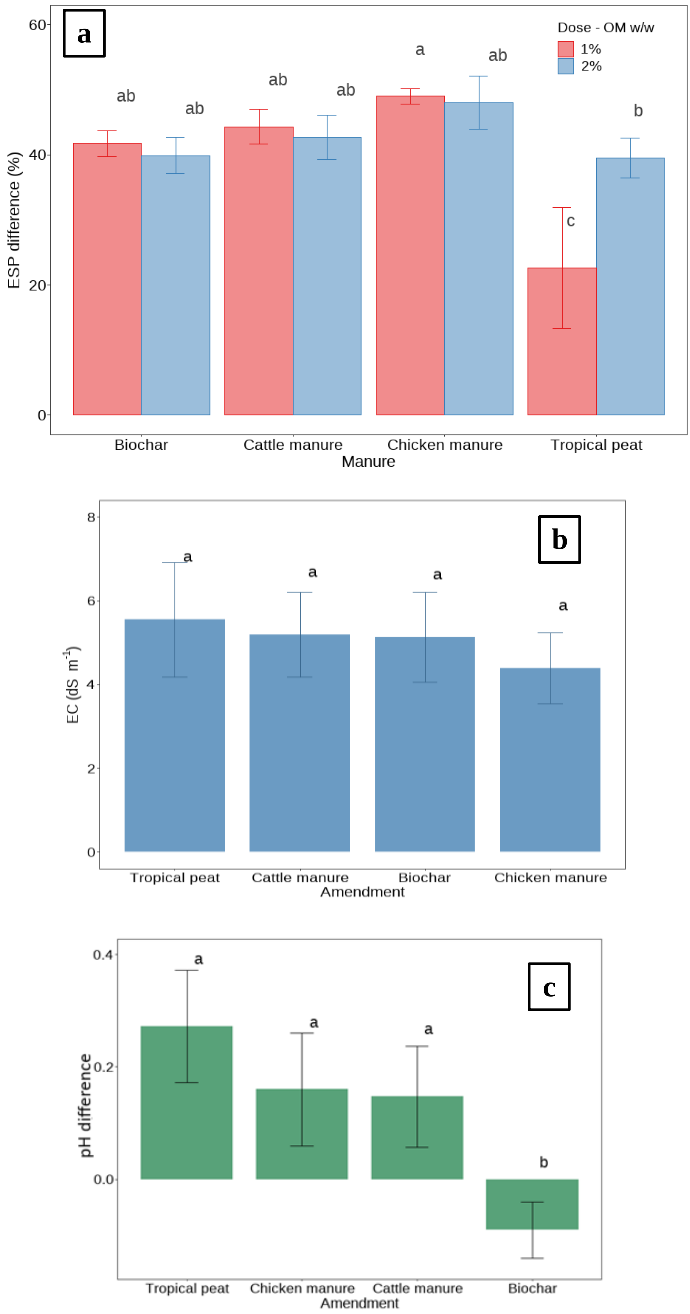

Figure A6.1 Effect of organic amendments on soil ESP (a), ECe (b); and pH (c). The ESP and pH differences represent the subtractions between before and after remediation. Means sharing a letter are not significantly different and the bars indicate the standard error. Tukey test ($p < 0.05$).

ANNEX 7

Summary of the article: Application of gypsum and organic amendments for reclaiming a saline-sodic soil

Quispe Zenteno I.; Gutiérrez Rodríguez E.; Andrade Foronda D. (2020). Aplicación de yeso agrícola y enmiendas orgánicas para la remediación de suelos salino-sódicos. *Rev. Agric*.62, 57–64. (Coauthor)

The objective of the study was to evaluate the effect of adding gypsum, cattle manure and chicken manure on the sodium exchangeable percentage (ESP), electrical conductivity (EC) and pH of a saline-sodic soil. The study was carried out at the location (17°32'38.6" S, 65°51'41. 9" W) of Santa Ana - High Valley of Cochabamba, through an experimental plot. The treatments were: Control, cattle manure, chicken manure, cattle manure and gypsum, chicken manure and gypsum, and sole gypsum. The dose for manures was 26 t/ha as 1% of organic matter (w/w), and 16 t/ha for gypsum as the requirement to reach the ESP threshold value of 15%. The soil before properties were a soil ESP of 80.2%, EC of 13.1 dS m^{-1} and pH of 8.53. All treatments except the control were equally effective in lowering the soil ESP, any amendment was not effective in decreasing the soil EC, and gypsum alone and chicken manure + gypsum were more effective in reducing the soil pH (Table A7.1), but without reaching the USSL threshold values. Further validation is needed in the early stage of the rainy period.

Table A7.1 Average values of soil ESP, EC and pH in the reclaimed soil, for the treatments with manures and gypsum, besides the control (Based on Quispe Zenteno et al., 2020)

Treatment	pH	EC (dS m^{-1})	ESP (%)
Control	8.49 a	14.38 a	89.11 a
Cattle manure	8.10 ab	17.20 a	30.80 b
Chicken manure	7.73 ab	26.48 a	33.90 b
Bovine manure + gypsum	7.86 ab	29.88 a	38.31 b
Chicken manure + gypsum	7.58 b	16.77 a	26.66 b
Gypsum	7.28 b	9.92 a	22.48 b

Means sharing a letter are not significantly different, according to the test Tukey ($P < 0.05$).

Moreover, in the year of the field experiment (2019) the average costs of the amendments were approximately: gypsum (~2,300 USD ha^{-1}), bovine manure (~2,990 USD ha^{-1}) and chicken manure (~3,180 USD ha^{-1}), these costs are affordable considering some average incomes per hectare from agricultural and livestock production in the area; however to have a proper economical evaluation and comparison, further assessment should consider farmers' income alternatives, including grains, vegetables, and forage crops, cultivated on the reclaimed soil.

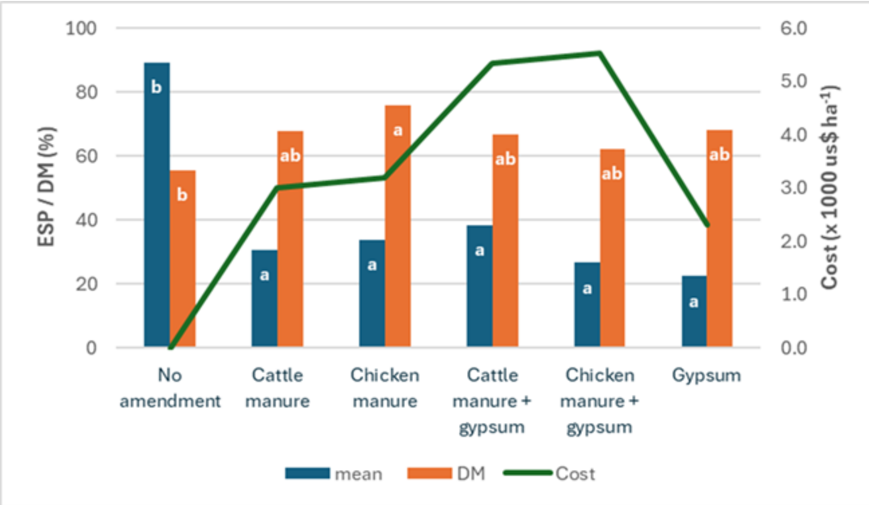

Figure A7.1 Effect of manures or/and gypsum on soil ESP and %DM after remediation, where means sharing a letter are not significantly different (Tukey test, $p< 0.05$), besides costs (a). Setup and addition of amendments in the experimental plots (b) by Quispe Zenteno et al. (2020).

ANNEX 8

Summary of the article: Evaluation of phytodesalination capacity of four halophytes for a saline-sodic soil

Mamani Flores J.; Arzabe Maure O.; Andrade Foronda D. (2020). Evaluación de la capacidad de fitodesalinización de cuatro halófitas en un suelo salino-sódico. *Rev. Agric*.62, 57–64. (Coauthor)

Phytoremediation can be considered a low-cost alternative to chemical amelioration. Halophytes are plant species with a significant removal capacity of salts and Na^+ from salt-affected soils. The study aimed to evaluate the potential of four halophytes to desalinize saline-sodic soil. The target soil (EC_e of 47.0 dS m^{-1} and 3.4 g Na^+ kg^{-1} soil) was collected from the High Valley of Cochabamba-Bolivia. The assessed halophytes were: *Suaeda fruticosa* Moq, *Sesuvium portulacastrum*, *Atriplex hortensis* and *Kochia scoparia* (Figure A8.1). The pot experiment was carried out under non-leaching conditions for 70 days and using 37-day-old seedlings.

Figure A8.1 Assessed halophytes for phytodesalination capacity (Mamani Flores et al., 2020).

Table A8.1 Soil EC_e and Na^+ values after phytoremediation ($p<0.05$). Based on Mamani Flores et al. (2020).

Halophyte	EC_e ($dS\ m^{-1}$)	Na^+ ($g\ kg^{-1}$ soil)
S. fruticosa Moq	35.5 a	3.18 a
S. portulacastrum	36.1 b	3.23 b
A. hortensis	36.8 c	3.24 b
K. scoparia	37.6 d	3.00 c

The results showed that *S. fruticosa* Moq. and *S. portulacastrum* were relatively better than the alien halophytes in decreasing the soil EC_e and Na^+ content compared to the soil before. *S. fruticosa* and *S. portu*lacastrum outperformed the alien halophytes in biomass production, sodium content in plant shoots and Phytodesalination capacity (Table A8.1 and Figure A8.2). Native halophytes were more effective than the alien species in soil desalination as well as in productivity, therefore, might be suitable for further field assessments in the study area.

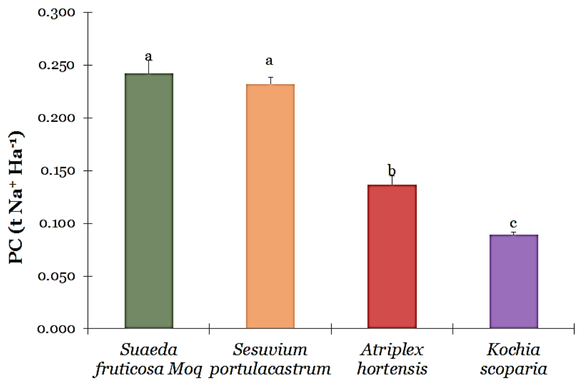

Figure A8.2 Phytodesalination capacity (t Na^+ Ha^{-1}) of halophytes based on their productivity as dry matter, and their sodium content in the aerial part (Adapted from Mamani Flores et al., 2020).

ANNEX 9

Summary of the article: Influence of three organic amendments and gypsum on physicochemical parameters of a saline-sodic soil from the High Valley

Zambrana Yañez N.; Arzabe Maure O.; Andrade Foronda D.; Troncoso Joffre A. (2020). Influencia de tres enmiendas orgánicas y yeso agrícola sobre los parámetros fisicoquímicos de un suelo salino sódico del Valle Alto de Cochabamba. *Rev. Agric.*62, 57–64. (Coauthor)

The farmers from the high Valley of Cochabamba suffer production losses due to the negative effects of salt-affected soils on plant growth and soil quality. The objective of this study was to evaluate the effect of adding organic amendments, namely, cattle manure, litter topsoil (*Schinus molle* L.) and activated charcoal compared to gypsum on soil pH, electrical conductivity (EC), exchangeable sodium percentage (ESP), and sodium adsorption ratio (SAR) and CO_2 emissions, under controlled and non-leaching conditions. The amendments were added to a saline-sodic soil and incubated for three months, then, the soil after remediation was analyzed. It was found that the application of organic amendments and gypsum showed a significant effect in decreasing the soil pH, but not the soil EC, and an increase in exchangeable /soluble sodium.

Table A9.1 Soil pH, electrical conductivity and exchangeable sodium percentage of the soil before and after reclamation (Based on Zambrana Yañez. et al, 2020)

Treatment	Soil before			Soil after		
	pH	**EC (dS m^{-1})**	**ESP**	**pH**	**EC (dS m^{-1})**	**ESP**
Charcoal	7	38.5	46	7.1 (a)	35.36 (a)	57 (a)
Cattle manure	8.19	46.21	66	7.89 *	42.43 (a)	64
Plant litter	8.06	39.15	54	7.6 (a)	46.39 (a)	66
Gypsum	7.94	40.28	45	7.33 (a)	40.95 (a)	57 (a)

Dunnett's clustering test (confidence of 95%). Means not labelled with the letter (a) are significantly different (*) from the control (gypsum) mean.

ANNEX 10

Figure A10.1 Pot experiment (by Castellón, D., 2018) to evaluate the effect of organic amendments in reclaiming a saline-sodic soil.


a


b

Figure A10.2 Preparation and setup of soil columns (a) and extraction of soil column sample after reclamation (b).

Figure A 10.3 Field plot to test adaptation of salt-tolerant forage crop in the High Valley.

Figure A 10.4 Collection of native halophytes for the research by Mamani, J. (2019) in a saline-sodic soil patch (High Valley)