Designing Technosols to Reduce Salinity and Water Stress of Crops Growing Under Arid Conditions

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ABSTRACT

Salt- and plant-water stress are widely considered to be major abiotic stresses threatening crop production in dry areas. Innovative methods to alleviate salt and plant-water stress that are both practical and economically efficient are in great demand. While the most common reclamation strategy for salt-affected soils is to flush the salts out of the root zone with low salinity/sodicity water, this is challenged by the fact that water is commonly scarce in areas affected by salt stress. The use of specific soil amendments or a combination of them in such areas may well solve some of these problems. Biochar has, in fact, been shown that, in some instances, it is able to effectively reduce salt stress to plants. Other porous materials, such as pumice, have not yet been considered although pumice has been reported to contribute to water retention under arid conditions. Further potential amendments include organic residues, as they can produce beneficial impacts on plant growth by improving soil functions. To date, however, limited research has attempted to unravel (and compare) the effects of either pumice and/or biochar in alleviating salt and plant-water stress. There is also scant information on (i) how to minimise the impact of biochar on the salinity of soils in dry regions; (ii) the underlying mechanisms explaining how the use of either pumice or biochar amendments can decrease soil salinity under arid conditions; and (iii) whether individual or combined additions of either pumice and/or an organic amendment, algae, to a sandy soil alleviates salt and water-stress on plant growth. Therefore, my objective in this study is to investigate whether these

amendments can be used in the formulation of Technosols specifically designed to reduce salinity and water-stress of crops growing under arid environments.

A quantitative review of literature was carried out to evaluate what type of biochar and under what conditions its use is suitable in dryland soils. For this, a meta-analysis of 40 studies published between 2013 and 2020 using pairwise comparisons was carried out to evaluate the short-term effect of biochar on the salinity using electrical conductivity (EC) as the proxy for soils under dry environments (Mediterranean, arid, semi-arid climates, or under simulated dry and saline conditions). The results indicated that in terms of the risk of biochar increasing soil salinity, (i) biochars made from high-ash material should not be applied to soils in dry regions; and (ii) the addition of biochars made from relatively low-ash ligneous material at application rates ≤ 20 t ha^{-1} is suitable as an amendment to soils under dry environments. The use of a leaching fraction is recommended.

Water-borne salt transport in soils under arid conditions is strongly related to the influence of amendments on the soil's mobile-immobile water fractions. For this, the influence of the porosity and pore-size distribution of pumice and biochar (produced from willow wood chips at a highest heating temperature of 350 °C) on the mobile-water content when added to a sandy soil were investigated. Pumice and biochar (of 1.5-, 3-, and 6-cm Ø) were characterised using Scanning Electron Microscope (SEM) technology. The fraction of mobile-water present in these amendments, previously added to a sandy soil at different application rates and particle sizes, was determined using a tracer (Na^+) technique. The results showed that the overall larger contribution of pumice to the water mobility than that of biochar under near-saturated conditions could be related to its relatively higher levels of macro-scale plus meso-scale porosity, and this increased as the pumice particle size increased. Both pumice and biochar had a predominance of pores with a Ø < 30 μm and relatively high total porosity, which are expected to contribute to water retention dilution of salinity when these amendments are added to salt-affected sandy soils.

In order to evaluate the effects of pumice and biochar amendments on water retention and salinity of a sandy soil under simulated arid conditions, pumice and biochar of different particle sizes (1.5-, 3-, and 6-cm Ø) were separately added at different rates (3, 6, and 12%, v/v basis) to the soil. This was drip irrigated with an artificial saline water under non-draining conditions. Pebbles applied at identical rates and sizes as pumice and biochar, were used as positive controls, whereas no amendment was the negative control. Treatments underwent 10 wetting and drying cycles at 35 °C at the end of which, the residual soil was separated from the amendments. We found that (i) the EC of the residual soil followed the order pumice < biochar < positive control = negative control, with differences where existing, being significant at $p < 0.05$; (ii) the smallest EC and sodium adsorption ratio (SAR) values of the residual soil were achieved when applying 12% pumice, regardless of the particle size; the opposite pattern (12% > 6% > 3%) was observed in the pumice when analysed separately from residual soil; (iii) pumice and biochar treatments retained an increasing amount of water in the soil after each drying cycle (significant at $p < 0.05$); and (iv) at the end of the experiment, the EC values of the leachates indicated that

salts retained in pumice were more slowly mobilised than those in the biochar. The application of either pumice or biochar can contribute to a decrease soil salinity, but pumice could additionally serve as a tool to remove salts from salt-affected soils.

In order to investigate whether individual or combined additions of either pumice (PU) and/or algae (AL) to a sandy soil could alleviate the impact of irrigation with saline water on the growth of lucerne (*Medicago sativa* L.) under simulated semi-arid conditions. A plant growth chamber study was conducted that included six treatments that received saline water (6.4 dS m^{-1}): T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL). A seventh treatment was T7 (sand – negative control), to which deionised water was added. All treatments underwent 14 cycles of irrigation wetting and drying events (at 27 ± 1 °C/ 16 ± 1 °C day/night). Results showed that, at the end of the experiment and compared with the positive control (T1), the two treatments with the largest application rate of PU (T5 and T3) showed the largest (significant at $p < 0.05$) reduction in soil EC, SAR, and water-extractable ions among those treatments receiving saline water (T1-T6). Lucerne in treatments T1-T6 always had a smaller ($p < 0.05$) biomass, leaf dry weight (DW), and relative growth rate than the treatment receiving deionised water (T7) (DW: 2.3 g m^{-2}), but values for treatment T5 (DW: 1.7 g m^{-2}) were significantly larger ($p < 0.05$) than for treatments T1-T4 and T6 (DW < 1.1 g m^{-2}). Overall, the results obtained suggest that, if proven feasible at a field scale, the combined addition of PU (12%), by reducing salinity and contributing to water retention, and AL (2%), by adding nutrients and/or bioactive compounds, could be used to mitigate salt stress and improve plant growth in sandy soils under arid conditions.

The information obtained in this thesis supports the use of pumice and algal amendments as ingredients of Technosols designed to reduce salinity and water-stress of crops growing under arid conditions. Both materials are easily available (if to be used in areas close to a volcanic region and at the seaside), low cost, and their use in agriculture may open new doors to deal with the current problems faced in dry regions.

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Abstracts/proceedings and posters/presentations in Conference/Workshop

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Al^{3+}	Aluminium ions
Al_2O_3	Aluminium oxide
AL	Algae
B/BC/Bi	Biochar
$B(OH)_3$	Hydrogen borate
C	Carbon
Ca^{2+}	Calcium
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
$Ca_3(PO_4)_2$	Calcium phosphate
$CaHPO_4$	Calcium hydrophosphate
$CaSO_4 \cdot 2H_2O$	Gypsum
CEC	Cation exchange capacity
CI	Confidence interval
CO_3^{2-}	Carbonate
CO_2	Carbon dioxide
Cr^{3+}	Chromium
Cu^{2+}	Copper
DDL	Diffuse double layer

DI water	Distilled water
DM	Dry matter
DW	Dry weight
EC	Electrical conductivity
EC_e	Electrical conductivity of saturated soil extract
ESP	Exchangeable sodium percentage
FAO	Food and Agriculture Organization of the United Nations
Fe	Iron
Fe_2O_3	Iron oxide
FW	Fresh weight
HCO_3^-	Bicarbonate
$H_2PO_4^-$	Dihydric phosphate
HHT	Highest heating temperature
HNO_3	Nitric acid
IC	Ion chromatography system
IF	Inorganic fertiliser
IR	Irrigation
K	Potassium
KCl	Potassium chloride
K_2O	Potassium oxide
LDMC	Leaf dry matter content
Mg^{2+}	Magnesium

$MgCO_3$	Magnesium carbonate
$MgHPO_4$	Magnesium hydrogen phosphate
MgO	Magnesium oxide
$Mg(OH)_2$	Magnesium hydroxide
$Mg_3(PO_4)_2$	Magnesium phosphate
$MgSO_4$	Magnesium sulphate
MP-AES	Microwave plasma atomic emission spectrometer
N	Nitrogen
Na^+	Sodium
NaCl	Sodium chloride
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
$Na_3H(CO_3)_2$	Sodium sesquicarbonate
Na_2O	Sodium oxide
Na_2SO_4	Sodium sulfate
NO_3^-	Nitrate
NMR	Nuclear magnetic resonance
OA	Organic amendment
OC	Organic carbon
P	Phosphorus
Pe	Pebble
PO_4^{3-}	Phosphate

PV	Pore volume
Pu/PU	Pumice
RGR	Relative growth rate
ROS	Reactive oxygen species
RS	Residual sandy soil
S	Sandy soil
SAR	Sodium adsorption ratio
S.D.	Standard division
SEM	Scanning electron microscopy
Si	Silicon
SiO_2	Silicon dioxide
SO_4^{2-}	Sulphate
TiO_2	Titanium oxide
WFPS	Water filled pore space
Zn	Zinc
Ø	Diameter

Chapter 1

GENERAL INTRODUCTION

This general introduction chapter provides (i) a general background of this research; (ii) the research objectives; and (iii) the outline of this thesis.

1.1. General background

Nowadays, a key challenge faced by intensive agriculture is the high salinity and sodicity of soils and irrigation water in many parts of the world (Yamaguchi and Blumwald, 2005; Shahbaz and Ashraf, 2013). Increased soil degradation of arable land due to salt stress is expected to result in around 30% of land loss within the next 25 years, and up to 50% by the year 2050 (Wang and Altman, 2003). This will decrease our ability to meet food security for a growing world population. Therefore, exploiting effective restoration techniques for alleviating salt and plant-water stress should be given a high research priority.

The restoration of salt-affected soils to recover soil functioning, and thus its ability to sustainably grow crops, is a challenging work (Aboukila, 2013). Several conventional approaches including scraping and removal of surface soil, land leveling, subsoiling and deep ploughing, mulching, continuous ponding, sprinkling, balanced fertilisation, application of biofertiliser, addition of gypsum, and application of elemental sulfur are used to rehabilitate the soils that have been degraded through salinization and/or sodification processes (Horneck et al., 2007). In fact, leaching is considered the most effective strategy to flush large amounts of water-soluble salts out of the root zone with the application of better-quality water (Saifullah et al., 2018). However, this is challenged by the scarcity of better-quality water in arid areas, although the use of blue and grey water in the saline and hyper-arid desert environments for the irrigation of tree species is becoming a success (Al-Muaini et al., 2019). The application of reclamation strategies is high cost, as with the use of furrow or bed with mulch (Klocke et al., 2009; Devkota et al., 2015); usage of combinations of agrochemicals such as $CaCl_2{:}2H_2O$ and phosphate of gypsum, and organic solutions (Walker and Bernal, 2008; Singh et al., 2019). These are either still unavailable or unsuitable for many poor areas in the world. Hence, practical and economically feasible salt-reclamation methods are in great demand (Seenivasan et al., 2015).

Technosols (soils whose properties and pedogenesis are dominated by their technical origin) have been use to remediate mining areas (Macías and Camps-Arbestain, 2010; Asensio et al., 2013; Manuel et al., 2016), and as an alternative to environmental-friendly manage other types of degraded areas, such as industrial wastelands (Hafeez et al., 2012; Macía et al., 2014), but direct evidence supporting its influence in alleviating salt and plant water-stress is still lacking. Several potential ingredients for the production of Technosols could be used to remediate salt-affected areas. In soils under dry environments, the interest in using biochar resides on the fact that it may help, in some instances, increase soil water retention and reduce salinity stress to plants (Mulcahy et al., 2013; Ali et al., 2017; Munera-Echeverri et al., 2018). However, some studies have reported a distinct increase in salinity and/or sodicity, especially when biochar is applied at high rates (> 30 t ha^{-1}) (Song and Guo, 2012; Fernandes et al., 2018). These specific studies highlight the need for a careful selection of the biochar feedstock with low ash content, low Na content to alleviate successfully salt and water-stress to plants. Other porous materials, such as pumice, have not yet been considered although pumice has been reported to trap salts during desiccation (Doak, 1972) and provide good results to retain moisture under arid environments (Noland et al. 1992; Lura et al., 2004). Further potential ingredients include organic amendments, such as sewage sludge or manure compost, as suggested for the reclamation of sodic soils, due to its positive effects on water infiltration, lowering the electrical conductivity (due to the provision of cation exchange sites), and the displacement of Na^+ from exchange sites by other cations present in these amendments (El-Shakweer et al., 2008).

The use of either pumice and/or biochar in the treatment of salt and plant-water stress is part of the focus of this thesis. Both ingredients are easily available (if needed in an area close to a volcanic region in the case of pumice), low cost, and their possible use as nuclei ingredients of specially-designed Technosols may open new doors to deal with the current problems faced in salt-affected dry areas.

1.2. **Research objectives**

1.2.1 Main objective

This study intends to investigate the suitability of specific soil amendments (potentially used as ingredients in tailor-made Technosols) for reducing salinity and water stress of crops growing under arid environments.

1.2.2 Specific objectives

Five sub-objectives are associated/derived from the main objectives, including:

Sub-objective 1 To evaluate the short-term (≤ 1 year) effect of biochar on soil salinity (using EC as a proxy) under dry environments (Mediterranean, arid, semi-arid climates, or under simulated dry and saline conditions).

Sub-objective 2 To investigate the influence of the porosity and pore-size distribution of amendments of a pumice (from New Zealand) and a biochar (produced from willow wood chips at a highest heating temperature of 350 °C) on the mobile-water content when added to a sandy soil.

Sub-objective 3 To evaluate the effects of pumice (from New Zealand) and biochar (produced from willow wood chips at a highest heating temperature of 350 °C) amendments on water retention and salinity of a sandy soil under simulated arid conditions.

Sub-objective 4 To investigate whether individual, or combined additions, of either pumice and/or algae to a sandy soil could alleviate the impact of irrigation with saline water on the growth of lucerne (*Medicago sativa* L., Kaituna superstrike) under a simulated arid environment.

Sub-objective 5 To reveal the mechanisms through which pumice and biochar alleviate salinity and water stress.

1.3. Thesis outline

The whole thesis includes 7 chapters described briefly as follows:

Chapter 1 (this chapter) is an introduction to the entire thesis and presents general background information and specifies the objectives of the current research and the outline of this dissertation.

Chapter 2 is a literature review that provides an overview on (i) soil salinity, sodicity and arid environment; (ii) the potential for pumice and biochar to alleviate salinity and water stress; (iii) the potential for Technosols to restore salt-affected soils in arid conditions; and (iv) research gaps and priorities.

Chapter 3 conducts a meta-analysis to evaluate the effect of biochar on soil salinity (using EC as a proxy) under dry environments (Mediterranean, arid, and semi-arid climatic conditions, or under simulated dry and saline conditions).

Chapter 4 characterises the porosity and pore-size distribution of pumice (from New Zealand) and biochar (produced from willow wood chips at a maximum heating temperature of 350 °C). It also evaluates the amount of mobile-water present in these amendments when added to a sandy soil.

Chapter 5 explores the possibility of using either pumice (from New Zealand) or biochar (produced from willow wood chips at a maximum heating temperature of

350 °C) amendments to decrease soil salinity under arid conditions.

Chapter 6 evaluates the responses of the lucerne (*Medicago sativa* L., Kaituna superstrike) and soil salinity to individual, or combined additions, of either pumice and/or algal amendments and investigates the underlying mechanisms.

Chapter 7 is a general summary of the whole thesis and a discussion on some future research recommendations.

Note that (i) The content of Chapter 3–6 have been submitted to or are in the process of submission for journal publications – this information is provided in each chapter. As these standalone chapters were written according to the format requirements from different journals, the structure of each chapter may differ slightly; and overlapping and repetition occur between some sections.

Chapter 2

LITERATURE REVIEW

This literature review provides an overview on (i) soil salinity, sodicity and arid environments; (ii) the potential for pumice and biochar to alleviate salinity and water stress; (iii) the potential for Technosols to restore salt-affected soils in arid conditions; and (iv) research gaps and priorities.

2.1. An overview of soil salinity, sodicity and arid environments

Three of the most severe and prevalent abiotic stresses limiting the productivity of agricultural crops globally are salinity, sodicity and water stress, which are common in arid environments (Bray et al., 2000; Zhao et al., 2007). Worldwide, over 800 million hectares of land are influenced by either sodicity or salinity stress, or both (Martinez-Beltran and Manzur, 2005) (Figure 2–1). Soil salinity occurs through the accumulation of water-soluble salts in the soil. These include chlorides and sulfates of sodium ($NaCl$, Na_2SO_4), sodium, calcium and magnesium carbonates (Na_2CO_3, $CaCO_3$, $MgCO_3$) and bicarbonates ($NaHCO_3$, $Na_3H(CO_3)_2$) (Rengasamy, 2010). Sodicity is caused by a high proportion of sodium ions relative to other cations (Mg^{2+}, Ca^{2+}) at exchange sites (Bernstein, 1975). A plant is considered to experience water stress during intense transpiration rates and/or limited water supply to the root system (Bhattacharjee, 2012). Limited water supply could be caused not only by a deficiency in water but also due to an osmotic decrease of water potential caused by salinity (Salehi-Lisar and Bakhshayeshan-Agdam, 2016). An understanding of salinity-, sodicity-, and plant-water stress mechanisms and management practices to overcome them is important for long-term sustainable arid zone agriculture.

Figure 2-1 Global distribution of salt-affected soils (Spark, 1995).

2.1.1 Salinity, sodicity and salt-affected soils

There are several main causes for the development of soil salinity. Primary salinity is currently linked to climatic and geologic factors such as high evaporative conditions that favour the precipitation of soluble salts, and the weathering of rocks rich in soluble salts (Thomas and Middleton, 1993). Secondary salinity is caused by inadequate farming practices such as (i) the long-term use of salt-rich irrigation water; (ii) the increase in the level of the water table through irrigation in areas naturally rich in salts, which facilitates the capillary rise of saline groundwater; and (iii) unreasonable agronomic practices such as excessive fertiliser and pesticide application (Manchanda and Garg, 2008).

Sodicity degrades soil physical properties by impairing soil structural stability. This results in the dispersion of aggregates during rainfall, causing sealing, which then impedes water infiltration, reduces water availability for crops growing in the soil, and increases the risk of erosion. On drying, the seal hardens as a crust through the accumulation of salts at the surface, which can prevent emergence of germinating seeds resulting in poor crop establishment. In addition, the influence of Na^+ on the clay fraction in the soil makes the sodic soil difficult to cultivate and with poor load-bearing capacity (Menzies et al., 2015). This dispersion is due to the displacement of Ca^{2+} and Mg^{2+} from exchange sites by Na^+, which causes a broadening of the diffuse double layer (DDL) (Figure 2–2) and creates repulsive forces at much greater distances than the short-range van der Waals attractive forces (Figure 2–3). This decreases the ability of particles to flocculate, leading to the dispersion and/or swelling of the soil particles (Srivastava et al., 2014). Sodicity also causes cation nutrition (Ca^{2+}, Mg^{2+}, K^+) deficiency, direct Na^+ toxicity, and aluminate toxicity to plants (Menzies et al., 2015).

Figure 2-2 Schematic representation of the soil surface charge (cation exchange capacity) being balanced by an excess of cations and deficit of anions in a volume of solution extending some distance from the surface (Menzies et al., 2015).

Figure 2-3 Representation of the strength (y axis) and distance of influence from the soil surface (x axis) of the van der Waals forces which attract particles together (force of attraction V_A) and double layer repulsion (force of repulsion V_R). The force of repulsion is plotted for three different soil solution concentrations (the effect of concentration on diffuse double layer thickness will be discussed shortly). The van der Waals forces are not affected by environmental influences, hence only one line is needed to represent these (Menzies et al., 2015).

Salinity, in contrast, favours flocculation of soil particles, since high levels of soluble salts narrows diffuse double layer and weakens repulsive forces (Rodriguez et al., 2000; Mavi, 2012). However, it can also cause soil crusting, due to the accumulation of soluble salts in soil surface (Rietz and Haynes, 2003). The greatest impairment of salinity on plant growth is caused by (i) osmotic stress (Qadir and Schubert, 2002), which makes water uptake by plants difficult, and (ii) ionic imbalance (Wong, 2007; Yan et al., 2015).

Generally, salt-affected soils can be categorised into three groups: saline, sodic and saline-sodic soils as defined by Rengasamy (2010) on the basis of chemical properties such as soil pH, electrical conductivity of saturated soil extract (EC_e), sodium absorption ratio (SAR), and exchangeable sodium percentage (ESP) (Figure 2–4).

Figure 2-4 Classification of salt-affected soils based on sodium adsorption ratio (SAR) and electrical conductivity (EC_e) measured in soil saturation extract, $pH_{1:5}$ measured in soil water suspension, and possible mechanisms of impact on plants (Rengasamy, 2010).

2.1.2 The effects of salinity and sodicity stress on plant growth

A high level of salts in soils cause damaging effects on plant physiological processes such as seed germination, photosynthesis, cellular respiration, plant nutrition, and antioxidant function (Wang and Altman, 2003; Sairam and Tyagi, 2004). Osmotic stress causes a rapid decrease in the movement of water across the plant cell membrane (Finan and Guilak, 2010), thus decreasing water availability and causing water in plant tissues to be diverted. This leads to various physiological changes, such as interruption of membranes, and impairment of the ability to detoxify reactive oxygen species (ROS). Further, it leads to differences in the antioxidant enzymes, decreased photosynthetic activity, and decrease in stomatal aperture, which ultimately results in the plant drying out (Munns, 2002). Ionic stress is related to toxic ions being transported to the cytoplasm or the cell wall and building up to toxic levels within the plant (Allakhverdiev et al., 2000). It is a slower process than that caused by osmotic stress and causes nutrient deficiencies and specific-ion toxicities such as that of B, Na, and Cl, which in turn, lead to the reduction of crop yield (Figure 2–5) (Munns, 2005).

The effects of sodicity on plant growth differ depending on whether the soil is just sodic or saline and sodic. When soils are sodic only, total soluble salt concentrations are low. An unbalanced ratio of exchangeable Na/Ca+Mg would lead to Ca and Mg deficiencies. In saline-sodic soils, salinity effects predominate, these being osmotic effects, specific-ion effects, and nutritional imbalances. The adverse effects of high concentrations of salts in the soil with respect to their implications on plant-available water, and nutrient balances are introduced in the following sections.

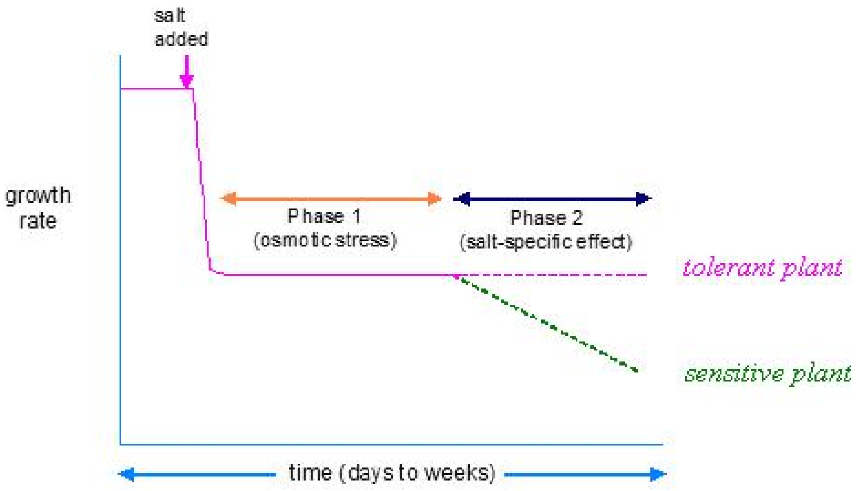

Figure 2-5 Scheme of the two-phase growth response to salt stress (Munns, 1995).

2.1.2.1 Plant-water uptake

The primary challenge that salinity poses to cropland is the impact on plant-water relations (Ahmad et al., 2014). The presence of excessive amount of soluble salts in soil reduces the soil water potential, and thus decreases the amount of plant-available water and nutrients, and forces the plant to spend more energy to exclude salts and take up water (Ghoulam et al., 2002; Sobahan et al., 2009). If soil salinity is too high (> 100 mM NaCl), water may be pulled out of the plant cell into soil solution, causing root cells to shrink and collapse (Munns, 2002; Tuteja, 2007).

The osmotic shock on the plant produces symptoms similar to those of physiological drought stress, i.e., stunted growth, poor germination, leaf burn, wilting, and possibly plant death (Duncans and Carrow, 1998). It has been well reported that leaf water potential, leaf stomatal conductance, leaf relative water content, root hydraulic conductivity and water use efficiency in whole, or in part, decrease in response to an increase in the concentration of salts in various plants such as *Beta vulgaris* (Ghoulam et al., 2002), *Shepherdia argentea* (Qin et al., 2010), *Brassica juncea* (Hayat et al., 2011), *Lycopersicon esculentum* and L. *pennellii* (Alarcón et al., 1993), *Thymus vulgaris* L. (Najafian et al., 2009), *Phaseolus vulgares* L. (Stoeva and Kaymakanova, 2008), and *Cicer aritinum* L. (Ashraf and Waheed, 1993).

2.1.2.2 Plant nutrient uptake and ion toxicity

When split into ions, the most common soluble salts in saline soils are mainly comprised of five anions (Cl^-, $B(HO)_4^-$, SO_4^{2-}, HCO_3^-, and rarely NO_3^-), and four cations (Mg^{2+}, Ca^{2+}, Na^+, and rarely K^+), with chloride (Cl^-) and sodium (Na^+) being the most deleterious anion and cation for plant growth, respectively (Rengasamy, 2002; Munns and Tester, 2008). Excessive accumulation of sodium ions competes with other ions during nutrient uptake in plants and can result in intracellular ion imbalance, limiting the uptake of nutrient ions such as K^+, Mg^{2+} and Ca^{2+} and further affecting the normal metabolic processes of plant cells, thus restricting plant growth and yield (Suhayda et al., 1990; Watad et al., 1991; Schroeder et al., 1994; Hu and Schmidhalter, 1997; Grattan and Grieve, 1998; Asch et al., 2001; Hu and Schmidhalter, 2005). Toxic accumulations of sodium in plants lead to necrosis, burn of leaf tips and margins, and eventual death (Bohn et al., 1985). High level of Cl^- (600–800 mg kg^{-1} and/or above 800 mg kg^{-1}) reduces the uptake and accumulation of K^+, NO_3^-, and $H_2PO_4^-$ ions by plants (Bar et al., 1997). An example of the antagonistic effect of Cl^- ions is the suppression of phosphorus transport from root to the above-ground tissues in potato due to a disorder in the cell membrane system and the cell metabolism system under salt-affected conditions (Leacox and Syvertsen, 1991; Sheldon et al., 2004). Excess Cl^- can be toxic to plants, with critical concentrations for toxicity estimated to be 4–7 mg g^{-1} for chloride-sensitive species and 15–50 mg g^{-1} for chloride-tolerant species (White and Broadley, 2001; Xu et al., 2002). An excess of sulfate in soil may also cause negative effects on plant growth and performance with reported toxic effects on plant metabolism via an inhibition of photophosphorylation (Cerović et al., 1982). Boron toxicity is regarded as the most common specific-ion effect on plants (Bohn et al., 1985; Princi et al., 2016). It is more difficult to control than salinity in general. Boron present in high concentration in soil is an important concern because of its narrow range between deficiency and toxicity, about 30 to 80 mg kg^{-1} B (Hall, 2010). The solubility of B is high and it can be readily leached from soils as $B(OH)_3$ (boric acid) in high rainfall areas. B availability to plants decreases with increasing soil pH, because of the formation of $B(OH)_4^-$ and associated anion adsorption. Drought can also sharply decrease boron availability, which may be attributed to both, decrease of boron mobility and the polymerisation of boric acid (Marschner, 1986).

2.1.3 Management of soils affected by salinity and sodicity

There are several ways to manage and restore salt-affected soils, including (i) scraping and removal of surface soil; (ii) land leveling; (iii) subsoiling and deep ploughing; (iv) sanding; (v) leaching plus artificial drainage; (vi) irrigation water management; (vii) mulch management; (viii) the use of inorganic amendments; (ix) the use of organic amendments; (x) salt phytoremediation; (xi) balanced fertilisation; and (xii) biofertiliser application (Abou-Baker and Ei-Dardiry, 2016). From a reclamation point of view, salt-affected soils can be categorised into two types: (i) saline, and (ii) saline-sodic/sodic.

The restoration of saline soils can be general done by sufficient leaching with good quality irrigation water that carries water-soluble salts to the deeper soil layers (Muhammad et al., 2017). Sodic/saline-sodic soils can be reclaimed by the addition of Ca amendments such as gypsum ($CaSO_4 \cdot 2H_2O$), followed by irrigation with good quality water (Hanay et al., 2004). Application of Ca-rich amendments to sodic/saline-sodic soils can help to increase the concentration of Ca^{2+} in soil solution, which results in Ca^{2+} displacing exchangeable Na^+ at clay surfaces. Displaced Na^+ is then removed from root zone along with dissolved salts in leaching water (Richards et al., 1954; Hanay et al., 2004; Rashad and Dultz, 2007; Ondrasek et al., 2011). Thus, reclamation of both soils (saline, and sodic/saline-sodic) requires the downward flow of water through the soil profile.

Of all these methods, the most classic and straightforward option for salt-affected soils reclamation is to scrape off the salt-accumulated topsoil, exposing the low salinity subsoil, which can support crop growth well (Rakshit et al., 2009). Land leveling could be more suitable for farming and mechanised management, resulting in uniform application of water for better leaching and salt control (Abou-Baker and Ei-Dardiry, 2016). Deep tillage/ploughing tends to give effective control of salinity level around root zones through enhanced salt leaching, homogenisation of soil layers of different salinities (which causes the dilution of salt concentration), as well as improving water permeability (Botta et al., 2006). Leaching is considered the most effective method for the management and rehabilitation of salt-affected soils (Richards et al., 1954). In the case of regions with a shallower water table, the efficiency of leaching is increased by adopting artificial drainage systems (Barac et al., 2012). Amelioration of salt-affected soils can also be accomplished by adequately managing irrigation water, such as the efficient use of available water supplies including fresh water (for leaching) and acidified saline irrigation water (to modify soil water pH and enable the crops to response better to soil physicochemical properties) (Elhady and Shaaban, 2010). Acidification of saline irrigation water is commonly carried out through injection of sulfuric or phosphoric acid, which lowers the soil pH and dissolved Ca/Mg carbonates thus increasing Ca^{2+} and Mg^{2+} in solution and their ability to displace Na^+ from exchange sites (Christians, 1999). Likewise, application of inorganic amendments such as elemental sulfur is a desirable option for reclaiming sodic/saline-sodic soils as it causes a similar effect through oxidation to sulfuric acid (H_2SO_4) (Abou-Baker and Ei-Dardiry, 2016). The mulch technique employs crop residue mulch and a plastic mulch technique to effectively reduce evaporative water losses, thereby limiting the upward movement of salt into the root zone. This helps retain moisture and shows potential to alleviate salt stress (Ramalan and Nwokeocha, 2000; Klocke et al., 2009; Zhang et al., 2009; Zhao et al., 2010; Abou-Baker and Ei-Dardiry, 2016).

Addition of materials such as zeolite clay or perlite glass may also favour the decrease of Na^+ at exchange sites, given that they are rich in Ca^{2+} (Yasuda et al., 1998). The unique porous structure of zeolite and associated capillary properties assists water retention in the soil (Yamamoto, 2008). The application of organic amendments such as sewage sludge or manure compost has also been suggested for the reclamation of sodic soils, due to its positive effects on water infiltration, lowering the electrical conductivity (due to the provision of cation exchange sites), and the displacement of Na^+ from exchange sites by other cations present in these amendments (El-Shakweer et al., 2008).

Salt phytoremediation technology, the most cost-effective and environmentally-friendly method to reduce soil salinity, involves the use of halophytes as desalinisation plants (Panta et al., 2016). Common halophytes include

Mesembryanthemum crystallinum L., *Suaeda australis*, *Chenopodium album* L., *Salsola vermiculata* L., *Sarcocornia quinqueflora*, *Portulaca oleracea* L., *Allenrolfea occidentails*, *Salicornia europaea* L., *Sesuvium portulacastrum* L., *Crambe maritima* L., *Kochia indica*, *and Suaeda maritima* L. (Hasanuzzaman et al., 2014). Those commonly used in salt phytoremediation are *Sarcocornia quinqueflora*, *Allenrolfea occidentails*, *Salicornia europaea* L., and *Kochia indica* (Hasanuzzaman et al., 2014; Panta et al., 2016; Santos et al., 2017). It has been reported that halophytes are capable of completing their life cycle under high levels of salinity through their diversified adaptation mechanisms including osmotic adjustment, ion compartmentalisation, succulence, ion transport and uptake, antioxidant systems, salt inclusion or excretion, and maintenance of redox status (Barrett-Lennard, 2002). Balanced fertilisation could bring ionic equilibrium in the plant cell and facilitate cell metabolism, as well as promoting cell division and expansion, which in turn induces tolerance to overcome salinity stress (Sharif and Khan, 2009). Microorganisms such as fungi, or *Azolla* bacterium applied as a biofertiliser significantly increased the nutrient content, the enzymatic activities of soil, and further improved plant salt tolerance capacity (Sap et al., 2005; Irshad et al., 2013; Abd El-All et al., 2013).

2.1.4 Arid environments: drought and plant-water stress

Arid environments cover 30% of the world’s land surface and have erratic (often concentrated in a few rainstorms) and limited rainfall (less than 500 mm precipitation per annum), together with high temperatures and strong dry winds (Oweis et al., 2004). Globally, millions of people live in arid environments and are suffering from food and water shortage problems (FAO, 2018). Plants are adversely affected during drought due to changes in the water supply (Al-Kaisi et al., 2013). The intense transpiration rate can result in the rapid plant water loss or even death (Hsiao, 2002). Additionally, under drought situations, crops are not able to take up nutrients, as water is the major medium for their transport into plants (Canavar and Kaptan, 2014).

In addition to the effects on plants, drought can also severely affect soil structure through desiccation, which in turn affects water storage and movement, and solute transportation (Wu et al., 2008). Microbial activity decreases under drought conditions and thus the cycling of carbon and nutrients is reduced (Hueso et al., 2012; Al-Kaisi et al., 2013).

2.1.5 The relationship between water and salinity stress

In arid and semi-arid regions, salt and drought stress often occur at the same time. Inefficient irrigation methods lead to the rise of groundwater to the soil surface through capillary action, along with salts from the deeper ground (Eissa et al., 2016) (Figure 2–6). During evaporation, these salts are precipitated on the surface, and when in concentrations above 0.3%, this results in salt stress (Nie et al., 2011). Furthermore, the large evapotranspiration and associated plant-water demand that occur under evaporitic environments may further increase soil salinity (Katerji et al., 1998).

The components of drought and salinity stress interact as both ultimately result in the dehydration of the cell and osmotic imbalance (Mahajan and Tuteja, 2005; Hui et al., 2014). In addition, high salinity causes ionic stress and can lead to plant death (Figure 2–7). In fact, almost every aspect of plant physiology and cell metabolism is affected by water and salt stress.

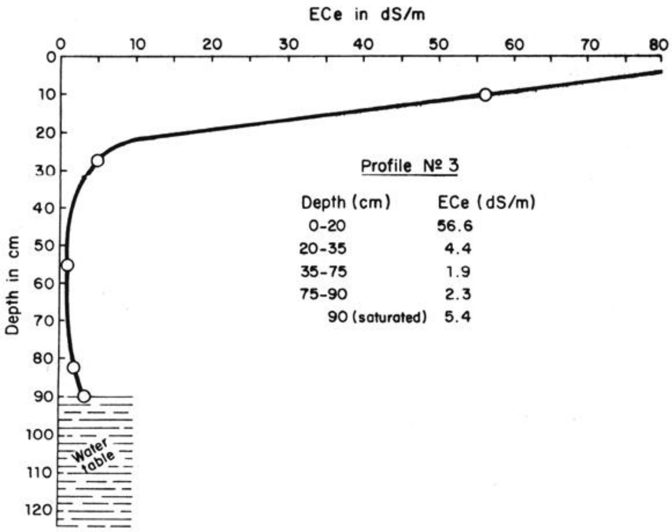

Figure 2-6 Typical salinity profile in soil with a high water table (Ayers and Westcot, 1976).

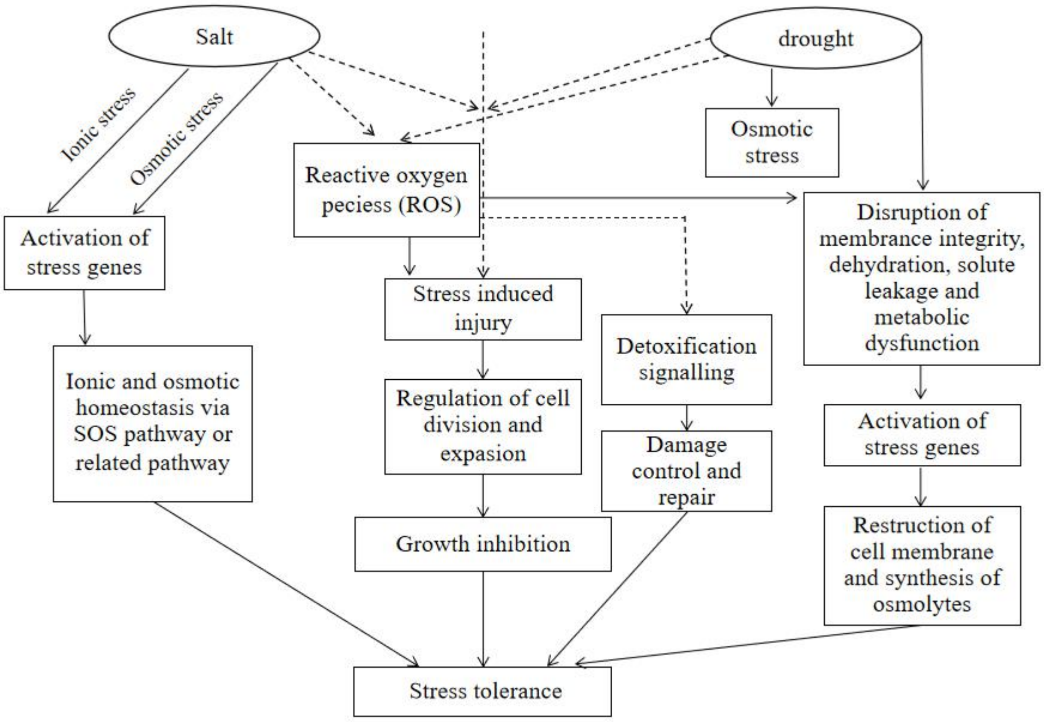

Figure 2-7 Salt and water stress tolerance mechanisms in plants (Modified from Mahajan and Tuteja, 2005).

2.1.6 The effects of water stress on plant growth

Water stress reduces the normal plant growth (Jaleel et al., 2009; Bhargava and Sawant, 2013). Low plant water potential and turgor under dehydration conditions results in the dysfunction of plant cells (Keyvan, 2010), which further affects plant's morphological and anatomical characteristics, plant-water relationships, root respiration rate, plant photosynthesis, and plant mineral nutrition and ion homeostasis (Salehi-Lisar and Bakhshayeshan-Agdamand, 2016). The symptoms of water deficit in plants varies from plant species, growth environments, and developmental stage (Arbona et al., 2013; Nezhadahmadi et al., 2013). In general, drought symptoms in plants include loss of leaf turgor, wilting, yellowing, drooping, and premature leaf downfall (Farooq et al., 2009; Zare et al., 2011; Akhtar and Nazir, 2013; Sapeta et al., 2013). Under drought stress, the growth, dry matter and harvest yield of a large number of plant species are significantly inhibited (Jaleel et al., 2009). The effects of water stress on plant growth and yield of various species are summarized in the Table 2–1.

Table 2-1 Effect of water stress on plant growth and yield in various plant species

Plant species	Effects	References
Glycine max L.	Fewer pods and seeds per unit area	Specht et al., 2001
Triticum aestivum L.	Significantly reduced grain number and grain size	Edward and David, 2008
Maize	Marked reduction in grain yield	Ndiso et al., 2012
Vitis vinifera L.	Distinctively decreased the growth of root	Kamiloglu et al., 2014
Lycopersicon esculentum Mill	Reduction in yield, flower number, fruit set percentage and dry matter production	Rahman et al., 1999
Zea mays L.	Reduction in plant height and leaf area	Çakir, 2004
Oryza sativa L.	Grain yield, total biomass, filled spikelet, 1000 grain weight, total panicle, tillers mortality, plant height and number of tillers per plant decreased with increased duration of water stress cycles	Zain et al., 2014
Vicia faba L.	Reduction in nitrogenase activity and yield of the plants	Plies-Balzer et al., 1995

2.1.7 Management of soils in arid environments

Substantial methods and practices have been adopted for managing soils in evaporitic environments. These aim at improving soil water retention capacity and nutrient status, alleviating drought stress on plants so the deleterious effect on crop yield is minimised. No-tillage or less tillage is a relatively widely adopted management practice in arid environments, owing to its beneficial role in improving soil structure and enhancing soil biological activity, nutrient cycling, soil water holding capacity, water infiltration, and water use efficiency (Al-Kaisi et al., 2013). Inorganic mulches such as lava rock gravel, rubber chips, or plastic film, with the purpose of decreasing soil moisture evaporation and soil erosion, and releasing nutrients to the soil are other measures to manage arid soils (Troll et al., 2017). Application of organic materials such as plant residue, wood chips, straw and animal manure has been found to enhance the organic matter content of the soil, and thus further improve soil nutrient status and water holding capacity (Song et al., 2008; Murakami and Kuroyanagi, 2009). Water saving irrigation practices such as the use of drip and sprinkler irrigation, could directly deliver water to plant roots, reducing the evaporation that occurs with the spray watering systems, and substantially improve the water use efficiency (Thompson et al., 2009). Proper irrigation scheduling can also help maintain soil moisture in the range between permanent wilting point and field capacity, thus markedly reducing the water loss caused by over-irrigation (Jones, 2004).

2.2. Potential use of pumice and biochar to alleviate salinity and water stress

Innovative methods to alleviate salt stress that are both practical and economically efficient are in great demand. The use of either pumice and/or biochar in the treatment of salt stress in arid regions is part of the focus of this thesis. Both ingredients are easily available (if needed in an area close to a volcanic region in the case of pumice), low cost, and their possible use in agriculture may open new doors to deal with the current problems faced in arid and semi-arid regions.

2.2.1 Potential use of pumice to alleviate salinity and water stress

Three important properties (structure, density and chemical composition) makes pumice a valuable material (Çifçi and Meriç, 2015). Pumice is a light and siliceous rock that forms during volcanic eruptions (Whitham and Sparks, 1986). The ample number of vesicles formed inside the mineral structure provides pumice with an appearance similar to a sponge (Sarkar et al., 2017). As it is made of inorganic material, it will not decompose over time (it does weather but only evident at a geological time scale), meaning that it can be recycled and reused (Wang et al., 2013). Its high porosity confers pumice with a high specific surface area (Anwar-Hossain, 2004). The large proportion of free silica sites at the grain surface results in a negatively charged surface (Yavuz et al., 2008). Due to its unique structure and chemical composition, pumice is used as an adsorbent to remove metal ions such as cobalt, copper, chromium and cadmium from wastewater (Abedi-Koupai et al., 2015; Çifçi and Meriç, 2015). Yavuz et al. (2008) observed that over 80% of Cu^{2+} and Cr^{3+} were removed by pumice from aqueous solutions. It is also used as a support material and/or amendment in agricultural and horticultural soils (Dyrness et al., 1966; Hermann et al., 1969; Troll et al., 2017). So far, there exists limited empirical evidence related to the application of pumice as a soil desalinization material. The skeletal structure of pumice allows water and ions to travel into and out of the porous structure and retain cations at negatively charged sites (Yavuz et al., 2008).

Diatoms growing in pumice may also contribute towards a decrease in soil salinity (Troll et al., 2017) (Figure 2–8). Diatoms are a major group of microorganisms found in the oceans, waterways and soils of the world and are the world’s largest contributors to bio-silicification (Round et al., 1990; Martinjézéquel, 2010). They are characterised by a unique feature: a cell wall made of silica (hydrated silicon dioxide) and functioning with several ionic pumps and transporters that are Na-dependent (Rusinova et al., 2011). Some of the diatom species such as C. *gracilis* and *Navicula lanceolata* can thrive in high saline environments (Roubeix et al., 2011;

Tokushima et al., 2016). A scanning electron microscopy (SEM) image of pumice pores from Troll et al. (2017) shows a variety of micro-organisms, these being dominantly diatoms, possibly of the genera *Pinnularia* and *Luticola*. The micro-environment inside the vesicles of pumice may contain sufficient moisture and nutrients (i.e., relatively high concentrations of iron and silica) to sustain diatoms alive. When diatoms die, salts entrapped therein are no longer available to the system. Moreover, the high silica content in plants plays an essential role in mitigating drought stress and salinity stress during plant growth process (Liang et al., 2007; Rusinova et al., 2011). To sum up, the combined effect of (i) the vesicular structure of pumice as nuclei for salts precipitation; and (ii) the potential presence of diatoms within the pumice structure that contribute to salt entrapment and also in nutrient supply in the form of silica suggests that pumice could be an efficient additive to alleviate salt stress and promote plant growth.

Soil amended with pumice has been shown to effectively increase the number of macropores important for drainage and aeration in loamy soils (Sahin et al., 2006). When salt-affected soils are well drained, salts are more easily leached out of the soil. Pumice may also contribute to water retention, as it has large numbers of micropores and can entrap water from excessive irrigation, rain or from liquid fertilizers, and can slowly release water to plant roots, as needed (Noland et al. 1992; Malekian et al., 2012). Pumice with a range of pore sizes can be used as an efficient soil conditioner, which can not only enhance the water retention capacity of sandy soils (Verdonck, 1984), but also increase the hydraulic conductivity of medium-fine textured soil

(Boyraz and Nalbant, 2015). However, the degree of inter-connectivity of the pores considerably affects the water retention capacity, and this depends on the origin of the pumice (Whitham and Sparks, 1986; Lura et al., 2004). If this is high, pumice is able to hold water–up to 55% of its own volume (Muralitharan and Ramasamy, 2015). The addition of pumice to soil has been shown to increase crop yield through its effects on soil physical properties (Noland et al., 1992; Kiss et al., 1998; Sahin et al., 2006; Zalewski, 2014; Boyraz and Nalbant, 2015). Overall, pumice can help improve water and nutrient retention, decrease compaction resistance, and increase drainage and runoff filtration, and can be effectively used as a long-term soil conditioner (Sahin et al., 2006; Troll et al., 2017). Thus, pumice has a high potential to be used as a core salt precipitation and water retention material for salt-affected soil amelioration in arid environments.

Figure 2-8 SEM images of diatoms and other micro-organisms found in pumice (a. several frustules in a vesicle; b. frustules of *Pinnularia* sp. and *Luticola* sp.; c. *Luticola* sp.; d. *Pinnularia* sp.) (Troll et al., 2017).

2.2.2 Potential use of biochar to alleviate salinity and water stress

Biochar is a fine-grained and porous carbonaceous material obtained from the pyrolysis of organic residues under oxygen-limited conditions (Sharma et al., 2018). It has attracted interest around the world for its potential to improve soil physicochemical and biological functions, mitigate CO_2 emissions, and enhance crop productivity (Herath et al., 2013; Burrell et al., 2016). Biochar use in soils may modify soil chemical properties such as pH, CEC, and nutritional content (Chintala et al., 2013; Mukherjee et al., 2014; Wang et al., 2014). Soil amended with biochar has also been shown to improve the physical properties of the soil, water retention and drainage characteristics (Yu et al., 2006; Downie et al., 2009; Burrell et al., 2016). Biochar addition has also been demonstrated to alter the biological status of the soil mostly due to its highly porous nature (Zhang et al., 2012) and presence of a small fraction of labile carbon (Herath et al., 2013). More interestingly and especially relevant to this study, several studies reported that biochar has an important effect on reducing soil salinity (Glaser et al., 2002; Liang et al., 2006; Atkinson et al., 2010; Sohi et al., 2010; Yue et al., 2014).

The potential beneficial impacts of biochar addition on salt-affected soils can be categorised into the physical, chemical and biological effects (Novak et al., 2012; Diacono and Montemurro, 2015; Bhaduri et al., 2016; Ali et al., 2017; Saifullah et al., 2018). Yue et al. (2016) reported that biochar addition reduced EC_e of soil through the biochar-induced improvement in soil porosity and hydraulic conductivity that accelerated leaching of salts. Tomas et al. (2013), Lashari et al. (2015) and Fazal and Bano. (2016) ascribed the reduction in salinity with biochar amendments to the adsorption of cations on the surface, or physical entrapment of salts in fine pores. Hammer et al. (2015) indicated that biochar application reduced evaporation (the upward movement of saline water) resulting in decreased salt accumulation in surface soils.

Biochar affects the chemical properties of salt-affected soils by altering the nutrient status (Ingestad and Ägren, 1991; Hammer et al., 2015; Akhtar et al., 2015; Usman et al., 2016; Luo et al., 2017), soil pH (Chen et al., 2008; Wang et al., 2017) and SAR/ESP (Chaganti et al., 2015). Biochar can also improve the growth and development of soil microbes in salt-affected soils through (i) improving aggregate formation (Quilliam et al., 2013); (ii) enhancing water retention and availability to microbes (Ajayi and Rainer, 2017); (iii) releasing nutrients such as organic C, nitrogen and microbial biomass C in soil for microbes; and (iv) alleviating salinity and sodicity stress (Zhang et al., 2016).

Effects of biochar on soil water retention highly depends upon feedstock, pyrolysis conditions, particle size, application rate, and the type of soil (Basso et al., 2013). A study in 2011 using a biochar made from black locust (*Robinia pseudoacacia* L.) in a sandy soil showed a significant increase in available (by 97%) and saturated water content (by 56%), and a smaller hydraulic conductivity with increasing moisture content when compared with unamended sand (Uzoma et al., 2011). Researchers reported an increase in saturated hydraulic conductivity and soil water-holding capacity in upland rice production in Northern Laos after applying wood residues biochar (Asai et al., 2009). Application of biochars produced from the pyrolysis of corn stover to silt loam soils increased the volumetric water content at each matric potential (Herath et al., 2013).

Given that some studies have reported an increase in soil salinity and sodicity with biochar addition at high rates, with effects varying depending on the type of feedstock, these results highlight the need for careful selection of biochar (with lower soluble salts and/or Na content) to successfully alleviate salinity and sodicity stress to plants, improve water use efficiency, as well as to enhance productivity in water-limiting conditions.

2.3. Potential use of tailor-made Technosols to restore salt-affected soils in arid conditions

While the most common reclamation strategy for salt-affected soils is to flush the salts out of the root zone with low salinity water, this is challenged by the fact that water is scarce in areas affected by salinity. The use of an artificial soil in such areas may well solve some of these problems when formulated adequately.

2.3.1 Technosols

Technosols is a new Reference Soil Group officially announced at the 18th World Congress of Soil Science that combines soils whose properties and pedogenesis are dominated by their technical origin (IUSS Working Group WRB, 2006). They contain significant amounts of artifacts and materials of natural and anthropic origin. Their ingredients include organic and inorganic waste material (e.g., sewage sludge, manure, fly ash, red-mud gypsum, foundry sand, and dolomite residues). In recent years, the preparation of tailor-made Technosols has been recognised as a novel and prospective method of re-using waste products and regenerating degraded or polluted areas (Camps-Arbestain et al., 2008; Asensio et al., 2012; Macía et al., 2014). An efficient Technosol should be made of an environmentally-sound mixture, and have adequate mineralogical and biogeochemical conditions, a balanced content of essential nutrients, adequate physical characteristics, and high content of stabilised organic C (Camps-Arbestain et al., 2008). An example of a Technosol and its benefits is provided in the study by Asensio et al. (2012), where Technosols made of mussel residues, wood fragments, paper mill ashes and sewage sludge were used to ameliorate mine tailing soils and caused an increase in soil pH, CEC, base saturation, organic C, and significantly decreased extractable Na^+ and Al^{3+}. Macía et al. (2014) reported that a tailor-made Technosol made of dredged sediment, sewage sludge, wood chips, peat moss, perlite and compost was employed in degraded areas as a manufactured soil and led to germination indices for *Lepidium sativum* by over 320%. Thus, it is worthwhile to investigate whether specific materials could be used as ingredients of Technosols, so that these can be especially designed for restoring salt-affected soils in arid environments.

2.3.2 Potential ingredients of Technosols other than pumice and biochar to be used to alleviate water, salt and sodic stress in plants growing in arid conditions

Considering the properties that a Technosol to be used under arid environments should have, potential ingredients of this artificial soil, in addition to pumice and/or biochar could be the following:

(i) Sand. Sand may help impair the capillary rise of water and salts to the surface soil (Figure 2–9). A sandy soil is dominated by macro-pores, which are wide enough that water is poorly held against the force of gravity. In this way, the salt accumulation caused by evaporation of ascending capillary water will be impaired;

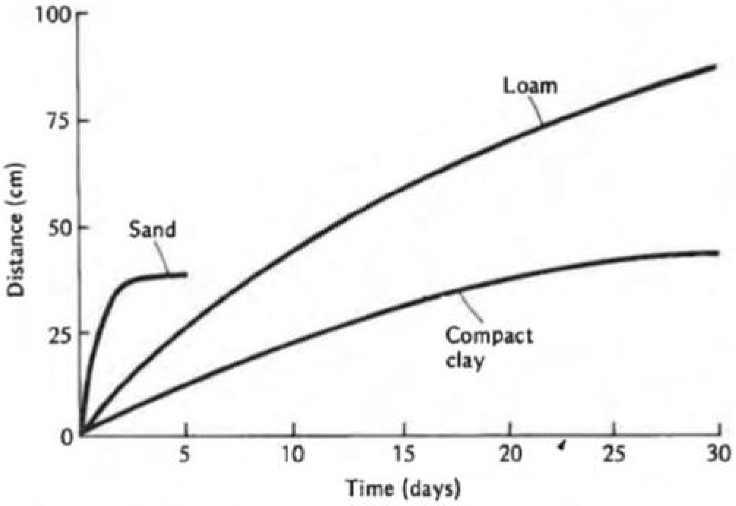

Figure 2-9 The distance (cm) of capillary rise for different soil types in time (days) (Brady and Weil, 2008).

(ii) Compounds rich in available silicon. The use of a compound rich in plant-available silicon may help provide Si to plants and increase their resistance to numerous abiotic and biotic stresses, including water and salinity stress (Zhu and Gong, 2014). Compounds such as calcium (magnesium) silicate, supplied in the form of metallurgical slags (Gascho, 2001); carbonized rice husk and straw (Ugheoke and Mamat, 2012); alkaline Si sources, such as calcium silicate slag, cement, and granulated ground blast furnace slag (Keeping et al., 2017), have been proven to be effective in supplying plant-available Si.

(iii) Diatoms. As reported above, they may help trap salts and render them unavailable to plants. They may grow within pumice pores (Matichenkov and Bocharnikova, 2004);

(iv) Organic material. An organic source will be needed to help aggregation, retain moisture, and provide a source of carbon and nutrients to soil microorganisms and nutrients to plants (Michalak et al., 2016). A combined amendment of these potential ingredients might help combat salt and water stress in crops and thus improve crop productivity in arid areas (Figure 2–10).

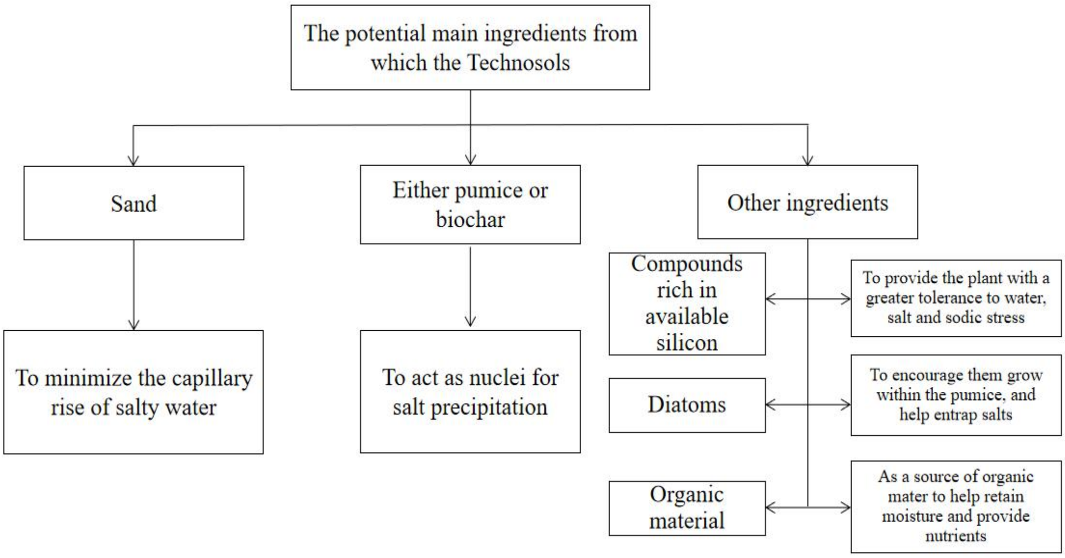

Figure 2-10 Potential formulation of Technosols especially designed for reclaiming salt-affected soils in arid areas.

2.4. Current research gaps and priorities in the understanding of the use of specific soil amendments to be used in formulation of

Technosols for reducing salinity and water stress of crops growing under arid environments

There are a number of research gaps and priorities in the study of the formulation of Technosols to reduce salinity and water stress of crops growing under arid conditions, which are as follows:

(i) While extensive research efforts have been made to investigate the effects of Technosols on restoring mine tailing soils and heavy metal contaminated soils, less is known about the influence of specific materials that could serve as ingredients for tailor-made Technosols to be used to alleviate salinity and water stress of crops growing under arid environments.

(ii) While there is a growing body of research on the use of biochar to improve soil functions, the effect of the type of biochar (and type of feedstock) and application rate to mitigate salt-induced plant stress is yet to be summarised.

(iii) The effect of pumice on alleviating salinity and plant-water stress is still unknown, along with its effect compared with that of biochar or that of its combined application with algae.

(iv) Although the high capacity of biochars or pumice to sorb a variety of salts has been noted, the mechanisms behind the precipitation of salts on these ingredients remain largely unclear.

Chapter 3

HOW TO MINIMIZE THE IMPACT OF BIOCHAR ON THE SALINITY OF SOILS IN DRY REGIONS: A META-ANALYSIS

This chapter aims to conduct a meta-analysis to investigate the effect of biochar on the salinity using EC as the proxy of soils in dry environments (soils under Mediterranean, arid, semi-arid climatic conditions, or under simulated dry and saline conditions in glasshouse/incubation chamber experiments).

A paper from this study will be submitted for publication: **Chao Kong**, Marta Camps-Arbestain, Brent Clothier. How to minimize the impact of biochar on the salinity of soils in dry regions: a meta-analysis. *Soil Use and Management* (To be submitted).

Abstract

A meta-analysis of 40 studies published between 2013 and 2020 using pairwise comparisons was carried out to evaluate the short-term effect of biochar on the salinity of soil. We used electrical conductivity – EC – as a proxy for soils under Mediterranean, arid, and semi-arid climates, or under simulated dry and saline conditions. Compared with the control, a 16.8% increase in EC was observed with the addition of biochar. Yet it should be noted that 77% of the observations applied biochar at rates > 20 t ha^{-1}. The largest increase in EC was detected when (i) biochar produced from high-ash feedstock was used (61.4%); (ii) biochar was applied at high rates (> 20 t ha^{-1}) (21.8%); (iii) in soils with a low initial soil organic carbon (OC) concentrations (28.6%); and (iv) in soils not receiving a leaching fraction (23.3%). Data limitation precluded the identification of the influence of production conditions without bias. The results suggest that in terms of the risk of biochar increasing soil salinity, (i) biochars made from high-ash material such as seafood shell powder and peanut shell should not be applied to soils in dry regions; and (ii) the addition of biochars made from relatively low-ash ligneous material at application rates ≤ 20 t ha^{-1} is suitable as an amendment to soils under dry environments. The use of a leaching fraction is recommended.

Key words

Biochar; Salinity; Meta-analysis; Mediterranean climate; Arid; Semi-arid; Greenhouse; Chambers

3.1 Introduction

Biochar technology is currently being promoted because of its potential to improve soil properties while contributing to the mitigation of climate change (Atkinson et al., 2010; Lehmann and Joseph, 2015). For soils in dry environments, the interest in using biochar resides in the fact that it may help, in some instances, to increase soil water retention and decrease soil salinity (Mulcahy et al., 2013; Munera-Echeverri et al., 2018). As a low density, porous particulate material, when added to soil, biochar may alter soil physical properties. Whether biochar has an impact on soil water retention depends on the relative differences in these properties between the biochar and the receiving soil, as well as its particle size, application rate, and depth of application. This explains the contrasting results in the literature, with either an increase (Basso et al., 2012; Kinney et al., 2012; Novak et al., 2012; Herath et al., 2013), no effect (Laird et al., 2010; Abel et al., 2013), or a decrease in soil water holding capacity upon biochar addition (Hardie et al., 2014). In general, the greatest increases in soil water retention caused by biochar application have been observed with biochars produced from hard wood, and when added to soils with a low water-holding capacity (Kinney et al., 2012; Novak et al., 2012).

Contradictory results have also been reported on the effect of biochar on soil salinity. While Thomas et al. (2013), Hammer et al. (2015) and Amini et al. (2016) have all described a decrease in soil salinity after the application of biochar, other studies have reported a distinct increase in salinity, especially when biochar is applied at high rates (Sigua et al., 2016; Blok et al., 2017; Luo et al., 2017; Zheng et al., 2017). The influence of biochar on soil salinity depends primarily on the type of biochar, its initial content of soluble salts, application rate, soil properties (texture, pH, organic C, and electrical conductivity), plus irrigation water quality, and irrigation practices in terms of a leaching fraction (Gaskin et al., 2010; Novak et al., 2010; Mukherjee and Zimmerman, 2013; Sigua et al., 2015; Rafiq et al., 2016). The test most widely used to determine soil salinity is the measurement of the soil-solution electrical conductivity (EC) (Pansu and Gautheyrou, 2006). It is based on the principle that an increase in the concentration of dissolved salts causes an increase in the ability of the soil solution to conduct an electrical current. Hammer et al. (2015), Akhtar et al. (2015a, 2015b, 2015c) and Yue et al. (2016) have ascribed the reduction in soil EC with biochar amendments to (i) an increase in water retention within biochar pores, resulting in a dilution of soil salinity; (ii) the retention of salts within biochar through either adsorption on the biochar surfaces or physical entrapment within fine pores; and (iii) a decrease in the soil bulk density and an increase in the soil hydraulic conductivity, which facilitates the leaching of salts when a leaching fraction is applied. Other studies have observed an increase in soil EC caused by the contribution of soluble salts in the ash fraction of the biochar (Gray et al., 2014; Smider and Singh, 2014).

Given that an understanding of the influence of the amount of soluble salts in biochar on soils is needed to avoid any adverse effects on salt-sensitive plants and on soil functioning, the main objective of this study was to conduct a meta-analysis to investigate the effect of biochar on the salinity using EC as the proxy in soils under Mediterranean, arid, and semi-arid climatic conditions, or under simulated dry and saline conditions in glasshouse/incubation chamber experiments.

3.2 Materials and Methods

3.2.1 Data collection

We performed a literature search focused on peer-reviewed publications using the ISI Web of Science (http://apps.isiknowledge.com) and Google Scholar before July 2020. Publications were identified using the key words ‘biochar’ OR ‘charcoal’ OR ‘char’ OR ‘pyrogenic carbon’ AND ‘soil salinity’ OR ‘salinity’ AND ‘Mediterranean’ OR ‘arid’ OR ‘semi-arid’ OR ‘glasshouse’ OR ‘incubation chamber’. We selected studies that reported biochar and soil properties, including EC of biochar and soil, for (i) a treatment that did not receive biochar, referred to as the ‘control’;

AND (ii) a treatment that only differed from the ‘control’ by the addition of biochar, where possible, and referred to as the ‘treatment’. Thus, if the control was fertilised, so was the treatment and, where possible, in similar amounts of conventional fertiliser in both treatments. If one publication had treatments with different fertiliser rates, the more realistic scenario was chosen. The studies should have lasted a maximum of 1 year.

Altogether over 180 studies were reviewed, and we selected 40 studies (Maucieri et al., 2017; Chaganti and Crohn, 2015; Zhang et al., 2016; Usman et al., 2016; Teutscherova et al., 2018; Chaganti et al., 2015; Andrés et al., 2019; Arif et al., 2016; Pandian et al., 2016; Hammer et al., 2015; Huang et al., 2019; Agbna et al., 2017; Elshaikh et al., 2017; Smider and Singh, 2014; Wu et al., 2014; Singh et al., 2018; Thomas et al., 2013; Sigua et al., 2016; Luo et al., 2016; Zheng et al., 2017; Abbas et al., 2017a; Abbas et al., 2017b; Abrishamkesh et al., 2015; Zhang et al., 2019; Irfan et al., 2019; She et al., 2018; Vasconcelos et al., 2017; Zhang et al., 2020; Mohawesh et al., 2018; Chávez-García et al., 2019; Mahmoud et al., 2019; Shah et al., 2017; Martos et al., 2019; Alburquerque et al., 2014; Elshaikh and She, 2018; Ghorbani et al., 2019; Mickan et al., 2016; Rekaby et al., 2019; Mokhtar et al., 2016; Sekar et al., 2014), which met our criteria. Studies included in the meta-analysis are marked with an asterisk in the cited literature. The selected studies represented a range of geographical sites across 37 experimental locations in 14 different countries. We used 149 observations in the meta-analysis.

We extracted meta-data from each of the selected publications, including climatic, soil chemical and physical data, treatments and analytical methods. The specific data included in the meta-analysis were as follows: climatic conditions, initial soil properties, type of feedstock, which was then classified based on the ash content – high-ash material, cereal residue, and ligneous material –, biochar production conditions, biochar properties, biochar application rates, soil EC at the end of the experiment, irrigation practices, and addition of fertiliser. Where data were available in a graphic form only, the values were extracted using Plot Digitizer 2.6.8 (Huwaldt and Steinhorst, 2015). The categorical variables of climate, texture, initial soil pH, initial soil OC, initial soil EC, type of feedstock, HHT, biochar pH, biochar EC, leaching fraction, biochar application rate, addition of fertiliser were then grouped into different categories, which are described in Table 3–1 along with a description on how data were organised. For example, soil pH values were converted to pH measured in distilled water using a 1:2.5 soil/water ratio following van Lierop (1981), Conyers and Davey (1988), and Kabala et al. (2016). Soil EC values were converted to EC measured in distilled water using a 1:5 soil/water ratio at 25 °C following Al-Busaidi et al. (2006) and Pan et al. (2014). We acknowledged that there is uncertainly in the conversion of EC from different dilutions associated with mineral dissolution, ion hydrolysis, formation of ion pairs, and changes in exchangeable cation ratios (Al-Busaidi et al., 2006). Most soils considered in this study had pH > 6.5, as expected in poorly leached soils in drylands. Yet, the study included some soils with pH value ≤ 6.5, from wetter regions, that were subjected to simulated dry and saline conditions in glasshouse and incubation chambers.

Table 3-1 Categorical variables tested and their grouping

Variable	**Grouping**	**Notes**
Experimental Climate	Arid & Semi-arid Mediterranean Greenhouse & Chambers	
Soil texture	Sandy	Sand, loam sand, sandy loam
	Loam	Sandy clay loam, loam, clay loam, silty clay loam
	Clay	Clay, sandy clay, silty clay
Initial soil pH	≤ 6.5 > 6.5	Soil pH measured in DI water (1:1, 1:2.5, 1:5, 1:10, 1:20), $CaCl_2$ (1:2, 1:2.5, 1:5), and KCl (1:2, 1:2.5, 1:5) were converted to soil:water = 1:2.5 following Conyers and Davey (1988), van Lierop (1981) and Kabala et al. (2016). The initial soil $pH_{(1:2.5)}$ ranged from 3.9 to 10.2
Initial soil OC	≤ 5 g kg^{-1} 5–10 g kg^{-1} > 10 g kg^{-1}	When total C was reported in acidic soil, the values were considered as organic C. Initial soil organic C ranged from 0.44 to 70 g kg^{-1}
Initial soil EC	≤ 0.4 dS m^{-1} > 0.4 dS m^{-1}	Soil EC measured in DI water (1:1, 1:2.5, 1:5, 1:10, 1:20) were converted to soil:water = 1:5 at 25 ℃ following Al-Busaidi et al. (2006) and Pan et al. (2014). The initial soil $EC_{(1:5)}$ ranged from 0.02 to 217 dS m^{-1}
Feedstock	Animal & Human wastes	Cattle feedlot manure, cattle dung, poultry litter, farmyard manure, sewage sludge
	Cereal residues	Maize cobs, rice husk, miscanthus, straw
	Ligneous materials	Coniferous and deciduous wood residues, peanut hull, coconut shell, bamboo, cotton stalk
	Greenwastes	Plant pruning and grass clippings collected from parks, gardens, and agricultural fields
	Papermill residue	

	Mixed materials	
Pyrolysis highest heating temperature (HHT)	≤ 400 °C 400–550 °C > 550 °C	Biochars produced using traditional kiln were allocated in the group of 550–700 °C (http://www.fao.org/docrep/X5328E/x5328e07.htm). HHT classes have been established based on the changes in the chemical structure of biochar as HHT increases (these are described in Keiluweit et al., 2010)
Biochar pH	≤ 9 > 9	
Biochar EC	≤ 2 dS m^{-1} > 2 dS m^{-1}	Biochar EC measured in DI water (1:1, 1:2.5, 1:5, 1:10, 1:20) were converted to solid:water = 1:10 at 25 °C following Al-Busaidi et al. (2006), Pan et al. (2014) and Singh et al. (2017). Biochar EC$_{(1:10)}$ ranged from 0.011 to 110 dS m^{-1}
Leaching fraction	With the leaching fraction Without the leaching fraction	
Biochar application rate	≤ 20 t ha^{-1} yr^{-1} 20−40 t ha^{-1} yr^{-1} 40−80 t ha^{-1} yr^{-1} > 80 t ha^{-1} yr^{-1}	
Treatments	BC BC + IF BC + OA BC + IF + OA	

DI water, distilled water; OC, organic carbon; EC, electrical conductivity; BC, biochar; BC + IF, biochar + inorganic fertiliser; BC + OA, biochar + organic amendment; BC + IF +OA, biochar + inorganic fertiliser + organic amendment.

3.2.2 Meta-analysis

Statistical analyses and graphical representation were performed according to Hedges et al. (1999) and Cayuela et al. (2014) using Meta Win 2.0 software (Rosenberg et al., 2000). We used natural log-transformed response ratio (R) as a measure of the effect size:

$$\ln R = \ln\left(\frac{XE}{XC}\right) \qquad [3\text{–}1]$$

Where XE is the mean value of the treatment and XC is the mean value of the control. Mean effect sizes of each category and the 95% confidence intervals (CIs) were generated by bootstrapping (999 iterations) using MetaWin 2.0 Statistical software (Rosenberg et al., 2000).

A non-parametric function, based on the sample size and the number of replications, was used for weighting (Adams et al., 1997). We chose this function instead of the variance because many studies did not report a measure of variance for soil EC. The sample-size weight function used here was as follows:

$$\text{Weight} = \frac{N_E \times N_C}{N_E + N_C} \qquad [3\text{–}2]$$

Where N_E is the number of replicates of the experimental observation and N_C is the number of replicates of the control observation within the same experimental conditions. A categorical random effects model was used to calculate the grouped effect sizes. The pooled variance of the EC was ≤ 0, for which MetaWin 2.0 software automatically switched from a categorical random model to a categorical fixed model.

Graphically, the change in the EC is shown as a proportion of the control with the effect size exponentially transformed. Then, R−1 was calculated and multiplied by 100 to obtain the percentage change. The relative changes in soil EC within each category were considered to be significant from one another if their CIs did not overlap. The overall mean of the soil EC changes, either for each category or for the whole observation, was considered to be significantly different from the control, if the 95% CI did not overlap with zero (Scheiner and Gurevitch, 2001; Cumming and Finch, 2005). For grouping, a minimum of five pairwise comparisons coming from at least two independent studies were considered to form a category and was presented in the meta-analysis. Otherwise, ungrouped data contributed to the calculation of the overall mean effect size. The dataset used to generate different graphs are reported in the Tables 3–2 & 3–3.

3.3 Results

3.3.1 Effect of biochar on the grand mean

The application of biochar to soil caused a significant 16.8% grand-mean increase of soil EC (bootstrap CI 95%: 8.3%–29.3%, n = 60) when compared with the control (Figure 3–1). The variables that had the greatest influence on soil salinity were related to the biochar properties of type of feedstock, and EC, plus the initial soil properties of EC, pH, and OC content, along with the irrigation practices relating to the leaching fraction, as well as biochar application rate, and climatic conditions. With few exceptions, other categorical variables such as biochar pH, and application with or without IF had a generally smaller contribution to the variance.

3.3.2 Effect of biochar properties

As expected, as compared with the control, biochars with EC values > 2 dS m^{-1} caused a larger and significant ($p < 0.05$) increase in soil EC with a mean of 24.8% (bootstrap CI: 12.9%–39.9%). Those with EC values ≤ 2 dS m^{-1} had a mean of 2.1% (bootstrap CI: -5.7%–11.7%) (Figure 3–1). The latter did not contribute to increase soil salinity. Biochar pH did not contribute to explaining changes in soil salinity upon biochar application. The type of biochar feedstock was key in determining the effect of biochar application on soil salinity, with the biochars produced from high-ash materials such as seafood shell powder, and peanut shell causing the largest increase in EC (mean: 61.4%, bootstrap CI: 53.6%–80.3%) as compared with the control (Figure 3–1). Biochars from cereal residues also increased soil salinity (mean: 17.9%, bootstrap CI: 4.8%–35%) when compared with the control. Whereas biochar made from ligneous materials did not (mean: 8%, bootstrap CI: -0.6%–18.1%). Biochar produced at temperatures ≤ 400°C significantly increased soil EC (mean: 26.6%, bootstrap CI: 11.9%–41.4%) compared with the control (Figure 3–1). No significant increase was detected in the other two HHT classes (400 to 550 °C and > 550 °C) (Figure 3–1). Yet, no significant differences were detected between HHT groups (HHT ≤ 400 vs. 400–550 vs. > 550 °C) (Figure 3–1).

3.3.3 Effect of initial soil properties

Application of biochar to soils with sandy (mean: 19.8%; bootstrap CI: 7.1%–34.3%) and loam texture (mean: 14.5%; bootstrap CI: 4.3%–26.4%) increased soil EC, as compared with the control (Figure 3–1). But it did not increase that of clay soils (mean: 1.7%; bootstrap CI: -14.9%–28.8%). No significant differences were observed between the textural classes (Figure 3–1). Biochar application increased soil EC when added to soils with initial EC > 0.4 dS m^{-1} (mean: 23.5%; bootstrap CI: 13.8%–34.3%) compared with the control (Figure 3–1), as opposed to soils with an EC ≤ 0.4 dS m^{-1}. No significant differences between soil EC groups (EC ≤ 0.4 vs. > 0.4 dS m^{-1}) were detected (Figure 3–1). Large initial soil pH values (pH > 6.5) were associated with a larger response in soil salinity to biochar addition (mean: 20.2%; bootstrap CI: 11.5%–30%) compared with the control. For soils with an initial pH ≤ 6.5 (mean: -7.1%; bootstrap CI: -15.9%–6.2%) (Figure 3–1), there was no significant effect. The differences in salinity response between pH groups (pH ≤ 6.5 vs. > 6.5) were significant between each other. The application of biochar to soils with low OC contents (≤ 5 g kg^{-1}) resulted in significant increases in soil EC as compared with the control (mean: 28.6%; bootstrap CI: 16.7%–43.6%). The application to soils with OC values ranging from 5 to 10 g kg^{-1}, or > 10 g kg^{-1} showed no significant increase in soil EC (Figure 3–1). The low soil-OC group (≤ 5 g kg^{-1}) was significantly different from that of soils with an OC rates > 10 g kg^{-1} (mean: -6.1%; bootstrap CI: -14.7%–5.5%) (Figure 3–1).

3.3.4 Effect of climatic conditions and irrigation practices

Soils under arid and semi-arid climates showed the greatest increase in EC (mean: 30.1%; bootstrap CI: 19.8%–43.2%), followed by those under Mediterranean climates (mean: 8%; bootstrap CI: 0.1%–16.7%). There was no significant increase in soil salinity responses in soils under simulated dry and saline environments in greenhouse/incubation chambers (Figure 3–1). As expected, studies without the leaching fraction caused a larger and significant ($p < 0.05$) increase in soil EC (mean: 23.3%; bootstrap CI: 15.7%–32.3%), compared to those with a leaching fraction (mean: 1%; bootstrap CI: -5.7%–11.4%) (Figure 3–1). In fact, the application of the leaching fraction contributes to maintaining low soil salinity levels.

3.3.5 Effect of application rates and simultaneous addition of other amendments

Biochar application rates > 20 t ha^{-1} always caused a significant increase in soil EC, with no significant differences found between the classes of 20–40, 40–80, and > 80 t ha^{-1}) (Figure 3–1). Biochar application rates ≤ 20 t ha^{-1} had no effect on soil salinity in this meta-analysis (mean: 0.8%; bootstrap CI: -7.8%–11.9%) (Figure 3–1). The addition of either only biochar (mean: 15.9%; bootstrap CI: 4.6%–29.5%), or biochar + IF (mean: 9.7%; bootstrap CI: 1.6%–18.7%) did not have an influence on the soil EC (Figure 3–1).

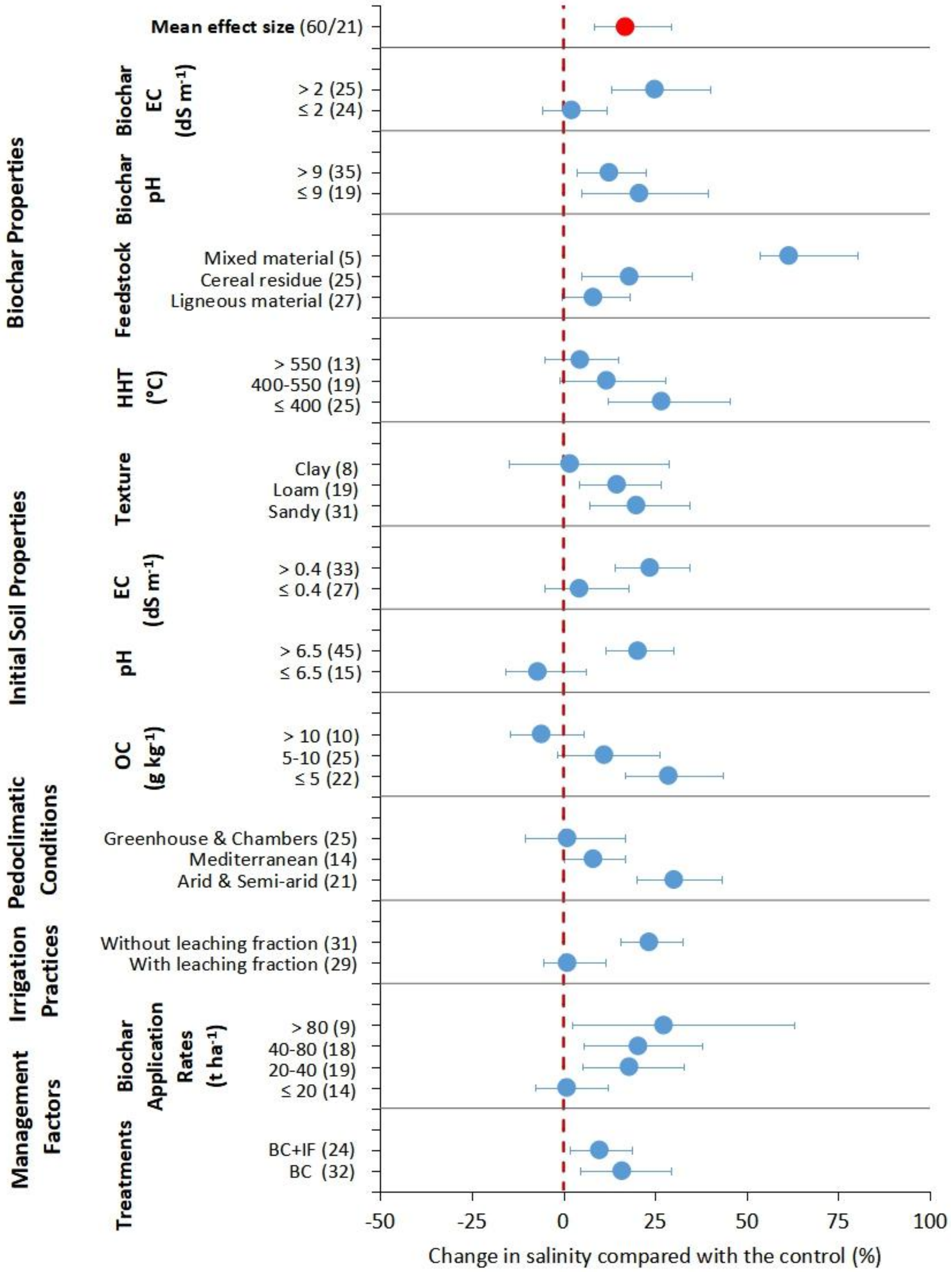

Figure 3-1 Proportional changes in soil salinity caused by biochar additions for each level of the individual categories over the control. The red dotted line represents the overall mean change in soil salinity among all studies combined. The numbers in

parentheses show the number of pairwise comparisons on which the statistic is based. The right number within parenthesis for the mean effect size is the number of independent publications from which the data are drawn. The data used to generate this figure are provided in Table 3–2. EC, electrical conductivity; HHT, pyrolysis highest heating temperature; OC, organic carbon; BC, biochar; BC + IF, biochar + inorganic fertiliser.

Table 3-2 Proportional changes (mean, and lower and upper confidential intervals) in soil salinity caused by biochar additions for each level of the individual categories over the control.

Category	Groups	n	Change (%)	Lower CI	Upper CI
Treatment	BC	32	15.9	4.6	29.5
	BC + IF	24	9.7	1.6	18.7
Biochar application rate	≤ 20	14	0.8	-7.8	11.9
	20−40	19	17.9	5.3	32.7
	40−80	18	20.3	5.6	37.8
	> 80	9	27.3	2.3	63.1
Leaching fraction	With the leaching fraction	29	1.0	-5.7	11.4
	Without the leaching fraction	31	23.3	15.7	32.3
Experimental climate	Arid & Semi-arid	21	30.1	19.8	43.2
	Mediterranean	14	8.0	0.1	16.7
	Greenhouse & Chambers	25	1.0	-10.7	16.7
Soil OC	≤ 5	22	28.6	16.7	43.6
	5−10	25	11	-1.8	26.2
	> 10	10	-6.1	-14.7	5.5
Soil pH	≤ 6.5	15	-7.1	-15.9	6.2
	> 6.5	45	20.2	11.5	30
Soil EC	≤ 0.4	27	4.2	-5.2	17.7
	> 0.4	33	23.5	13.8	34.3
Soil texture	Sandy	31	19.8	7.1	34.3
	Loam	19	14.5	4.3	26.4
	Clay	8	1.7	-14.9	28.8
Pyrolysis temperature	≤ 400	25	26.6	11.9	45.4
	400−550	19	11.7	-1.2	27.6
	> 550	13	4.4	-5.2	14.9

Feedstock	Ligneous material	27	8	-0.6	18.1
	Cereal residue	25	17.9	4.8	35
	Mixed material	5	61.4	53.6	80.3
Biochar pH	≤ 9	19	20.6	4.7	39.5
	> 9	35	12.4	3.5	22.4
Biochar EC	≤ 2	24	2.1	-5.7	11.7
	> 2	25	24.8	12.9	39.9
Grand mean		60	16.8	8.3	29.3

BC, biochar; BC + IF, biochar + inorganic fertiliser; OC, organic carbon; EC, electrical conductivity; CI, confidence interval.

3.4 Discussion

3.4.1 Selection and application of a biochar to dryland soils

Our meta-analysis has clearly shown that when biochars with an initial EC ≤ 2 dS m^{-1}, derived from ligneous materials that are poor in ash, and applied at rates ≤ 20 t ha^{-1}, then there is no apparent effect on soil EC. This is basically related to the application of a modicum of soluble salts. Soluble salts in biochar are found in its ash fraction, and this is mostly influenced by the type of feedstock from which the biochar is produced (Camps-Arbestain et al., 2015), with the ligneous materials having the smallest ash contents among all feedstocks used for the production of biochar. The ash fraction is enriched with inorganic non-crystalline amorphous compounds and poorly to well-crystallized mineral constituents (Singh et al, 2010; Yuan et al, 2011; Kloss et al, 2012). These are predominantly metal carbonates, silicates, phosphates, sulphates, chlorides and oxy-hydroxides (Singh et al, 2010; Vassilev et al, 2013a). Among these, chlorides and sulphates salts are those that contribute the most to salinity.

Although the main meta-analysis points towards the fact that biochars produced at temperatures ≤ 400 °C increased soil salinity, as opposed to biochars produced at higher HHT, after further analyses, this was proven to be an artefact caused by several masking effects. While about half of the biochars in the ≤ 400 °C category were mostly produced from intermediate to relatively high-ash feedstocks, the proportion of these materials decreased to 13% in the biochars produced at > 550 °C. To overcome this limitation, we compared the effect size of biochars made from ligneous feedstocks only when pyrolysed at three different HHT (≤ 400 °C, 400–550 °C, > 550 °C) (Figure 3–2). We then found that there was no mean effect size at low HHT, as opposed to the higher HHT classes, with a mean effect size on salinity of -12.1%, 18.8%, and 8.3%, respectively, for the three HHTs. There were no significant differences between them (Figure 3–2). When considering the cereal feedstocks by grouping them at HHT of ≤ 380 °C, 380–450 °C, > 450 °C, we found a trend of decreasing salinity with HHT increase, with a mean effect size of 37.1%, 7.1%, and -12.9%, respectively. This could be explained by the fact that when cereal feedstocks are pyrolysed at high temperatures, some of the salts become more insoluble. Carbonates became metal oxides and the CO_2 of carbonates are lost, thus decreasing the effect of biochar on soil salinity (Enders et al., 2012). It is possible that a data limitation precluded the identification of the influence of production conditions without bias.

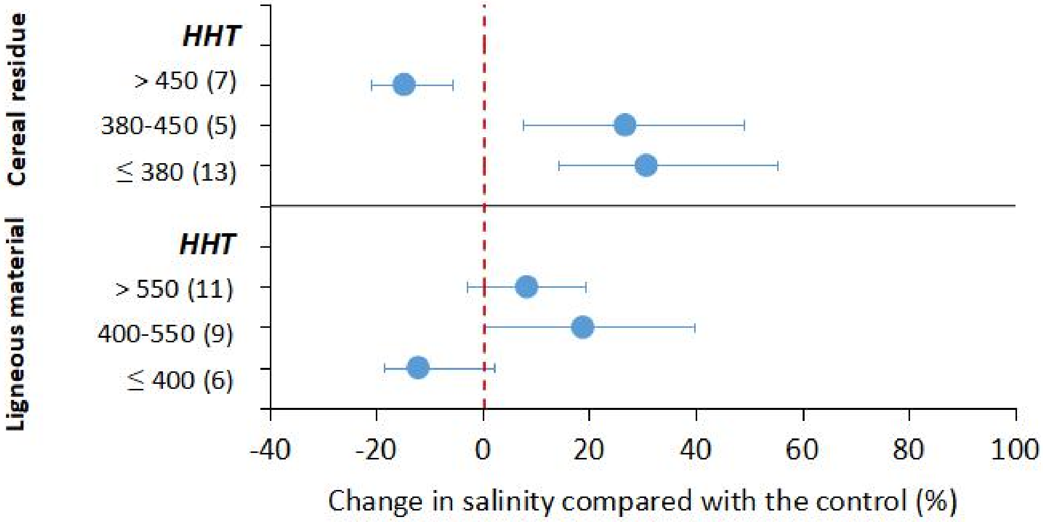

Figure 3-2 Proportional changes in soil salinity caused by biochar additions over the control for application of biochar produced from different feedstocks and pyrolysis highest heating temperature values (HHT). The red dotted line represents the overall mean change in soil salinity among all studies combined. The numbers in parentheses show the number of pairwise comparisons on which the statistic is based. The data used to generate this figure are provided in Table 3–3.

Table 3-3 Proportional changes (mean, and lower and upper confidential intervals) in soil salinity caused by biochar additions over the control for biochars with different feedstocks and pyrolysis highest heating temperatures.

Category	Groups	n	Change (%)	Lower CI	Upper CI
Ligneous material	≤ 400	6	-12.11	-18.58	2.19
	400−550	9	18.8	0.23	39.62
	> 550	11	8.27	-2.99	19.19
Cereal residue	≤ 400	13	37.05	15.41	65.35
	400−550	10	7.13	-9.06	29.85
	> 550	2	-12.89	-16.93	-8.48

CI, confidence interval.

3.4.2 Is the type of recipient soil important?

Soils in arid environments tend to have low OC because of limited plant growth, as well as pH > 6.5 because of the higher rate of evaporation compared with precipitation, which restrains leaching. And, in some instances, soil EC can be high where the parent material was originally a seabed or has arisen due to a poor irrigation management (Matar et al., 1992; Scotti et al., 2015). The results obtained from our meta-analysis implies that the drier the environment, the lower the soil OC, the higher the soil pH, and the poorer the soil leaching. Consequently, the higher the impact of biochar on soil salinity.

The fact that clay soils apparently buffered any increase in salinity added with the biochar could be explained by their larger CEC compared with sandy and loamy soils (Pignatello et al., 2015). However, again there was an imbalance in the dataset with biochars in the clay soils category being mostly produced from woody materials (68.7% of observations) as opposed to those used in sandy soils (17.3% of observations). The fact that addition of biochar to soils with initial EC $\leq$ 0.4 dS m^{-1} had no effect on soil salinity, as opposed to soils with EC > 0.4 dS m^{-1}, is consistent with the results obtained by Saifullah et al. (2018). The increase in soil EC relative to the control, observed when biochar addition to soils with initial EC > 0.4 dS m^{-1}, could be explained by the fact that in these soils, low soluble salts, such as phosphorous or sulphates, might already be saturated and thus unable to precipitate with cations from more soluble salts (Rajkovich et al., 2012; Smider and Singh, 2014).

The fact that soils with initial pH values $\leq$ 6.5 did not result in an increase in EC with biochar application, as opposed to soils with initial pH values > 6.5, deserves some clarification. Most soils used in this database had pH values > 6.5, as expected in poorly leached soils in dry regions where evaporation exceeds precipitation. Yet, the study included some soils with pH value $\leq$ 6.5, from wetter regions with average annual precipitation > 1000 mm. They had an initial low EC, and then were subjected to simulated dry and saline conditions under glasshouse and incubation chambers. Values of pH have an influence on the solubility of salts and, thus, this could explain the patterns observed. Yet, it should be noted that soils with a pH > 6.5 generally had a higher EC than soils with a pH $\leq$ 6.5, due to poor leaching. The fact that the addition of biochar to soils with initial OC concentrations > 10 g kg^{-1}, or between 5 and 10 g kg^{-1}, had no effect on soil salinity, as opposed to soils with an initial OC concentration ≤ 5 g kg^{-1} could be explained by the fact that these soils have a higher CEC. Thus, they probably had a higher ability to buffer those cations that had been added (Amini et al., 2016).

In arid & semi-arid or Mediterranean climates, the initial soil EC values were > 0.4 dS m^{-1} (72.2% and 71.4% of observations, respectively) whereas in greenhouse and incubation chambers they had initial soil EC values ≤ 0.4 dS m^{-1}. Given that our dataset only considered the studies that lasted a maximum of 1 year, and it may be possible initial soil EC (as influenced by climatic conditions) was more important than the climate itself during the experiment. Finally, the fact that soils with the leaching fraction did not result in an increase in EC with biochar application, as opposed to soils without the leaching fraction was expected and consistent with the work of Saifullah et al. (2018). They found that the combined application of biochar and leaching irrigation were shown to facilitate leaching of soluble salts out of the soil profile.

3.5 Conclusions

The results obtained in this study when evaluating the effects of biochar on soil salinity under dry environments could be useful in the development of guidelines on the use of the biochar feedstock and its ash content, temperature of pyrolysis, initial EC of biochar, and the application rate in dry areas. Overall, the results indicate that, when a moderate amount of soluble salts in biochar is added to a soil under a dry environment, and a leaching fraction is applied, in the risk of increasing soil EC is negligible.

Chapter 4

INFLUENCE OF THE PHYSICAL PROPERTIES OF PUMICE AND BIOCHAR AMENDMENTS ON SOIL'S MOBILE- AND IMMOBILE-WATER: IMPLICATIONS FOR USE IN SALINE ENVIRONMENTS

This chapter aims to evaluate how the physical properties of a pumice and a biochar, namely their particle size, and application rate affected their mobile-immobile water when added to a sandy soil.

A paper from this study will be submitted for publication: **Chao Kong**, Marta Camps-Arbestain, Brent Clothier. Influence of the physical properties of pumice and biochar amendments on soil's mobile- and immobile-water: implications for use in saline environments. *Soil Research* (Under review).

Abstract

We investigated the influence of the porosity and pore-size distribution of amendments of a pumice (from New Zealand) and a biochar (produced from willow wood chips at a highest heating temperature of 350 °C) on the mobile-water content when added to a sandy soil. Pumice and biochar (of 1.5-, 3-, and 6 cm Ø) were characterised using Scanning Electron Microscope (SEM) technology. The fraction of mobile-water present in these amendments, previously added to a sandy soil at different application rates and particle sizes, was determined using a tracer (Na^+) technique. The results showed that (i) pumice exhibited a wider pore-size span than biochar; and (ii) both materials had a predominance of pores with a Ø < 30 μm; but (iii) the total porosity in pumice and biochar was not significantly different; (iv) pumice had a significantly larger ($p < 0.05$) mean absolute micro-scale porosity than biochar; and (v) pumice had a significantly greater ($p < 0.05$) relative resident Na^+ concentration than biochar, irrespective of the particle size, which increased as pumice particle size increased. This reflects a larger fraction of the mobile-water in pumice than that of biochar under near-saturated conditions, irrespective of the biochar particle size; and this increased as the pumice particle size increased. Our results suggest that, while both materials are expected to contribute to water retention and thus might alleviate salt-stress by diluting salt concentration, pumice may perform better than biochar on improving the retention of plant-available water.

Key words

Pumice; Biochar; Porosity; Pore-size distribution; Miscible displacement; Mobile-water fraction

4.1 Introduction

The sustainability of agriculture in arid regions is challenged by the limited availability of water, and the need to manage salinity in soils and irrigation-water. This demands long-term economically- and environmentally-sound interventions (Alon et al., 2006). Despite the magnitude of these challenges, there are opportunities to overcome them by further exploring innovative techniques that alleviate salt- and plant-water stresses (Abou-Baker and Ei-Dardiry, 2016). One such potential option is the use of amendments such as the addition of either pumice or biochar to soils. Potentially these can contribute to improving the physical, chemical and biological properties of salt-affected soils, while promoting better plant growth (Gur et al., 1997; Saifullah et al., 2018). However, a deeper knowledge of the influence of the physical properties of the amendments is needed, as well as that of the impact of their particle size and application rate on soil-water retention so that their value in ameliorating soil salinity is better understood.

Both materials have in common the fact that they are very porous. For biochar, this is particularly the case when produced from woody material (Waldron, 2014). Pumice is characterised by having a porosity (64–85% by volume) that was generated by air bubbles created during its formation, which give this material a low bulk density (0.35–0.65 g cm^{-3}), and large pore-size span (from micrometre to millimetre) (Ersoy et al., 2010; Cekova et al., 2013). The physical properties of biochar mainly depend on the type of feedstock, which is influenced by the plant cellular structure, plus the type of pyrolyser, highest heating temperature and residence time of pyrolysis, and activating agents (Rasa et al., 2018). Biochar has been reported to have a bulk density ranging from 0.06 to 0.7 g cm^{-3}, with a specific surface area from 50 to 630 m^2 g^{-1} (Rajkovich et al., 2012), while its pore size distribution can vary greatly, ranging from sub-nanometre to hundreds of microns (Brewer et al., 2014). The physical properties of these amendments can directly or indirectly influence soil properties and plant growth.

Although the ability of pumice (Malekian et al., 2012) and biochar (Herath et al., 2013) to retain soil water has been reported, the mechanistic understanding of how their use affects water-borne salt transport in soils under arid conditions remains largely unclear (Noland et al., 1992; Lura et al., 2004; Batista et al., 2018). Given that this is strongly related to the influence of these materials on the soils mobile-immobile water fractions, in this study we aimed to evaluate how the physical properties of a pumice and a biochar, namely their particle size, and application rate affected their mobile-immobile water when added to a sandy soil. Our objectives were two-fold:

- We first characterised the porosity and pore-size distribution of a pumice from New Zealand's central North Island, and a biochar produced from willow wood chips at a highest heating temperature of 350 °C. We chose to use a low-temperature biochar to minimise the amount of ash, given that salts in the ash can contribute to soil salinity when applied to soils in arid environments.
- We then investigated the amount of mobile-water present in these amendments (previously added to a sandy soil at different rates and particle sizes) using a tracer (Na^+) during miscible displacement experiments.

4.2 Materials and Methods

4.2.1 Preparation of the experimental material

Pumice was taken from the Tongariro National Park New Zealand (39°12'36.5"S, 175°40'55.5"E), and was washed with deionised water, then dried at 30°C for 72 h to a constant weight prior to its use. The biochar was produced from weeping-willow chips (*Salix matsudana* L.) using a rotary kiln pyrolyser (25-L retort), at a heating rate of ca. 10 °C min^{-1} and a highest heating temperature of 350 °C, which was hold for 15 min. Both pumice and biochar were categorised into three different particle sizes (1.5-, 3-, and 6-cm Ø). The biochar was crushed before the particle size screening. Both materials were further milled to achieve a particle size < 0.3 mm for chemical analysis. The sandy soil (96.6% sand) for the miscible displacement experiment was obtained from the sand dunes at Himatangi Beach New Zealand (40°23'54.6"S, 175°13'33.8"E) and was air-dried before use. The mineralogy of the sandy soil was predominantly quartz and feldspar (Claridge, 1961). An artificial saline solution was prepared using Na_2SO_4, $CaCl_2$, NaCl and $MgSO_4$ salts at the following concentrations 0.285 g L^{-1}, 0.517 g L^{-1}, 2.865 g L^{-1}, and 0.924 g L^{-1}, respectively. The final solution had an electrical conductivity (EC) of 6.4 dS m^{-1} and a Na^+ concentration of 2300 mg L^{-1}. This is a moderate level of salinity typically found in the irrigation waters of the Middle East and North Africa (Hirich and Allah, 2018).

4.2.2 Scanning electron microscopy analysis

For measurements of porosity (pores > 300 nm Ø) and pore size distribution of pumice and biochar, samples were mounted on 0.5” aluminium specimen stubs equipped with SEMCarbon foils (Agar scientific, UK). The gold coating was applied to samples after air drying at 40 °C for 24 h. Micrographs were taken on a FEI Quanta 200 Environmental Scanning Electron Microscope (SEM; Quanta, Oregon, United States) at a magnification ranging from 60 to 260x, with an acceleration voltage of 20 kV. The digital micrographs processing and analysis were conducted with the software ImageJ Version 1.49s (National Institutes of Health, http://imagej.nih.gov/ij/) for porosity and pore size measurements. Pore sizes were functionally divided into four categories: the ultra-micropores (Ø < 3 μm), micropores (Ø of 3-30 μm), mesopores (Ø of 30-100 μm), and macropores (Ø > 100 μm) (Landis, 1990; Drzal et al., 1999). The macropores enable soil drainage and aeration, the mesopores contribute to soil-water conductivity, the micropores provide soil-water retention, with the water retained in ultra-micropores being unavailable for plant use (Landis, 1990; Drzal et al., 1999).

4.2.3 Miscible displacement analysis

4.2.3.1 Measurements of the pore volume of materials

The pore volume (PV) of the materials (Table 4–1) were estimated by immersing a known volume of the amendments (v_i) in water for 72 h and looking at the corresponding increases in weight (m_i). In this experiment, since the volume of the amendment only accounts for a small part of the total soil volume, we used the PV of sandy soil to represent the PV of the soil after amendment addition hereafter.

4.2.3.2 Measurement of the mobile-water fraction in pumice and biochar

The mobile-water fraction of pumice and biochar during near-saturated flow was determined following the tracer technique proposed by Clothier et al. (1992) with some modifications as detailed below, and in the Supplementary Information. Briefly, pumice and biochar of three particle sizes (1.5-, 3- and 6-cm Ø) were separately added to the sandy soil at three application rates (3, 6 and 12%, v/v basis). Thereafter, 1 L of mixed sandy soil and amendment (in triplicates) was added to a 2.3-L plastic container (16.5 x 15.5 x 9 cm^3) with free-water drainage at its bottom. Initial charging of the immobile fraction θ_{im} was achieved by first wetting the soil with 2 PV of deionised water until near-saturated conditions prevailed. The system was then rapidly rewet with an artificial saline solution containing a tracer (Na^+) at the C_m concentration of 2,300 mg L^{-1}. A total volume of 8 PV of saline solution was supplied to the soil. Subsequently the bottom 5-cm of soil was sampled. Pumice and biochar were completely separated from the sandy soil and then dried at 30°C for 72 h to a constant weight. Prior to chemical characterization, pumice and biochar particles, at the beginning and at the end of the experiment, were ground to a size < 0.25 mm and deionised water at a 1:5 w/v solid:water ratio was added and a subsample of the ground material was used after homogenisation. The suspension was then shaken on an end-to-end shaker for 2 h and stood overnight. Thereafter, it was filtered through a Whatman No.42 filter paper. The concentration of Na^+ in the water soluble-extract (referred to as C^* hereafter) was measured using a Microwave Plasma Atomic Emission Spectrometer (MP-AES). The ratio of the measured resident solute concentration C^* to applied solution concentration C_m, C^*/C_m, was the fraction of material's water that was effectively mobile. The concentration of Na^+ of pumice, biochar and the sandy soil at the beginning of the experiment are reported in Table 4–1, where it is shown that concentrations, on volume basis, were > 10 times smaller in the amendments than in the sandy soil. With this methodology, field irrigation was simulated using a burette as the wetting system through which the amount of water added to the soil and the rate of soil wetting could be accurately controlled.

Table 4-1 Pore volume and Na^+ concentration of pumice, biochar, and sandy soil. Values are mean ± S.D. of 3 replicates. Mean values with different letters indicate significant differences within the same material (Duncan's test, $p < 0.05$).

		Pore volume ($v\ v^{-1}$)	Na^+ ($mg\ cm^{-3}$)
Pumice	Pu-1.5	0.16 ± 0.02b	0.01 ± 0.01a
	Pu-3	0.19 ± 0.02a	0.01 ± 0.01a
	Pu-6	0.22 ± 0.01a	0.02 ± 0.01a
Biochar	Bi-1.5	0.35 ± 0.06a	0.03 ± 0.01a
	Bi-3	0.29 ± 0.04a	0.04 ± 0.01a
	Bi-6	0.31 ± 0.03a	0.04 ± 0.01a
Sandy soil	S	0.31 ± 0.03	0.50 ± 0.02

Pu-1.5, Pumice with 1.5-cm Ø; Pu-3, Pumice with 3-cm Ø; Pu-6, Pumice with 6-cm Ø; Bi-1.5, Biochar with 1.5-cm Ø; Bi-3, Biochar with 3-cm Ø; Bi-6, Biochar with 6-cm Ø; S, Sandy soil.

4.2.4 Data processing and statistical analysis

Data processing was performed with Microsoft Excel 2019. Statistical analyses were carried out using the SPSS version 14.0 software package (IBM, Armonk, New York, USA) and Graph pad prism 8 software. A one-way ANOVA with Duncan's test was used to detect significant differences (at $p < 0.05$) between the treatment means for parametric data (non-SEM data). The Kruskal-Wallis and Nemenyi tests were used to detect significant differences (at $p < 0.05$) between the treatment means for SEM data.

4.3 Results

4.3.1 Pore characteristics of pumice and biochar

Pumice exhibited a pore-size span ranging from 0.5 to 13,000 μm (Table 4–2). The maximum pore sizes observed under SEM followed the order of Pu-1.5 (5 mm) < Pu-3 (10 mm) < Pu-6 (13 mm). The pore-size span of biochar was smaller than that of the pumice and ranged from 0.3 to 651 μm (Table 4–2). The maximum pore size seen under SEM followed the order of Bi-1.5 (0.4 mm) < Bi-3 (0.5 mm) < Bi-6 (0.7 mm). There were no evident differences in the minimum pore sizes of either pumice, or biochar, between the three particle sizes. Significant differences ($p < 0.05$) in average pore-sizes of the pumice were only found between Pu-1.5 (492 μm) and Pu-6 (1,844 μm) (Table 4–2). For biochar, no significant differences in the average pore sizes were detected between the three particle sizes. The average pore size value under each particle size was always higher in pumice (range 492-1,844 μm) than in biochar (range 19-22 μm) (Table 4–2).

Table 4-2 Pore-size span and average pore size of pumice and biochar under three different particle sizes (1.5-, 3-, and 6 cm) based on the scanning electron microscope inspections. Where n is the number of pores. Data were analysed by Kruskal-Wallis and Nemenyi tests using the SPSS version 14.0 software package (IBM, Armonk, New York, USA) and expressed as mean ± S.D. Mean values with different letters indicate significant differences within the same material ($p < 0.05$).

		Pore-size span (μm)	Average pore size (μm)	n
Pumice	Pu-1.5	0.5 – 4,992	497.1 ± 144.2b	3,140
	Pu-3	1.7 – 9,625	1,004.1 ± 557.5ab	3,804
	Pu-6	0.8 – 13,308	1,843.9 ± 837.4a	3,340
Biochar	Bi-1.5	0.3 – 368	20.9 ± 13.9a	1,732
	Bi-3	0.3 – 453	18.5 ± 11.7a	2,069
	Bi-6	0.5 – 651	21.2 ± 12.6a	1,950

Pu-1.5, Pumice with 1.5-cm Ø; Pu-3, Pumice with 3-cm Ø; Pu-6, Pumice with 6-cm Ø; Bi-1.5, Biochar with 1.5-cm Ø; Bi-3, Biochar with 3-cm Ø; Bi-6, Biochar with 6-cm Ø.

In the pumice, the mean relative proportion of pores in each pore-size group out of the total pore volume followed the order ultra-micropore > micropore > mesopore > macropore, irrespective of the pumice particle size. All differences were significant at $p < 0.05$. In this material, the proportion of ultra-micropores plus micropores (87%) were more than six-fold that of the mesopores plus macropores

(13%), reflecting that pumice mainly consists of pores < 30 µm (Figure 4–1a). Similar patterns of pore-size distribution were observed for biochar, but the mean relative proportion of ultra-micropores plus micropores (95%) was significantly greater ($p < 0.05$) than those of pumice (87%). The relative proportion of micropores, which are those responsible for the retention of plant-available water, was significantly smaller ($p < 0.05$) in biochar (31%) than in pumice (41%), irrespective of their particle size. The relative proportion of mesopores plus macropores in pumice increased from Pu-1.5 (8%) to Pu-3 (12%) to Pu-6 (19%). All differences were significant at $p < 0.05$. There was no particle size effect in the pore-size distribution of biochar (Figure 4–1a & 4–1b).

Values of total SEM porosity in pumice were found to be significantly smaller ($p < 0.05$) in Pu-6 (58.5%) than in Pu-1.5 (65.6%). Differences in the absolute porosity, namely the volume of pores out of total volume of amendment, in the different pore size groups considered of the three pumice particle sizes were significantly different ($p < 0.05$). The highest values for both ultramicro- and micro-scale porosity were found in Pu-1.5 (32.7 and 27.2%), followed by Pu-3 (28.3 and 24.9%), and then Pu-6 (25.0 and 22.7%). An opposite pattern was observed in both meso- and macro-scale porosity with the lowest being under Pu-1.5 (3.5 and 2.1%), followed by Pu-3 (5.1 and 2.6%), and the highest in Pu-6 (6.4 and 4.5%) (Figure 4–1c).

For biochar, the absolute porosity in different pore size groups followed the order ultra- (44.2%) > micro- (20.7%) > meso- (1.8%), and > macro-scale porosity

(1.1%), irrespective of the biochar particle size. Absolute porosity in the different pore-size groups of biochar varied narrowly between the three particle sizes, with the most relevant difference found in the 3-cm biochar particle size, which had a significantly greater ($p < 0.05$) ultramicro-scale porosity than the 6-cm biochar. The opposite pattern was observed for micro-, meso-, and macro-scale porosity (Figure 4–1d).

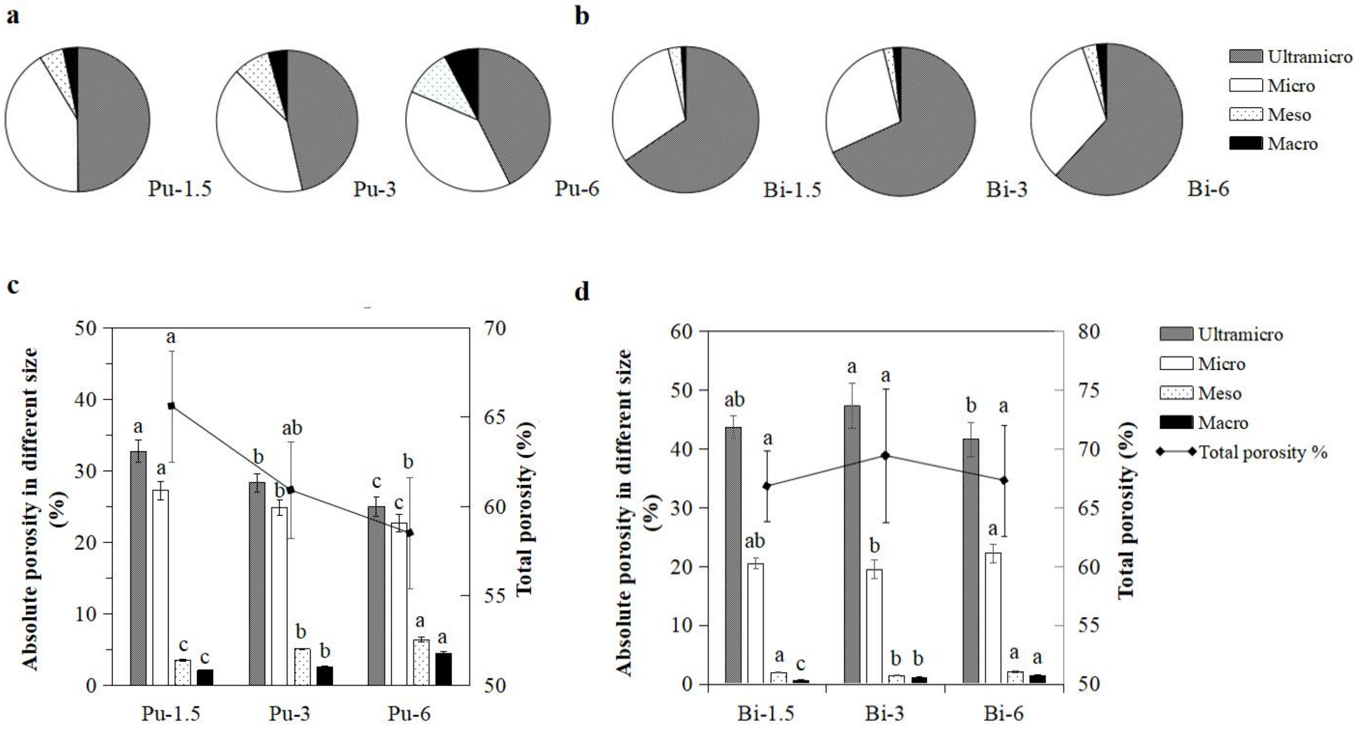

Figure 4-1 The mean relative proportion of pores in each pore size group out of total pore volume in (a) pumice and (b) biochar (n=6). Mean values of pumice pore parameters (absolute porosity for each pore size group out of total volume of the amendment and total porosity) in (c) pumice and (d) biochar (n=6). Ultramicropores represent vesicles with Ø smaller than 3 μm; micropores represent vesicles with Ø of

3-30 µm; mesopores represent vesicles with Ø of 30-100 µm; macropores represent vesicles with Ø larger than 100 µm. Pu-1.5, Pumice with 1.5-cm Ø; Pu-3, Pumice with 3-cm Ø; Pu-6, Pumice with 6-cm Ø; Bi-1.5, Biochar with 1.5-cm Ø; Bi-3, Biochar with 3-cm Ø; Bi-6, Biochar with 6-cm Ø. Data were analysed by Kruskal-Wallis and Nemenyi tests using the SPSS version 14.0 software package (IBM, Armonk, New York, USA). Different letters in the same colour block indicate significant differences between the treatments ($p < 0.05$).

4.3.2 Mobile-water fraction of pumice and biochar

The mobile-water fraction (θ_m) of the pumice and biochar amended sandy soil when subsequently leached was estimated based on the Na^+ concentration at the end of the experiment, relative to the amount added (C^*/C_m) (Figure 4–2). It should be noted that the amount of water-soluble Na^+ in the amendments before the experiment was < 0.05 mg cm^{-3}, and no significant differences between particle sizes were observed in either the pumice or the biochar (Table 4–1). When averaging C^*/C_m from the treatments grouped by pumice particle size, there was an increase in the mobile-water fraction (from 0.14 to 0.24) with increasing particle size of pumice. The differences between treatments were significant at $p < 0.05$, except between Pu-1.5 and Pu-3. When averaging the relative Na^+ concentration from the treatments grouped by the pumice application rate, no significant differences were observed between the three application rates.

With biochar, when averaging the relative Na^+ concentration from the different treatments grouped by biochar particle size, the mobile-water fraction showed a small decrease with an increasing particle size (from 0.085 to 0.080), and was only significant (p < 0.05) between Bi-1.5 and Bi-6 treatments. When averaging the relative Na^+ concentration from the treatments grouped by biochar application rate, no significant differences were detected between the three application rates (Figure 4–2).

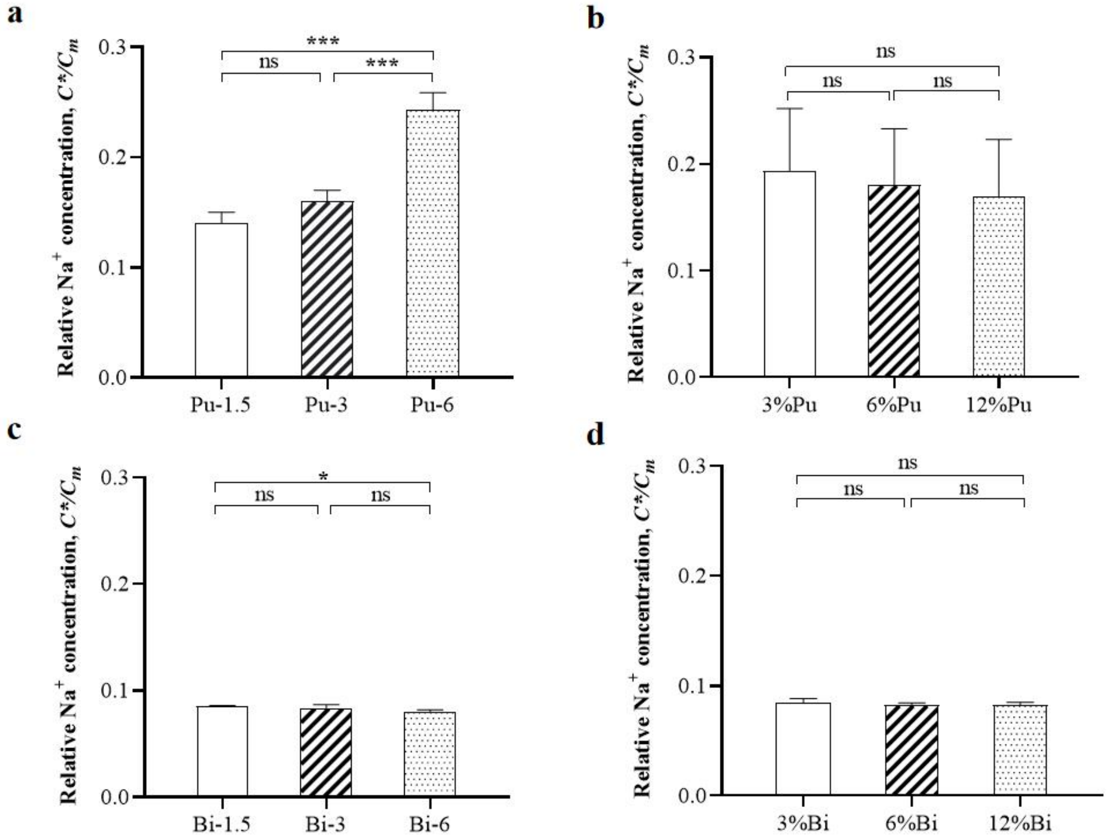

Figure 4-2 The relative Na^+ concentration of pumice and biochar at the end of the experiment. Bar charts showing: (a) when averaging the relative Na^+ from the treatments grouped by pumice particle size (1.5-, 3-, and 6-cm), (b) when averaging the relative Na^+ from the treatments grouped by pumice application rates (3%, 6%,

and 12%, v/v, basis), (c) when averaging the relative Na^+ from the treatments grouped by biochar particle size (1.5-, 3-, and 6-cm), (d) when averaging the relative Na^+ from the treatments grouped by biochar application rates (3%, 6%, and 12%, v/v, basis). Data were analysed by one-way ANOVA using Graph pad prism 8 software and expressed as mean ± S.D. * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. Differences were considered significant if $p < 0.05$.

4.4 Discussion

4.4.1 Pore characteristics of pumice and biochar

Porosity in terms of pore size and pore distribution greatly influence soil properties, particularly aeration, drainage, and water retention (Klug and Cashman, 1996). The wide pore-size range observed in the pumice under study is consistent with the observations of Ersoy et al. (2010) who were working with pumice (of particle size ranging between 0.5- and 4-cm Ø) from the Tatvan region of Turkey. This large variety of pore sizes is been attributed to the rapid release of pressure during volcanic eruptions, which leads to gas expansion and the formation of multiple bubbles (Whitham and Sparks, 1986). The elongation of micropores occurs due to the ductile elongation in the volcanic conduit (Figure 4–3a, 3b & 3c) or, in the case of pumiceous lavas during flow (Papadopoulos et al., 2008). Particle size of the pumice had an influence in the size of those pores, where the average pore size of Pu-6 (1.8

mm) was significantly higher than that of Pu-1.5 (0.5 mm). This is likely attributed to the differences in total volatile content of the magmas between the different particle size pumice. More volatiles and faster ascent results in more and larger vesicles (Mitchell et al., 2019). Our pumice samples were taken from the Tongariro National Park and originated from the 1994-1995 Mount Ruapehu eruption. This had a predominance of ultra-micropores (< 3 μm) and micropores (3-30 μm), under the three given particle sizes. This is probably associated to the rapid release of gas as a result of a large explosive force during the eruption (Pardo et al., 2012). These findings agree with a study of Lichtan et al. (2016), who found the SEM-observed peak in vesicle abundance at 25 μm in all pumice samples taken from the most recent eruption (1.8 ka) of the Taupo Volcano (New Zealand).

Total porosity of pumice, as estimated from segmented areas of pixels (ranging from 58.5 to 65.6%) was larger than that of estimated by Lichtan et al. (2016) using the mercury intrusion porosimetry method in pumice from the nearby region (Taupo 1.8 ka eruption) (ranging from 41.9 to 53.8%). The reason for this difference is probably the distinct geological formation conditions, as well as the different methods used for their measurement (Lubda et al., 2005; Ersoy et al., 2010).

The greater micro-scale porosity and the smaller macro-scale porosity in 1.5-cm Ø pumice is consistent with the results from the mobile-water fraction analyses. These showed that, compared to pumice of large particle sizes, smaller particle sized pumice had a smaller volume of mobile-water, due to its larger water holding porosity (microporosity) and larger hydraulic conductivity (Raviv et al., 2002) than the coarser pumice. On the other hand, pumice of large particle size (e.g., 6 cm) had a larger volume of air-filled porosity compared with the smaller particle sizes studied, and this may contribute to soil aeration (Raviv et al., 2002). Considering that pores > 100 μm drain easily, and those between 3 and 30 μm retain plant-available water (Landis, 1990), the pumice of all particle sizes under study could suit as amendment to enhance the permeability of clayey soils, as well as to improve the water holding capacity of sandy soils.

The larger relative proportion of pores able to retain plant-available water (41% vs 31%) of pumice at a similar total porosity than that of the specific biochar under study (Figure 4–1a & 4–1b) suggests that this pumice may perform better on improving plant-available water retention capacity, compared with this biochar produced from willow at a highest heating temperature of 350 °C. Additionally, it should be noted the properties of pumice and biochar differ in other aspects, such as the fact that biochar has been promoted as a technology to sequester carbon, for provision of nutrients, and as a liming material (Camps-Arbestain et al., 2015). Therefore, the selection of one material, or the other, should be based on the desired impact.

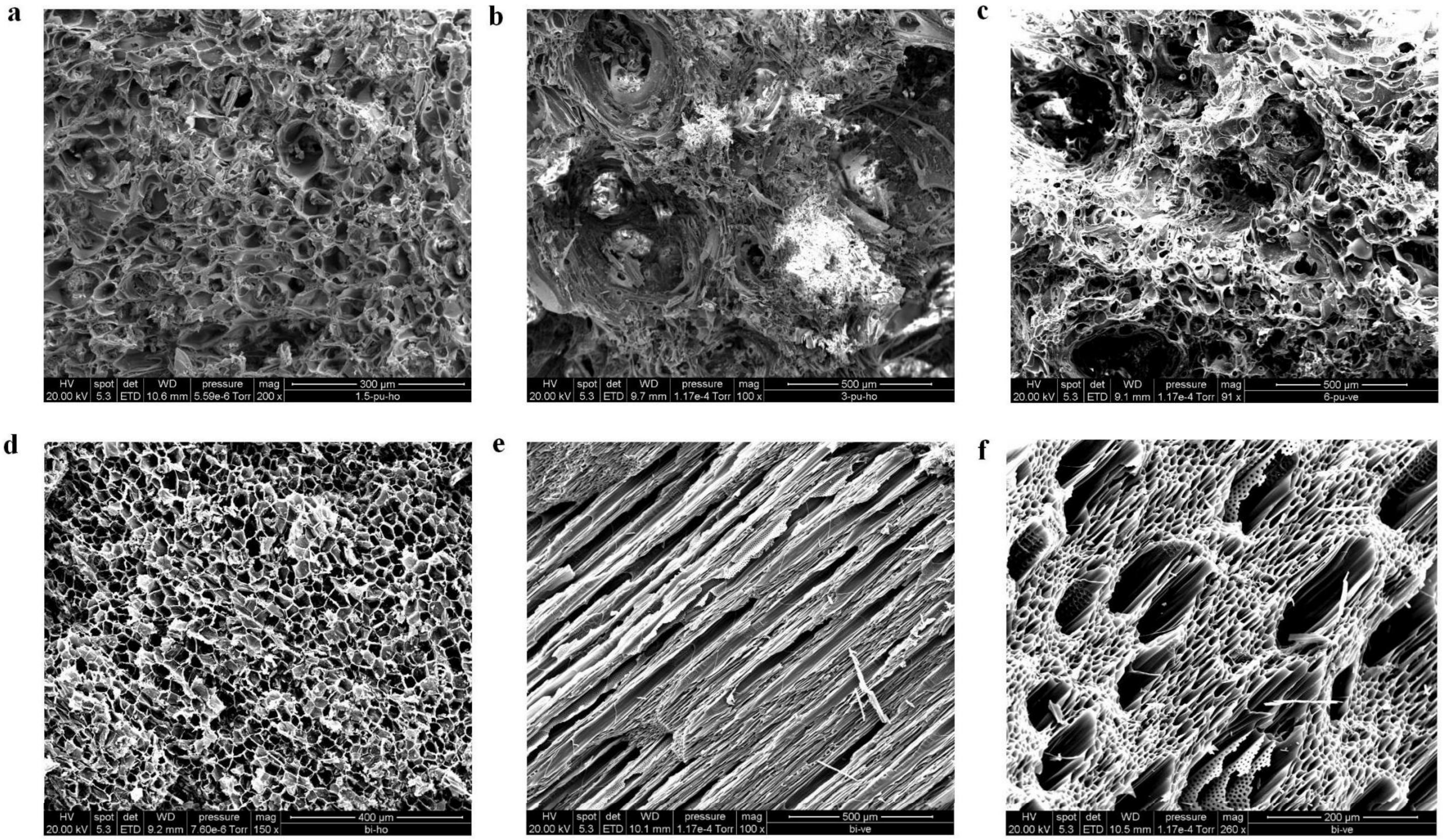

Figure 4-3 Representative SEM images of the studied pumice and biochar. Images showing: (a) pumice with 1.5-cm Ø, scale bar, 300 µm, (b) pumice with 3-cm Ø, scale bar, 500 µm, (c) pumice with 6-cm Ø, scale bar, 500 µm, (d) biochar with 1.5-cm Ø, scale bar, 400 µm, (e) biochar with 3-cm Ø, scale bar, 500 µm, (f) biochar with 6-cm Ø, scale bar, 200 µm.

4.4.2 Mobile-water fraction of pumice and biochar

The mobile-water fraction study supports the pattern that is commonly observed in pumice- and biochar-amended soils, with a larger soil moisture content where these amendments have been applied, as compared with the un-amended soils (Malekian et al., 2012; Downie et al., 2009; Burrell et al., 2016). This characteristic has commonly been attributed to the porous nature of these materials and, in particular, to their small 'mean' pore size (Clothier et al., 1995; Sahin et al., 2005). In fact, in this study, the fraction of immobile-water of pumice was nearly four-fold that of mobile-water (0.82 vs 0.18), and this ratio was eleven-fold in biochar (0.92 vs 0.08). A higher mobile-water fraction in a larger particle sized pumice agrees with its larger proportion of macro-scale and meso-scale porosity. Thus, the application of these two materials could contribute to alleviate salt- and plant-water stress by retaining more water and diluting salt concentration in the soil solution under arid conditions, when a biochar with a small ash fraction is used.

The fact that there were no obvious differences in the mobile-water fraction between the three particle sizes biochar under study could be explained by the fact that the three particle-size biochars originated from the same biochar, which was crushed before the particle screening, and the overall small contribution of biochar to the water mobility. Furthermore, in a previous study carried out with the same pumice and biochar (Kong et al., under review), accumulation of Na^+ within biochar was one fifth that of pumice (70 vs. 380 meq L^{-1}) reflecting the lower ability of biochar to retain Na^+. Here we only considered the effect of porosity and pore-size distribution on the mobile-water fraction of pumice and biochar. Other aspects such as the differences in pore morphology characteristics, such as the homogeneity of pores and pore sizes, and the connectivity of the pore structure (Ersoy et al., 2010; Sahin et al., 2005; Liu et al., 2017; Fauria et al., 2017) cannot be discarded. But these were not investigated in this study and so deserve further research.

4.5 Conclusions

The findings of our study have offered an insight into the relationship between the physical properties of the porosity and pore-size distribution of a pumice and a biochar and the fraction of mobile-immobile water present in these materials when added to a sandy soil. The results emphasise a predominance of pores with a Ø < 30 μm and relatively high total porosity under the three given particle sizes of both materials, which are expected to contribute to water retention when these amendments are used in sandy soil, and to the dilution of salinity in salt-affected sandy soils assuming a low ash biochar is used. The overall larger contribution of pumice to the water mobility than that of biochar under near-saturated conditions could be related to its relatively higher levels of macro-scale plus meso-scale porosity, and this increased as the pumice particle size increased. The knowledge generated in this study provides an enhanced understanding of the relationship between the pore characteristics and mobile-water fractions of pumice and biochar, and their implications for potential use in saline environments.

4.6 Acknowledgements

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Chapter 5

USE OF EITHER PUMICE OR WILLOW-BASED BIOCHAR AMENDMENTS TO DECREASE SOIL SALINITY UNDER ARID CONDITIONS

This chapter aims to evaluate the effects of pumice and biochar amendments on water retention and salinity of a sandy soil under simulated arid conditions.

A paper from this study will be submitted for publication: **Chao Kong**, Marta Camps-Arbestain, Brent Clothier, Peter Bishop, Felipe Macías Vázquez. Use of either pumice or willow-based biochar amendments to decrease soil salinity under arid conditions. *Environmental Technology and Innovation* (under review).

Abstract

In order to alleviate salt- and water-stress in plants, innovative and economically-feasible techniques are needed. In this study, pumice and biochar (made from willow at 350 °C) of different particle sizes (1.5-, 3-, and 6-cm Ø) were separately added at different rates (3, 6, and 12%, v/v basis) to a sandy soil and their effects on soil salinity and water retention were evaluated over time. Soils were drip irrigated with an artificial saline water under non-draining conditions. Pebbles applied at identical rates and sizes as pumice and biochar, were used as positive controls, whereas no amendment was the negative control. Treatments underwent 10 wetting and drying cycles at 35 °C at the end of which, the residual sandy soil (RS) was separated from the amendments. The electrical conductivity (EC) of RS followed the order pumice < biochar < positive control = negative control, with differences being significant at $p < 0.05$. The smallest EC and sodium adsorption ratio (SAR) values of the RS were achieved when applying 12% pumice, regardless of the particle size; the opposite pattern (12% > 6% > 3%) was observed in the pumice when analysed separately from RS. Pumice and biochar treatments also retained more water in the soil after each drying cycle (significant at $p < 0.05$). At the end of the experiment, the EC values of the leachates indicated that salts retained in pumice were more slowly mobilised than those in the biochar. The application of either pumice or biochar (made from willow at 350 °C) can contribute to decrease soil salinity, but pumice could

additionally serve as a tool to remove salts from salt-affected soils.

Key words

Salinity stress; Plant-water stress; Arid condition; Pumice; Biochar

5.1 Introduction

A key challenge for agriculture in arid ecosystems is the combined impact of soil salinity and water scarcity on crop production (Yamaguchi and Blumwald, 2005; Shahbaz and Ashraf, 2013). According to Hossain (2019), the total area of salt-affected soil is about 1,125 million ha. Increased soil degradation of arable land due to salt stress is expected to result in around 50% of land loss by 2050 (Wang and Altman, 2003). Salt stress impairs plant growth and development through either osmotic stress, which decreases water availability and photosynthetic activity (Finan and Guilak, 2010), or ionic stress, which causes nutrient deficiencies and specific-ion toxicities (Munns, 2005). Water scarcity stress causes a drop in plant-water potential and turgor, which further affects the plant's morphological and anatomical characteristics, along with root respiration rate, plant photosynthesis, and plant-mineral nutrition homeostasis (Salehi-Lisar and Bakhshayeshan-Agdamand, 2016). Salt and plant-water stress often occur concurrently in arid or semi-arid regions thereby exacerbating their impact on crops (Alexandre et al., 2013).

A variety of technologies and practices have been and are being used to manage and remediate salt-affected soils. These include scraping and removal of surface soil, land leveling, subsoiling and deep ploughing, mulching, application of organic or inorganic amendments, balanced fertilisation, application of biofertiliser, and salt phytoremediation, with artificial drainage, plus the application of a salt leaching fraction being a standard practice (Horneck et al., 2007). In fact, leaching is considered the most effective strategy to flush large amounts of water-soluble salts out of the root zone with the application of better-quality water (Saifullah et al., 2018). However, this is challenged by the scarcity of better-quality water in arid areas, although the use of blue and grey water in the saline and hyper-arid desert environments for the irrigation of tree species is becoming a success (Al-Muaini et al., 2019). The application of reclamation strategies is high cost, as is the use of furrow or mulching (Klocke et al., 2009; Devkota et al., 2015); usage of combinations of agrochemicals such as $CaCl_2{:}2H_2O$ and phosphate of gypsum, and organic solutions (Walker and Bernal, 2008; Singh et al., 2019). These are either still unavailable or unsuitable for many poor areas in the world. Hence, practical and economically feasible salt-reclamation methods are in great demand (Seenivasan et al., 2015). In this study, we investigate the potential use of either pumice or biochar as a tool to deal with soil salinity in arid environments.

Pumice is a light, porous siliceous rock that forms during volcanic eruptions (Whitham and Sparks, 1986). The high number of vesicles formed inside the rock structure provides pumice with a sponge-like appearance (Sarkar et al., 2017). Pumice is mainly composed of SiO_2 and Al_2O_3, has a low bulk density (0.35–0.65 g cm^{-3}), a high water retention capacity (20–30%, v/v) (Ersoy et al., 2010), and a skeleton structure that allows molecules and ions to travel into and reside within the framework (Yavuz et al., 2008). Due to its unique structure and chemical composition, pumice has been used for the removal of metal ions such as cadmium, cobalt, copper, and chromium (Yavuz et al., 2008; Abedi-Koupai et al., 2015), as well as the removal of phosphate ions from wastewater (Onar et al., 1996). However, there is still limited empirical evidence related to the application of pumice as a soil desalinisation material.

Biochar – a fine-grained and porous carbonaceous material – is obtained from the pyrolysis of various feedstocks under oxygen-limited conditions (Lehmann and Joseph, 2015). It has attracted considerable interest around the world for its potential to sequester carbon and improve other soil functions (Herath et al., 2013; Burrell et al., 2016). In general, biochar has been shown to have a pronounced effect on improving physical, chemical, and biological properties of salt-affected soils (Atkinson et al., 2010; Sohi et al., 2010; Lashari et al., 2015; Chaganti and Crohn, 2015; Ali et al., 2017; Ajayi and Rainer, 2017). Many studies have demonstrated a reduction in soil EC and salinity stress with biochar amendments (Tomas et al., 2013; Hammer et al., 2015; Yue et al., 2016). However, some studies have found an increase in soil salinity and/or sodicity with biochar addition at high application rates (> 30 t ha^{-1}) (Song and Guo, 2012; Fernandes et al., 2018). These specific studies highlight the need for a careful selection of the biochar feedstock with low ash content, low Na content to alleviate successfully salt and water-stress to plants. Our objective was to evaluate the effects of pumice and willow-based biochar amendments on water retention and salinity of a sandy soil under simulated arid conditions. The results of this study might also help justify whether individual, or combined additions, of either pumice and/or algae to a sandy soil could alleviate the impact of irrigation with saline water on the growth of lucerne (*Medicago sativa* L., Kaituna superstrike) under a simulated arid environment.

5.2 Materials and Methods

5.2.1 Preparation of the materials

The sandy soil (96.6% sand) for this study was taken from the sand dunes at Himatangi Beach, Manawatu, New Zealand (40°23'54.6"S, 175°13'33.8"E) and was air-dried before use. Pumice was obtained from the Tongariro National Park, Manawatu-Wanganui, New Zealand (39°12'36.5"S, 175°40'55.5"E), and was washed several times with deionised water prior to its use, then dried at 30°C for 72 h to a constant weight. The biochar was produced from weeping willow chips (*Salix matsudana* L.), taken from trees growing in the Manawatu, New Zealand (40°23'14.1"S, 175°36'23.2"E). The biochar was produced from weeping-willow chips *(Salix matsudana* L.) using a rotary kiln pyrolyser (25-L retort), at heating rate ca. 10 °C min^{-1} and a highest heating temperature of 350 °C, which was hold for 15 min. Both pumice and biochar were categorised into three different particle sizes (1.5-, 3-, and 6-cm Ø). The biochar was crushed before the particle size screening. Both materials were further milled to achieve a particle size < 0.3 mm for the chemical analyses described in section 2.3. Three different particle size pebbles (1.5-, 3- and 6-cm Ø) were collected from a low terrace of the Manawatu River, Palmerston North, New Zealand (40°22'36.6"S, 175°38'12.6"E), washed with deionised water, and then dried at 30°C for 72 h to a constant weight before use. An artificial saline irrigation solution was prepared using Na_2SO_4, $CaCl_2$, NaCl and $MgSO_4$ salts at the following concentrations 0.285 g L^{-1}, 0.517 g L^{-1}, 2.865 g L^{-1}, and 0.924 g L^{-1}, respectively. The final electrical conductivity (EC) and pH of the solution was 6.4 dS m^{-1} and 7.4, respectively. This is a moderate level of salinity typically found in the Middle East and North African regions (Hirich and Allah, 2018).

5.2.2 Measurement of the bulk density, and pore volume of the materials

The apparent bulk density (m_i/v_i) of pumice, biochar and pebble (Table 5–1) was determined by adding different amounts of known dry mass (m_i) to the sandy soil and measuring the corresponding increases in volumes (v_i). The pore volume, referred to as PV hereafter, of the materials were measured by immersing them in water for 72 h and looking at their corresponding increases in weight.

Table 5-1 Chemical and physical properties of pumice, biochar, pebbles and sandy soil

	Pu	Bi	Pe	S
Na^+ (mg L^{-1})*	12	40	10	500
Ca^{2+} (mg L^{-1})	30	100	12	20
Mg^{2+} (mg L^{-1})	13	52	17	20
K^+ (mg L^{-1})	10	30	13	40
Cl^- (mg L^{-1})	50	10	20	680
SO_4^{2-} (mg L^{-1})	10	9	10	20
PO_4^{3-} (mg L^{-1})	50	60	30	40
NO_3^- (mg L^{-1})	30	17	40	30
HCO_3^- (mg L^{-1})	40	90	40	20
$pH_{1:2.5}$	7.12	8.21	6.93	6.76
EC (µS cm^{-1})	126	175	16	41
CEC (cmol (+) kg^{-1})	0.16	26.42	–	–
Surface charge (mV)	-10.39	-35.68	–	–
Apparent density (g cm^{-3})	0.67	0.24	2.38	1.40
Pore volume (v v^{-1}, cm^3)	0.19	0.32	0	0.31

* The concentration of ions was measured in a 1:5 w/v extract. Values are mean of three replicates. S, sandy soil; Pu, pumice; Bi, biochar; Pe, pebbles; EC, electrical conductivity; CEC, cation exchange capacity; —, no data.

5.2.3 Characterisation of the materials used

The characteristics of the materials used are listed in Table 5–1. Concentrations of water-soluble cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were measured by Microwave Plasma Atomic Emission Spectrometer (4200MP-AES, AGILENT, USA) after water extraction at a 1:5 w/v solid:water ratio. The concentration of Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- in the same extracts was measured using the Ion Chromatography (IC5000, LACHAT, USA) and that of HCO_3^- using an Automatic Potentiometric Titrator (AT-700, KEM, JPN). The pH was measured in 1:2.5 w/v solid:water ratio suspension. The electrical conductivity (EC) was determined using a conductivity electrode in a 1:5 w/v solid:water ratio suspension. The cation exchange capacity (CEC) of pumice and biochar were determined by 1 M ammonium acetate (pH = 7) (Rayment and Lyons, 2011). The surface charge of pumice was carried out using the ZetaSizer 3000 (Malvern Instrument Co., Ltd. UK) and determined following the method of Ontiveros-Ortega et al. (2014) with some modifications as follows. The ground material was conditioned for 24 h in 500 mL of the aqueous solution containing 1 mM NaCl electrolyte. The surface charge of biochar was carried out following the method of Hong et al. (2019) using a Zeta potential analyser (Malvern

Instrument Co., Ltd. UK).

5.2.4 Experimental procedure

The wetting and drying experiment was carried out in the Plant Growth Unit of Massey University, Palmerston North, New Zealand. The three different ingredients (pumice, biochar, and pebble) of the three particle sizes (1.5-, 3- and 6-cm Ø) were separately added to the sandy soil at three application rates (3, 6 and 12%, v/v basis) in four replicates. Thereafter, 1 L of either the soil without amendment, or the soil + amendments was added to a 2.3-L plastic container (16.5 x 15.5 x 9 cm^3). The pebble treatment was considered the positive control, and the 100% sandy soil treatment with no amendment, the negative control. When referring specific treatments (e.g., 3%-Pu-1.5cm), these were identified as: S, sandy soil; Pu, pumice; B, biochar; Pe, pebble, with the application rate being a prefix and the particle size as a suffix.

Soils were drip irrigated with the artificial saline water. At cycle 1, the amount of irrigated water was 188 mL, which corresponds to the water-filled pore space (WFPS) of the sandy soil at saturation (40%, v/v). Thereafter, the average amount of water lost from all treatments at each cycle was added as irrigation water in the following cycle. Two hours after irrigation, the *in situ* EC was measured using a GroLine HI98331 soil EC tester (Hanna instruments, Romania). The soil was then placed in a Conviron CMP6050 incubation chamber at 35 °C for 8 h, removed from the chamber thereafter, and left to cool down to room temperature for 16 h until the next irrigation cycle. Prior to the next irrigation, the soil was weighed. This cycle was repeated for a total of 10 times.

5.2.5 Characterisation of the samples at the end of the experiment

5.2.5.1. Chemical characterisation

In three out of the four replicates used, the amendments were completely separated from the sandy soil and characterized separately. Measurements of the EC and main soluble ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^- and HCO_3^-) in the water extracts (1:5 w/v ratio) of the amendments after their removal from the sandy soil and without grinding, plus that of the residual sandy soil were separately carried out using the same methods as described above for the materials. The sodium adsorption ratio (SAR) was calculated thereafter.

To evaluate the potential precipitation of secondary minerals, saturation indices were calculated based on the chemical characterisation of the water extracts from the pumice and biochar amendments using the geochemical equilibrium Visual MINTEQ, version 3.1 (Cid et al., 2018) after correcting the ionic concentration to water content in the amendments at the end of the 10 wetting and drying cycles. This was measured after drying the amendments in an oven at 105 °C for 72 h to a constant weight.

5.2.5.2. Miscible displacement

The fourth replicate of each treatment underwent a series of leaching events and changes in EC of the effluent were measured in order to evaluate the miscible displacement of dissolved salts occurring at each event. For this, increasing amounts of deionised water, sequentially 0.5, 0.5, 0.5, 0.5, 1, 1, and 1 PV of the sandy soil, were added to the treatments. The EC of the effluents after each leaching event was determined using a GroLine HI98331 EC tester (Hanna instruments, Romania). At the end of the leaching experiment, samples of pumice and biochar were separated from the sandy soil and then taken for Scanning Electron Microscopy (SEM) measurements.

5.2.6 Data processing and statistical analysis

Data processing was performed with Microsoft Excel 2019. Statistical analyses were carried out using the SPSS version 14.0 software package (IBM, Armonk, New York, USA). One-way ANOVA (Analysis of variance) was used to compare significance for differences between the treatment means, with a probability defined at 0.05.

5.3 Results

5.3.1 Water lost from the different treatments

The cumulative water lost (Figure 5–1; Supplementary Information – Figure S5–1) at the end of the wetting and drying cycles followed the order pumice < biochar < negative control < positive control, regardless of particle sizes and application rates, with these differences being generally significant at $p < 0.05$. When averaging water loss by application rates of each amendment, regardless of the particles size (Supplementary Information – Table S5–1), this tended to decrease as pumice- and biochar application rates increased. The opposite trend was observed with pebbles with differences being generally significant at $p < 0.05$ when comparing 3% and 12% application rates. When averaging water loss by particle sizes (Supplementary Information – Table S5–1), differences between treatments tended to attenuate. Compared with the negative control, the largest additional water retention (13.5 and 7.2%) was observed in pumice and biochar, respectively, when applied at 12% rate (and smallest particle size, with differences between these values and the rest of the treatments being significant at $p < 0.05$). The largest water loss (12%) was observed in pebbles when applied at 12% rate (at intermediate particle size), with differences between this value and the rest of the treatments being significant at $p < 0.05$) (Supplementary Information – Figure S5–1).

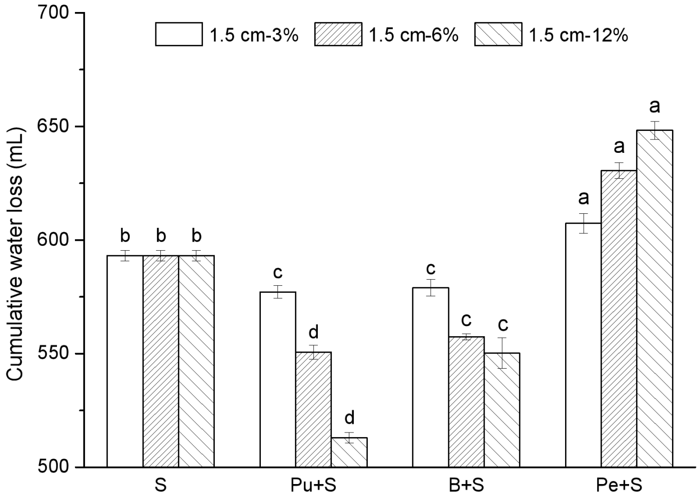

Figure 5-1 Cumulative water loss in sandy soil with, or without, amendment (pumice, biochar, and pebble) additions. Bar charts showing the amendments with 1.5 cm diameter. Values are means of four replicates. Error bars represent the standard error. Different letters in columns with similar filling pattern indicate significant difference between treatments according to Duncan's test ($p < 0.05$). S, sandy soil; Pu + S, pumice + sandy soil; B + S, biochar + sandy soil; Pe + S, pebble + sandy soil.

5.3.2 Changes of *in situ* EC over time

Significant differences ($p < 0.05$) in *in situ* EC measurements between treatments were already evidenced after cycle 2 (Figure 5–2; Supplementary Information – Figure S5–2), from which values followed the order of pumice < biochar < negative control = positive control, irrespective of either the particle size or the application rate, with differences between pumice-treatment and negative control, and between biochar-treatment and negative control at each specific application rate and particle size combination being significant at $p < 0.05$. By the end of the 10th irrigation, the presence of either pumice or biochar dropped the *in situ* EC by up to 26.2% and 20.9%, respectively (significant at $p < 0.05$), with maximum decreases compared with the non-amended soil corresponding to the 12%Pu-3 and 12%B-6 treatments (Supplementary Information – Figure S5–2).

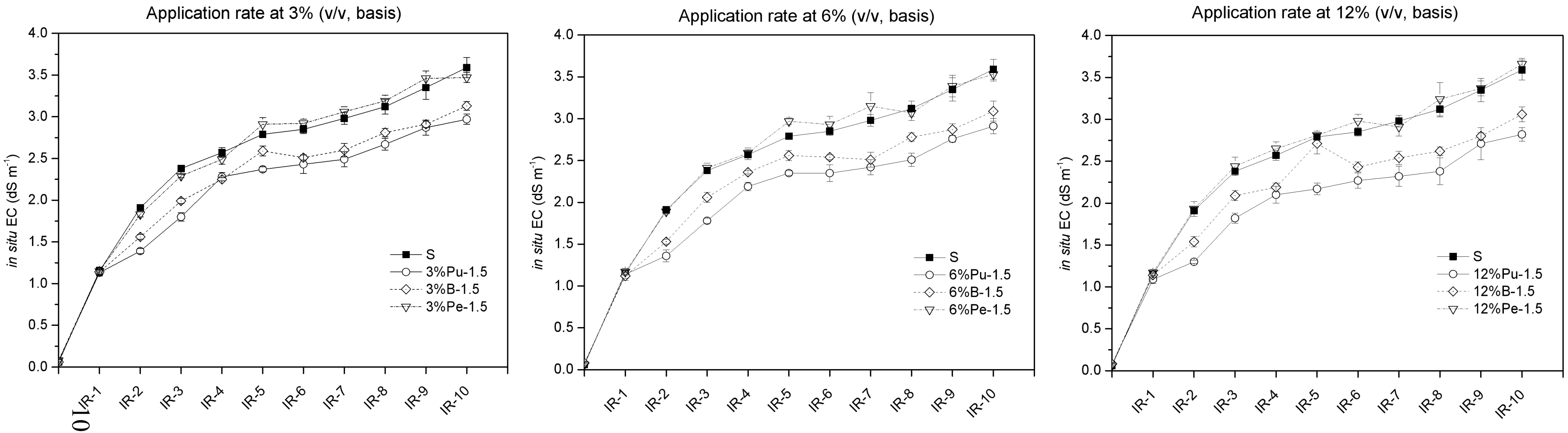

Figure 5-2 *In situ* EC in sandy soil with, or without, amendment (pumice, biochar, and pebble) additions after each cycle of irrigation. Line charts showing the amendments with 1.5-cm diameter. Values are means of four replicates. EC, electrical conductivity; S, sandy soil; Pu-1.5, pumice with 1.5-cm diameter; B-1.5, biochar with 1.5-cm diameter; Pe-1.5, pebble with 1.5-cm diameter.

5.3.3 EC values of the amendments after their removal at the end of the experiment and of the residual sandy soil

Remarkably, the EC values of the amendments after their removal from the mixtures (Figure 5–3a; Supplementary Information – Figure S5–3a & S5–3c) were clearly influenced by the type of amendment, regardless of their particle size, and followed the order of sandy soil = pebble < biochar < pumice, with differences between pumice and sandy soil, and between biochar and sandy soil being significant at $p < 0.05$.

In the residual sandy soil fraction (Figure 5–3b; Supplementary Information – Figure S5–3b & S5–3d), EC values were significantly ($p < 0.05$) smaller in the pumice-treated sandy soil than in the rest of the treatments, with the smallest value of 0.41 dS m^{-1} being observed in S-12%Pu-3 treatment. Values of EC followed the order of sandy soil-pumice < sandy soil-biochar = sandy soil-pebble = sandy soil, irrespective of either particle size or application rate, with differences being significant at $p < 0.05$ where indicated.

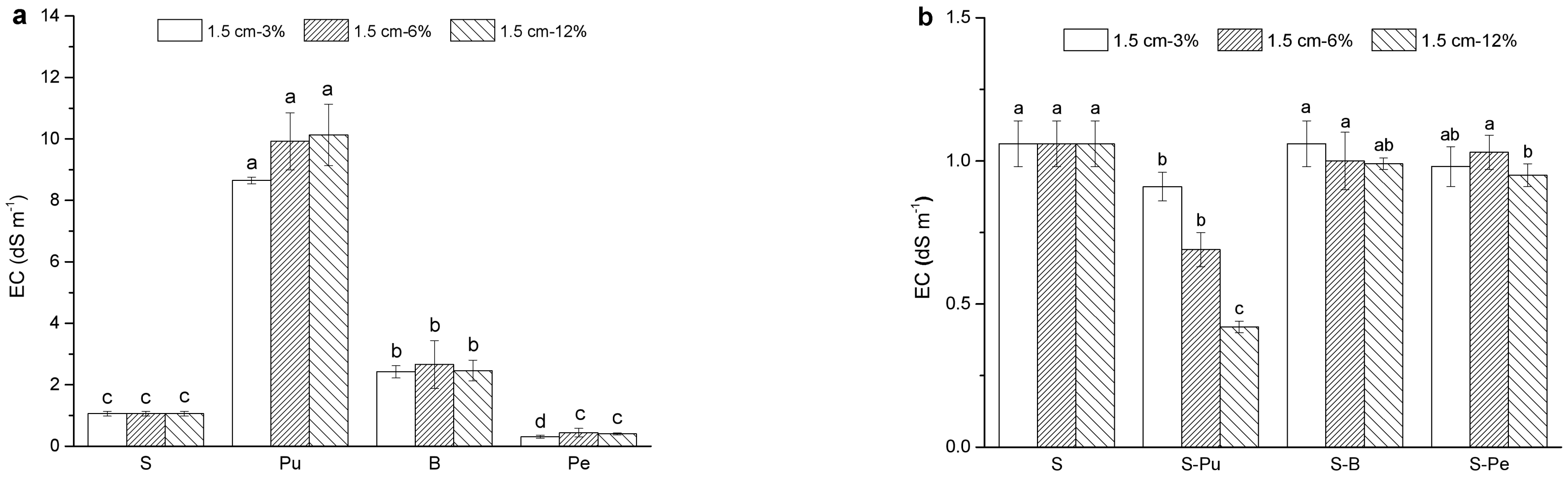

Figure 5-3 The electrical conductivity (EC) of the amendments and sandy soil after the experiment (1:5 w/v ratio). Bar charts showing: (a) the amendments with 1.5-cm diameter, (b) sandy soil treated by amendments with 1.5-cm diameter. Values are means of three replicates. Error bars represent the standard error. Different letters in columns with similar filling pattern indicate significant difference between treatments according to Duncan's test ($p < 0.05$). S, sandy soil; Pu, pumice; B, biochar; Pe, pebble; S-Pu, the residual sandy soil after the removal of pumice; S-B, the residual sandy soil after the removal of biochar; S-Pe, the residual sandy soil after the removal of pebble.

5.3.4 Chemistry of the amendments after their removal at the end of the experiment and of the residual sandy soil

5.3.4.1 Exchangeable ions and charge balance

The ionic concentration of water extracts from (i) the amendments after their removal from the mixture, and (ii) the residual sandy soil, varied widely between pumice, biochar and pebble amendments (Figure 5–4; Supplementary Information – Figure S5–4). When considering the water chemistry of the amendments, it was apparent that the largest accumulation of soluble salts occurred within pumice, whose total ionic concentration, on moles of charge basis, was up to four times that of biochar, and forty-fold that of pebble (Figure 5–4a; Supplementary Information – Figure S5–4c & S5–4e). Pumice had significantly greater ($p < 0.05$) concentrations of Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, and NO_3^- than biochar and pebbles. No significant differences in PO_4^{3-} and HCO_3^- concentrations were detected between the amendments (Figure 5–4a; Supplementary Information – Figure S5–4c & S5–4e).

In the residual sandy soil (Figure 5–4b; Supplementary Information – Figure S5–4d & S5–4f), the total ionic concentration in the pumice-treated sandy soil was 0.3-0.8 times smaller than that of the negative control. This effect was accentuated with increasing pumice application rate at all particle sizes considered, with the lowest value being found in S-12%Pu-6 treatment. The reduction in total ionic concentration found in the residual pumice-treated sandy soil was mostly caused by a decrease in Na^+, Ca^{2+}, and Mg^{2+}, with the charge balanced by a decrease in Cl^- (Figure 5–4b; Supplementary Information – Figure S5–4d & S5–4f). Overall, the concentrations of Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, and SO_4^{2-} were significantly smaller ($p < 0.05$) in pumice-treated sandy soil than in the negative control, with no significant changes in the concentrations of PO_4^{3-} and HCO_3^- being detected between these treatments (Figure 5–4b; Supplementary Information – Figure S5–4d & S5–4f). In the sandy soil treated with both biochar and pebbles, there were no significant differences ($p < 0.05$) in the ionic concentration of the remaining sandy soil compared with the negative control (Figure 5–4b; Supplementary Information – Figure S5–4d & S5–4f).

The charge deficit was always negative, both in the amendment and residual sandy soil fractions under all treatments (Figure 5–4; Supplementary Information – Figure S5–4).

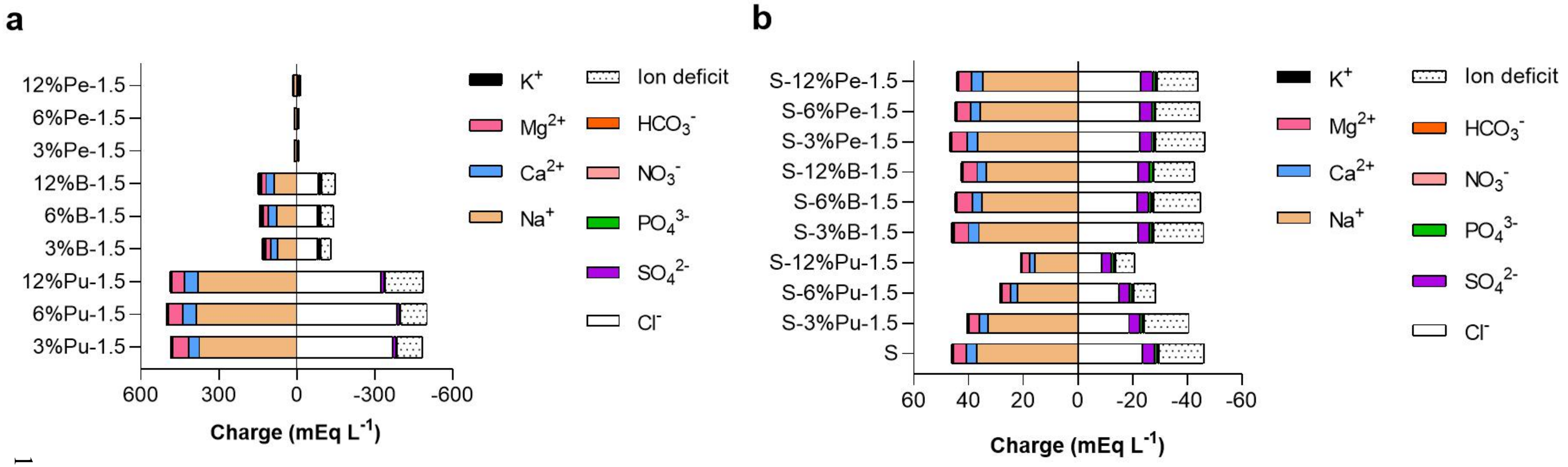

Figure 5-4 Charge balance (units in mEq L^{-1}) of the water extraction of (a) the amendments and (b) sandy soil after the experiment (1:5 w/v ratio). Values are means of three replicates. Pu-1.5, pumice with 1.5-cm diameter; B-1.5, biochar with 1.5-cm diameter; Pe-1.5, pebble with 1.5-cm diameter; S, sandy soil; S-Pu, the residual sandy soil after the removal of pumice; S-B, the residual sandy soil after the removal of biochar; S-Pe, the residual sandy soil after the removal of pebble.

5.3.4.2 Sodium adsorption ratio

The sodium adsorption ratio (SAR) of the pumice amendment after its removal from the mixture at the end of the experiment was 2.6-3.6 fold that of the negative control (Figure 5–5a; Supplementary Information – Figure S5–5c & 5–5e). This effect was more accentuated with increasing pumice application rates for the particles sizes of 3 and 6 cm, with the highest value being obtained in the 12%Pu-3 treatment. The residual sandy soil from the 12% pumice treatment (irrespective of the Ø) had the lowest SAR values (significant at $p < 0.05$), when compared with the negative control, indicating that the residual sandy soil was not relatively enriched in Na^+ over Ca^{2+} and Mg^{2+}. The largest reduction in SAR in the residual sandy soil was observed in the S-12%Pu-3 treatment, which exhibited a 2-fold reduction compared with the negative control (Figure 5–5b; Supplementary Information – Figure S5–5d & 5–5f). The application of biochar did not significantly ($p < 0.05$) influence SAR values of either the amendment, or the residual sandy soil when compared with the negative control, except for the S-12%B-1.5 treatment (Figure 5–5; Supplementary Information – Figure S5–5).

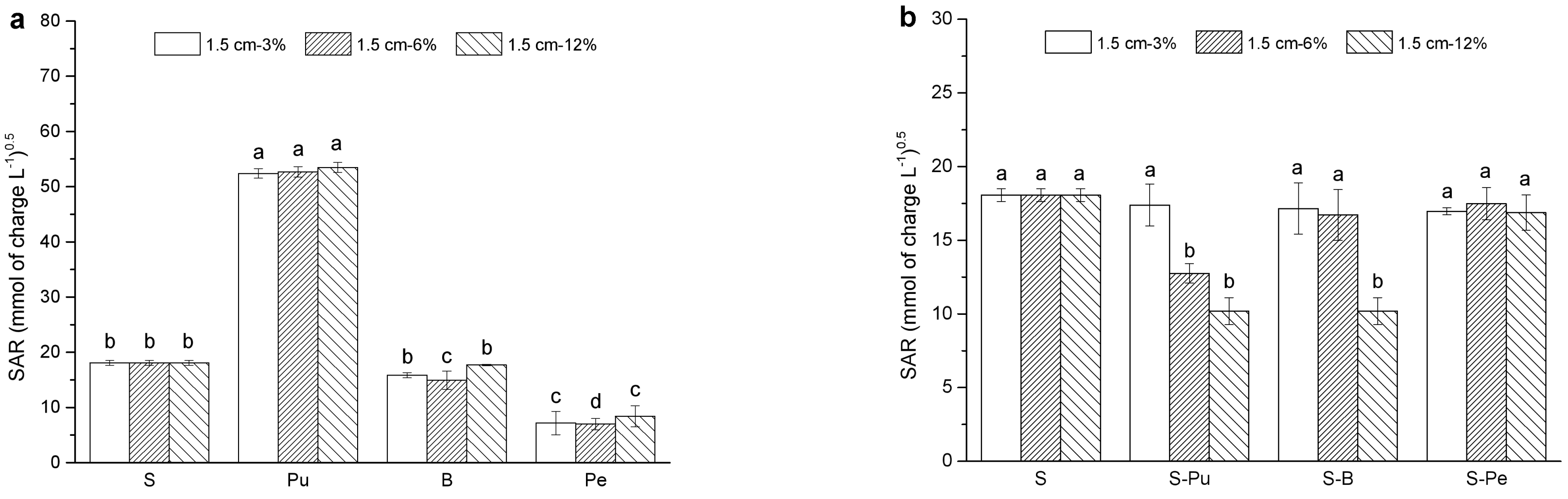

Figure 5-5 Sodium adsorption ratio (SAR) of the amendments and sandy soil after the experiment (1:5 w/v ratio). Bar charts showing: (a) the amendments with 1.5-cm diameter, (b) sandy soil treated by amendments with 1.5-cm diameter. Values are means of three replicates. Error bars represent the standard error. Different letters in columns with similar filling pattern indicate significant difference between treatments according to Duncan's test ($p < 0.05$). S, sandy soil; Pu, pumice; B, biochar; Pe, pebble; S-Pu, the residual sandy soil after the removal of pumice; S-B, the residual sandy soil after the removal of biochar; S-Pe, the residual sandy soil after the removal of pebble.

5.3.4.3. Visual MINTEQ modelling

Saturation indices (SI) for salts in biochar and pumice obtained from the geochemical software are provided in Table S5–2. Both amendments were saturated (SI > 0) with respect to phosphate salts such as $Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3{:}3H_2O(s)$, $CaHPO_4(s)$, $CaHPO_4{:}2H_2O(s)$, hydroxyapatite, and $MgHPO_4{:}3H_2O(s)$. But biochar had significantly greater ($p < 0.05$) SI values for these salts than pumice, irrespective of either the particle size or the application rate. Regarding the salts for which the solution was unsaturated (SI < 0), pumice had significantly greater ($p < 0.05$) SI values than biochar for anhydrite, epsomite, gypsum, halite, KCl(s), mirabilite and thenardite, irrespective of either the particle size or the application rate, with the opposite trend being observed with brucite, lime, $Mg(OH)_2$(active), $Mg_2(OH)_3Cl{:}4H_2O(s)$, and $Mg_3(PO_4)_2(s)$.

5.3.5 Miscible displacement of dissolved salts occurring at pumice-, biochar- and pebble-amended soil and unamended soil

The EC of the effluent after each PV addition was highest at the start of the leaching event (Figure 5–6; Supplementary Information – Figure S5–6), but the EC of the pumice treatments was 13.7 – 41.1% smaller than that rest of the treatments after only 0.5 PV. Thereafter, the EC decreased with increasing amounts of deionised water, this becoming close to that of the deionised water (< 0.3 dS m^{-1}) after 5 PV, with the exception of the pumice treatments, which ended with the highest EC value (up to 0.6 mS cm^{-1} under 12%-Pu-6).

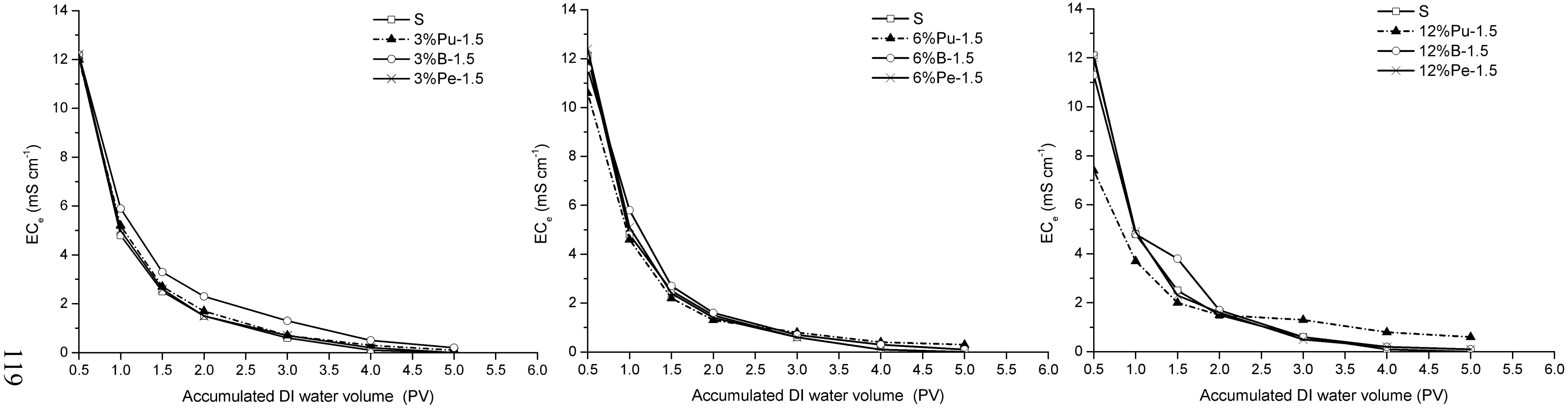

Figure 5-6 Graphical trend of electrical conductivity (EC) of the leachate to accumulated deionised water volume using pumice, biochar, and pebble as amendments. Line charts showing the amendments with 1.5-cm diameter. Here EC_e, electrical conductivity of the effluent; DI, deionized water; PV, pore volume; S, sandy soil; Pu-1.5, pumice with 1.5-cm diameter; B-1.5, biochar with 1.5-cm diameter; Pe-1.5, pebble with 1.5-cm diameter.

5.3.6 SEM images of pumice and biochar after leaching fraction

SEM images showed the horizontal and longitudinal section morphology of the pumice and biochar amendments after the leaching events at a magnification ranging from 100 to 220x (Figure 5–7). Salt precipitates were visible as shiny crusts and/or crystals at the surface of biochar and pumice. The salt precipitates on biochar surfaces and pore channels formed a flat and thin crust, whereas pumice presented smooth and regular films distributed in external flattened areas, and granular crystals distributed in the vesicles.

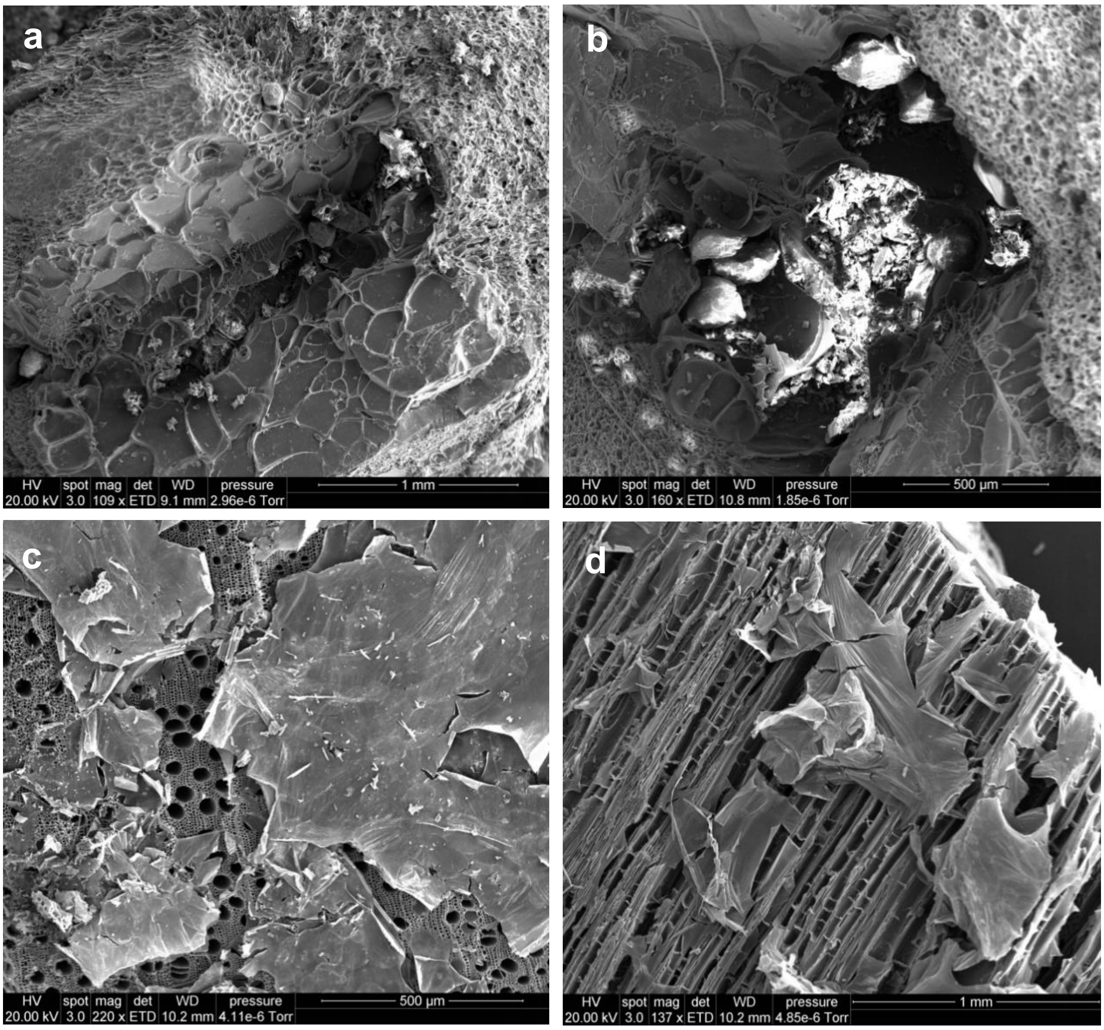

Figure 5-7 The Scanning Electron Microscopy (SEM) images of the pumice and biochar after the leaching events. Images showing: (a) horizontal section of pumice, (b) longitudinal section of pumice, (c) horizontal section of biochar, and (d) longitudinal section of biochar.

5.4 Discussion

5.4.1 Effects of pumice and biochar on water retention of salt-affected soils under arid conditions

The large water retention in both pumice- and biochar-treatments was attributed to well-known porosity of these two materials, and especially to their micro-scale porosity. As reported in a previous study from our team (Kong et al., under review), both materials exhibit a high total porosity (> 60%), and a predominance of pores with a Ø < 30 µm, reflecting the fact that both amendments can provide a micro-scale pore space to this sandy soil and contribute to its water retention, which is critical under arid conditions. The generally smaller (significant at $p < 0.05$) water loss under pumice than under biochar (regardless of either the application rate or particles size) was attributed to the greater micro-scale porosity (Ø of 3-30 µm) in pumice than that of biochar (24.9% vs. 20.7%, respectively) (Kong et al., under review). It should be noted though that, these authors also found that pumice had a large proportion of pores able to supply plant-available water than biochar (41% vs. 31%, respectively).

5.4.2 Effects of pumice and biochar on soil salinity under arid environments

The fact that pumice caused the largest decrease in the *in situ* EC of the sandy soil complex, and also the largest decrease in EC, SAR, and the concentration of Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, and SO_4^{2-} of the residual sand, namely an EC decrease by a maximum of 61%, compared with all other treatments, reflects the higher ability of this amendment in trapping ions therein, and thus in alleviating salt-stress in plants. The mechanisms through which this occurs can be several fold. Surface adsorption and ion exchange has been reported as being the driving forces for the removal of metal ions by pumice (Kraepiel et al., 1999; Panuccio et al. 2009; Sepher et al., 2013). But the CEC values of the pumice under study were small compared to that of biochar (Table 5–1), even when considering them on a volume basis (0.1 vs. 6.3 cmol (+) L^{-1}), as well as the pumice surface charge. Therefore, the chemical retention of ions at the surface of pumice could not explain the differences observed. Information provided by MINTEQ on the SI of the different salts (Supplementary Information – Table S5–2) indicates that in biochar there was a more predominant precipitation of phosphate salts than in pumice. Yet these were always in very small amounts, and this was attributed to the larger concentration of water-extractable Ca and Mg in the former (Table 5–1). Sodium salts (halite, thenardite, mirabilite) and also KCl were always undersaturated at the moisture conditions at the end of the wetting and drying cycles, but closer to saturation in pumice than in biochar, reflecting the ability of pumice to withdraw ions from highly soluble salts from soil solution. Yet chemical retention at pumice internal surfaces could not explain this behaviour of sodium and potassium salts. We hypothesise, based on the observations found by Doak (1972) working with pumice, that drying could induce salt trapping by the breaking of the hydraulic connections within the water column, thereby induced by the formation of entrapped air blocks in the pumice cavities during desiccation. Confined environments within pumice cavities may favour supersaturation conditions, as described by Adamo et al. (2001) for spheroidal halloysite. In the presence of saline water, the presence of salt crusts (as observed by SEM images; Figure 5–7) may further also impede the entrance of water (Kong et al., under review). These would result in a significant volume of immobile solution (deionised water/saline water), becoming more concentrated in the centre of pumice particles with respect to soluble salts and water than the outside solution (Doak, 1972).

The decrease in the *in situ* EC and EC in biochar-treated sandy soils compared with the unamended sandy soils was likely attributed to the adsorption of cations on the biochar surfaces − considering that biochar had relatively high surface charge (-35.68 mV) and cation exchange capacity (6.3 cmol (+) L^{-1}) (Table 5–1). Also some precipitation of phosphate salts was detected (Supplementary Information –Table S5–2), although these were in very small amounts. Additionally, physical entrapment of salts in the macro- and meso-pores of biochar (Akhtar et al., 2015a; Akhtar et al., 2015b), and biochar-induced enhancement in soil water retention capacity, resulting in dilution effect on the concentration of salt ions should not be disregarded.

5.4.3 Miscible displacement and scanning electron micrographs

During the miscible displacement experiment, the lower initial EC of the leachates under pumice-treatments was likely attributed to the presence of air bubbles that were trapped by imbibition and the filling of pores through capillary forces, impeding the access of water into pores in which salts had accumulated, along with salt crusts impeding the entrance of water (Finstad et al., 2016; Kong et al., under review) despite the high negative osmotic potential therein leading to a slow solute equilibration process (Doak, 1972). The generally greater final EC value of the leachates after applying 5 PV water under pumice-treated sandy soils than without its presence, as well as the smaller and slower drop in EC values of leachates under pumice-treatments (93.5% drop) compared to the rest of the treatments (98.3% drop) during the leaching process, reflects slower mobilisation of the larger amount of salts retained in the pumice compared with the other materials.

5.5 Conclusions

Pumice (from the 1994–1995 Ruapehu eruption, New Zealand) has shown to be a promising amendment to alleviate salt- and water-stresses under arid conditions. The slower salt mobilization process with pumice-treated sandy soils compared with the other treatments tested during the miscible displacement experiment corroborates its strong salt-trapping capacity. Additional advantages of applying pumice to salt-affected soils, as already pointed out by other authors (Noland et al., 1992; Sahin et al., 2005; Malakootian et al., 2011; Wang et al., 2013) include: i) a promising low cost; ii) easily available, especially if needed in an area close to a volcanic region; iii) reusable; and iv) inorganic. It can be regarded as a "green material". We therefore propose the application of pumice of large particle size to salt-affected soils in arid and semi-arid regions. Its removal once saturated with salts, using technologies already available, such as those used to harvest tubers, is a promising tool that deserves further attention. Our results also pave the way for further research on the effects of pumice application on the growth of lucerne (irrigation with saline water) under a simulated arid environment.

5.6 Acknowledgements

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Chapter 6

RECLAMATION OF SALT-AFFECTED SOILS USING PUMICE AND ALGAL AMENDMENTS: IMPACTS ON SOIL SALINITY AND THE GROWTH OF LUCERNE

This chapter aims to investigate whether individual, or combined additions, of either pumice (PU) and/or algae (AL) to a sandy soil could alleviate the impact of irrigation with saline water on the growth of lucerne (*Medicago sativa* L., Kaituna superstrike) under a simulated arid environment.

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Abstract

We investigated whether individual or combined additions of either pumice (PU) and/or algae (AL) to a sandy soil could alleviate the impact of irrigation with saline water on the growth of lucerne (*Medicago sativa* L.) under simulated semi-arid conditions. The study included six treatments that received saline water (6.4 dS m^{-1}): T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL) A seventh treatment was T7 (sand – negative control), to which deionised water was added. All treatments underwent 14 cycles of irrigation wetting and drying events (at 27 ± 1 °C/ 16 ± 1 °C day/night). At the end of the experiment and compared with the positive control (T1) (EC: 2.3 dS m^{-1}; SAR: 21.8 meq L^{-1}), the two treatments with the largest application rate of PU (T5 and T3) showed the largest (significant at $p < 0.05$) reduction in soil EC, SAR, and water-extractable ions among those treatments receiving saline water (T1-T6). Lucerne in treatments T1-T6 always had a smaller ($p < 0.05$) biomass, leaf DM content, and relative growth rate than the treatment receiving deionised water (T7) (DW: 2.29 g m^{-2}), but values for treatment T5 (DW: 1.69 g m^{-2}) were significantly larger ($p < 0.05$) than for treatments T1-T4 and T6 (DW < 1.13 g m^{-2}). Overall, the results obtained suggest that, if proven feasible at a field scale, the combined addition of PU (12%), by reducing salinity and contributing to water retention, and AL (2%), by adding nutrients and/or bioactive compounds, could

be used to mitigate salt stress and improve plant growth in sandy soils under arid conditions.

Key words

Lucerne; Saline water; Irrigation; Pumice; Algae

6.1 Introduction

In arid and semi-arid ecosystems, freshwater resources are becoming increasingly scarce and their use for urban water and food security is being prioritized. As a result, the use of low-quality water such as saline groundwater for land irrigation and potable supply, is receiving increasing attention (Beltrán, 1999; Li et al., 2015). However, the utilization of saline water with an insufficient leaching fraction can cause the build-up of soluble salts in the soil over time, as the low rainfall of these ecosystems has limited ability to remove them out from the root zone (Cui et al., 2010; Mavi et al., 2012). This causes osmotic and ionic stress to plants (Munns, 2002; Munns, 2005; Finan and Guilak, 2010), as well as nutritional imbalances (Hesami et al., 2020), which ultimately result in the reduction of crop yield (Khanam et al., 2018).

Saline-water irrigation can also cause soil crusting, due to the accumulation and precipitation of soluble salts at the soil surface (Rietz and Haynes, 2003). If the ratio of Na^+ to Ca^{2+} and Mg^{2+} increases, this favours soil particle dispersion and/or swelling, which causes a reduction in soil permeability, soil porosity, and soil hydraulic conductivity (Srivastava et al., 2014). In addition to these physical impacts, an increase in soil salinity impairs soil biological activity, with a decrease in soil respiration, enzyme activities, and microbial biomass (Rietz and Haynes, 2003; Wichern et al., 2006; Ghollarata and Raiesi, 2007).

The removal of soluble salts once added to a soil is difficult unless they are flushed out from the root zone by leaching with an excess of irrigation water (preferable of low salinity), which is challenging due to water scarcity in arid and semi-arid regions (Mahmoodabadi et al., 2013). The ability of pumice to retain water has been reported in previous studies (Noland et al. 1992; Lura et al., 2004; Kong et al., under review). However, none of these studies investigated its potential use to alleviate plant salinity stress. In a previous study from our group (Kong et al., under review) where different amendments were added to a sandy soil irrigated with saline water under simulated arid conditions, compared with the unamended control, the addition of 3-12% (v/v) of pumice (of 1.5-6 cm particle size) resulted in a reduction of soil EC (1:5 soil-water suspension) from > 1.3 dS m^{-1} to < 0.8 dS m^{-1}. Electronic microscope images showed the precipitation of salts at the surface of the pumice's skeleton framework, as already observed by Yavuz et al. (2008). Chemical characterisation pointed towards the accumulation of sodium salts as being dominant.

The authors, based on the study of Doak (1972), hypothesised that drying could induce salt trapping and sequestration through the breaking of the water connections induced by the formation of entrapped air in the pumice pores during desiccation.

Soils in arid and semi-arid environments have inherently low organic matter content – ranging from 0.1 to 3% (Matar et al., 1992), due to limited plant and microbiological growth (Scotti et al., 2015). This further challenges the ability of crops to cope with water stress, soil salinity and nutrient imbalances (Leogrande and Vitti, 2019). Numerous studies have reported several benefits of the application of algal residues as a source of organic matter and nutrients on plant growth and performance, including early seed germination, improved crop yield, and elevated resistance to biotic and abiotic stress (Eyras et al., 1998; Eyras et al., 2008; Khan et al., 2009; Saadaoui et al., 2019). Algal residues have been proven to lower EC due to the provision of cation exchange sites and they can decrease SAR by the displacement of Na^+ by other cations added with these residues (El-Shakweer et al., 2008).

Our objective in this study was to investigate whether individual, or combined additions, of either pumice (PU) and/or algae (AL) to a sandy soil could alleviate the impact of irrigation with saline water on the growth of lucerne (*Medicago sativa* L., Kaituna superstrike) under a simulated arid environment. Lucerne is moderately sensitive to salinity (Maas and Hoffman, 1977) and it is considered one of the most important legume forages in the world, being widely cultivated in dryland regions (Zhang et al., 2019). If proven suitable, these materials could be used in the formulation of low-cost Technosols aimed to be applied to areas under arid conditions where there is irrigation using saline water.

6.2 Materials and Methods

6.2.1 Source of sand, pumice and algae

A sandy soil (96.6% sand) was collected from the sand dunes of Himatangi Beach, Manawatu, New Zealand (40°23'54.6"S, 175°13'33.8"E) and air-dried before use. Pumice fragments (ca. 1.5-cm width) were collected from Tongariro National Park, Manawatu-Wanganui, New Zealand (39°12'36.5"S, 175°40'55.5"E). These were washed with deionised water to remove impurities, and then subsequently dried at 30 °C for 72 h to a constant weight. The algal residue was obtained from the Whanganui estuary, Manawatu-Wanganui, New Zealand (39°56'51.4"S, 174°58'52.2"E). Once in the laboratory, it was washed thoroughly with deionised water, and subsequently dried at 30 °C for 72 h to a constant weight prior to its use.

6.2.2 Measurement of the physicochemical properties of the materials used in the experiment

The concentrations of major elements in pumice and sand (the dried samples were crushed to pass through a 2-mm sieve and homogenized by mixing thoroughly) were measured by X-ray fluorescence, and their oxide concentrations (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, Na_2O, CaO, MgO, and K_2O) were subsequently calculated. Water-soluble cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) in the extracts obtained from the mixing of ground material (to < 0.25 mm) with deionised water (1:5 w/v solid:water ratio) were measured using an Agilent Technologies® 4200MP-AES microwave plasma atomic emission spectrophotometer (Agilent CrossLab, USA). The concentration of Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- in the same extracts was determined by an Ion Chromatography System (Dionex Aquion, USA), and that of HCO_3^- was measured using a TIM865 Automatic Potentiometric Acid-based Titrator (Radiometer Analytical SAS, France). The pH of the materials was measured in a 1:2.5 w/v solid to water ratio suspension. The electrical conductivity (EC) of the materials was measured in a 1:5 w/v solid to water ratio suspension. Total C and N concentrations in the algae were measured using a TruSpec CHNS analyser (LECO Corp. St. Joseph, MI). Total P concentration in the algae was determined using a Technicon Auto-Analyzer after Kjeldahl digestion (McKenzie and Wallace, 1954). The bulk density of the pumice (m_i/v_i) was determined by mixing sand with different amounts (of known mass; m_i) of pumice and measuring the corresponding increases in volume (v_i). The physicochemical properties of the materials are provided in Table 6–1.

Table 6-1 Chemical and physical properties of pumice, sand and algae before used for the experiment

	Pumice	Sand	Algae
SiO_2 (% wt)	72.2	80.4	_
Al_2O_3 (% wt)	12.9	7.6	_
TiO_2 (% wt)	0.1	_	_
Fe_2O_3 (% wt)	2.0	2.1	_
Na_2O (% wt)	_	0.9	_
CaO (% wt)	0.9	2.6	_
MgO (% wt)	0.1	2.1	_
K_2O (% wt)	4.7	0.2	_
Na^+ (mg L^{-1})*	10	500	2170
Ca^{2+} (mg L^{-1})	30	20	190
Mg^{2+} (mg L^{-1})	10	20	330
K^+ (mg L^{-1})	10	40	1960
Cl^-(mg L^{-1})	50	680	2110
SO_4^{2-}(mg L^{-1})	10	20	760
PO_4^{3-} (mg L^{-1})	50	40	1370
NO_3^-(mg L^{-1})	30	30	290
HCO_3^- (mg L^{-1})	40	20	130
pH	7.12	6.76	7.24
EC (µS cm^{-1})	126	41	527
Total C (mg g^{-1}dry algae)	_	_	374.2
Total N (mg g^{-1}dry algae)	_	_	50.2
Total P (mg g^{-1}dry algae)	_	_	0.11
Bulk density (g cm^{-3})	0.67	1.40	1.09

* The concentration of ions was measured in a 1:5 w/v extract.

6.2.3 Preparation of the saline irrigation water

An artificial saline irrigation water was prepared using Na_2SO_4, $CaCl_2$, NaCl and $MgSO_4$ salts at the following concentrations 0.285 g L^{-1}, 0.517 g L^{-1}, 2.865 g L^{-1}, and 0.924 g L^{-1}, respectively. The final solution had an electrical conductivity (EC) of 6.4 dS m^{-1}. This is a moderate level of salinity typically found in the irrigation waters of the Middle East and North African (Hirich and Allah, 2018).

6.2.4 Seed germination

Seeds of *Medicago sativa* L. (Kaituna superstrike) were obtained from PGG Wrightson Ltd, Feilding, New Zealand. Fifteen plastic pots of 2.25 L capacity with drainage holes were filled with 1 kg of potting mix (containing peat, bark, pumice, and 6 month-controlled release plant nutrients). Thirty lucerne seeds were sown in each pot, and then stored in a plant-growth room under controlled conditions (temperature 25 ± 1 °C; 16/8 h light/dark; average humidity 40%) for 30 d. The seeds were irrigated daily with tap water to keep the soil moist.

6.2.5 Preparation of the mixtures

The study included six treatments that received saline water: T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL). A seventh treatment, T7 (sand – negative control), had deionised water was added to it. For this, a total 2-L volume of either only sand or sand + amendments was added to 2.3 L pots (16.5 cm length, 15.5 cm width, 9 cm height) without drainage. Amendments were uniformly mixed with the sand. There were four replicates per treatment.

6.2.6 Experimental stages

At first trifoliate leaf stage (30 d after sowing), seedlings were removed from the trays, washed with deionised water, and transplanted to the pots at a density of 15 plants/pot. The soils of either the sand or sand + amendments were first wetted with deionised water until near-saturated conditions. The amount of water added to each pot was 376 mL, which corresponds to the sand water-filled pore volume at saturation (40%, v/v). The pots were then transferred to a plant growth chamber with light at each layer (temperature: 27 ± 1 °C/ 16 ± 1 °C day/night; 8/16 h light/dark; average humidity 45%) where the rest of the experiment was carried out. The lighting system consisted of six lamps of 18 W. Light intensity was 133 μmol m^{-2} s^{-1}. During a 7-d recovery period, referred to as P-I stage, the pots were covered with plastic film to keep the soil water content close to near-saturated conditions. Thereafter, during a 14-day period, referred to as P-II stage, the pots were drip irrigated with either saline (treatments T1 to T6), or deionised water (treatment T7), through 14 wetting and drying cycles. It should be noted that, compared with our previous study (Kong et al., under review), we increased the cycles from 10 to 14, as in here the system was first irrigated with non-saline water and 4 additional cycles with saline water were needed to achieve the similar salinity conditions as in cycle 1 of Kong et al. (under review). The daily amount of irrigation water was 90 ml, which was determined based on the average daily water loss from all treatments during a preliminary experiment (data not shown). After the completion of the P-II stage, during the following 7 days (P-III stage), the plants were kept growing under the same environmental conditions, but they were drip irrigated daily with 90 ml of deionised water. Plants were harvested after the P-I phase in one replicate (initial harvest) and after P-III in the other three replicates (final harvest).

6.2.7 Plant parameters

The survival of plants was recorded at the end of phases P-I and P-II. Fresh weight (FW) of harvested plants was measured immediately after these being rinsed in deionised water 3 times (during 5 s each) and gently blotted with soft paper towel to remove any surface moisture. Plant dry weight (DW) was measured after oven-drying the plants at 70 °C for 72 h (Katschnig et al., 2013). For the ash-free DW, the dried plants were charred in a muffle furnace at 500°C for 1 h, cooled and weighed (Boyer and Zedler, 2002). Leaf dry-matter contents (LDMC) were measured as the oven-dry weight (mg) of the leaves divided by their water-saturated fresh weight (g), expressed in mg g^{-1} (Cornelissen et al., 2003). The relative growth rate (RGR) was calculated using Equation (1), where w_1 and w_2 are either the DW or ash-free DW of the plants at initial and final harvest, respectively, and t_2 - t_1 is the time in days between the two harvests (Chakraborty et al., 2019).

$$RGR = \frac{\ln(w_2) - \ln(w_1)}{t_2 - t_1} \qquad [6\text{–}1]$$

6.2.8 Chemical soil analysis

Following harvest, the pumice particles were separated from the sand/sand+algae mixture. This extraction was intended to simulate a hypothetical mechanical removal of pumice from the soil under field conditions, which might be possible using larger pumice fragments. Measurements of pH, EC, and main soluble ions in a water extract of the sand fraction were carried out using the same methods as described above for the materials, and the sodium adsorption ratio (SAR) was calculated.

6.2.9 Retention of saline and non-saline water in pumice during a sequence of wetting and drying cycles

A separate experiment was carried out to gain a better understanding of the amount of water being retained in the pumice after successive wetting and drying cycles. Two hundred g of pumice of 1.5-cm Ø particle size were saturated with either deionised water or saline water with an identical composition as the one used for the plant experiment, under room temperature (25℃) in triplicates. After saturation, the pumice was weighed, then dried in an oven at 35 °C for 48 h, and reweighed. This wetting and drying cycle (and weighing) was repeated for a total of 10 times.

6.2.10 Data processing and statistical analysis

Statistical analyses were carried out using the SPSS version 14.0 software package (IBM, Armonk, New York, USA). One-way ANOVA with Duncan’s test was used to compare significance for differences between the treatment means, with a probability defined at 0.05.

6.3 Results

6.3.1 EC, SAR and pH of the residual sand at the end of the experiment

Values of EC, SAR and pH in the water extracts of the residual sand (i.e., after the removal of the pumice) from the different mixtures are provided in Table 6–2. As expected, sand under freshwater irrigation (T7) exhibited the smallest EC value (0.05 dS m^{-1}), this being significant smaller ($p < 0.05$) than that of the positive control (T1) (2.3 dS m^{-1}). The influence of the type of amendment on the EC of the residual sand was as follows: T6 > T1 > T4 = T2 > T3 = T5, with differences between treatments, where indicated, being significant at $P < 0.05$. The two treatments where pumice was added at a 12% rate (T3 and T5) showed the largest reduction (significant at $p < 0.05$) in soil EC (by > 33%) compared with that of the positive control (T1).

Values of the SAR (Table 6–2) showed similar trends to those observed for EC, with the negative control (T7) having the minimum value (12.8 meq L^{-1}), this being significantly ($p < 0.05$) smaller (by 41.5%) than the positive control (T1). SAR values of the residual sand followed the order of T6 = T1 = T4 = T2 > T3 = T5, with differences, where detected, being significant at $p < 0.05$. The combined application of 12% PU and 2% AL and that of 12% PU alone showed the largest soil improvement, with a significant reduction ($p < 0.05$) in soil SAR by 18.8 and 17.3%, respectively, over the positive control (T1). The pH value of the sand that received freshwater irrigation (T7) was significantly smaller ($p < 0.05$) than that of the positive control (T1) (6.04 vs. 6.74, respectively). The combined application of 12% PU + 2% AL (treatment T5) and that of 12% PU alone significantly ($p < 0.05$) decreased the pH value to 6.60 and 6.65, respectively, compared with the positive control (T1).

Table 6-2 Chemical properties (electrical conductivity (EC), sodium adsorption ratio (SAR), and pH in water) of the residual sand at the end of the P-III phase. The study included (i) treatments to which saline water was applied: T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL), and (ii) a treatment, T7 (sand – negative control), to which deionised water was added. Values are mean ± S.D. of 3 replicates. Mean values with different letters indicate significant differences within the same column (Duncan's test, $p < 0.05$).

Treatments	EC (dS m^{-1})	SAR (meq L^{-1})	pH (in H_2O)
T1	2.30 ± 0.07b	21.80 ± 0.36a	6.74 ± 0.10a
T2	2.16 ± 0.03c	21.46 ± 1.62a	6.70 ± 0.03ab
T3	1.58 ± 0.06d	18.02 ± 2.21b	6.65 ± 0.05bc
T4	2.20 ± 0.03c	21.60 ± 0.62a	6.68 ± 0.04abc
T5	1.53 ± 0.04d	17.70 ± 3.06b	6.60 ± 0.04c
T6	2.41 ± 0.03a	23.89 ± 0.86a	6.77 ± 0.06a
T7	0.05 ± 0.01e	12.76 ± 1.98c	6.04 ± 0.05d

P-III, period-III stage; PU, pumice; AL, algae

6.3.2 Exchangeable ions of the residual sand at the end of the experiment

The ionic concentration of water extracts from the residual sand, after the removal of pumice where applied, varied widely between the treatments (Figure 6–1). The positive control (T1) had significantly greater ($p < 0.05$) concentration of Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-} than the negative control (T7). No significant differences in the concentrations of other ions (K^+, PO_4^{3-}, NO_3^-, and HCO_3^-) were detected between the two control treatments. In the residual sand, the total ionic concentration (in moles of charge basis; Figure 6–1) followed the order of T6 = T1 = T4 = T2 > T5 = T3, with differences between treatments being significant at $P < 0.05$ where indicated. The application of either 12% PU (T3) or 12% PU + 2% AL (T5) resulted in a 40% reduction in the total ionic concentration compared with the positive control (T1). The decrease in ionic concentration was mostly caused by a decrease in cations, such as Na^+, and Ca^{2+}, with the charge of removed cations being predominantly balanced by Cl^- and SO_4^{2-}.

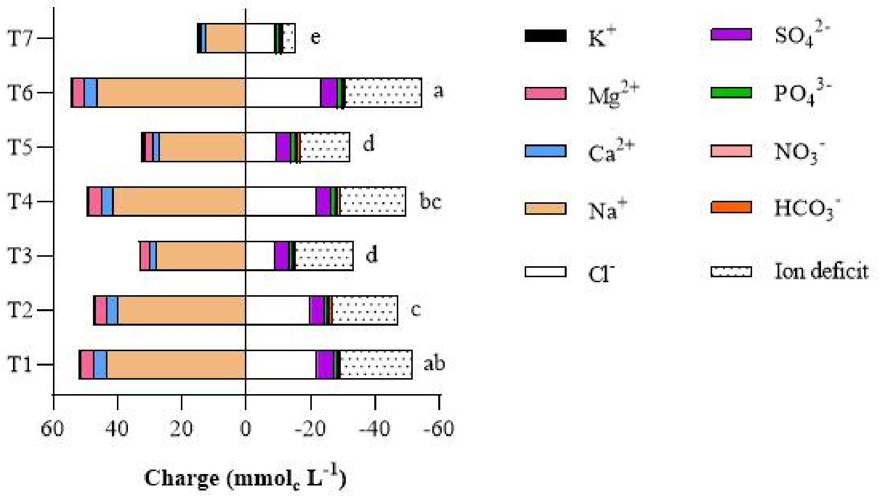

Figure 6-1 Charge balance (units in mmol$_c$ L^{-1}) of the water extraction of the residual sand under different treatments after the experiment (1:5 w/v ratio). The study included (i) treatments to which saline water was applied: T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL), and (ii) a treatment, T7 (sand – negative control), to which deionised water was added. Different letters over the bar indicate significant differences between the treatments according to Duncan's test ($p <$ 0.05).

6.3.3 Survival of lucerne after phase P-I and after phase P-II

At the end of phase P-I during which all treatments were irrigated with non-saline water (Figure 6–2a), the survival rate of plants always exceeded 80%, with no significant ($p < 0.05$) differences being observed between treatments. At the end of phase II (Figure 6–2b), there was an overall drop in the plant survival rate, including that of the negative control (T7) – the only treatment irrigated with non-saline water, which had the highest survival rate of all treatments (32%). The plant survival of the positive control (T1) (7.9%) was three-times smaller than that of the negative control (T7). Relative to the negative control (T7), the plant survival rates under treatments to which saline water was applied followed the order T5 (69.6%) > T3 (47.5%) = T4 (40.5%) = T2 (33.2%) = T1 (25%) = T6 (24.4%), with differences, where indicated, being significant at $p < 0.05$. The combined use of 12% PU and 2% AL (T5) rendered an increase in plant survival rate of 178.5%, compared with the positive control (T1) (Figure 6–2b).

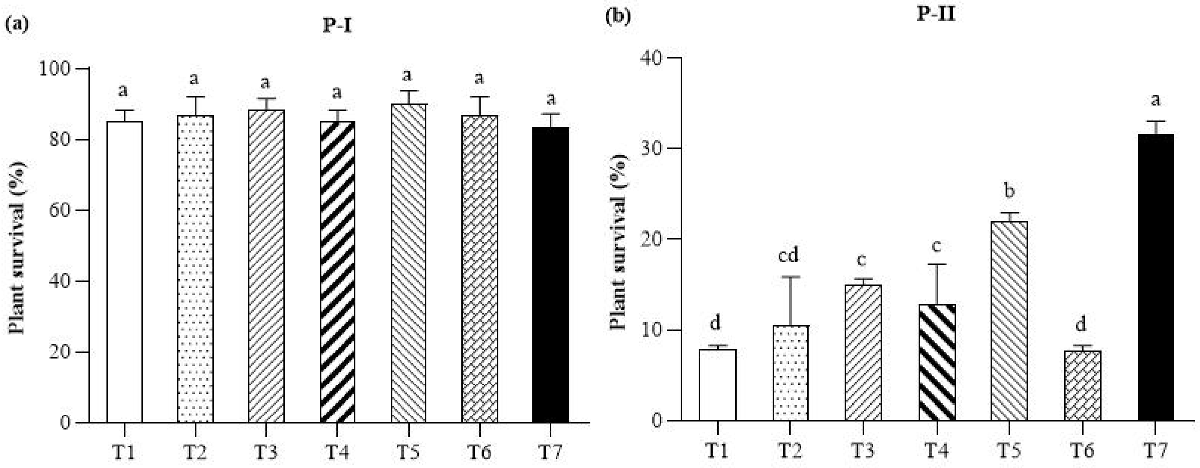

Figure 6-2 Plant survival of lucerne (*Medicago sativa* L.) at the end of (a) first recovery period (P-I) and (b) after phase II, which involved 14 cycles of wetting and drying, with plants irrigated with either saline water (T1-T6) or fresh water (T7). The study included (i) treatments to which saline water was applied: T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL), and (ii) a treatment, T7 (sand – negative control), to which deionised water was added. Different letters over the bar indicate significant differences between the treatments according to Duncan's test ($p < 0.05$).

6.3.4 Lucerne biomass at the end of the experiment

As expected, at the end of the 58-d experiment (phase III), the highest shoot and root biomass were observed in the negative control (T7) (shoot FW, DW, ash free DW:

12.7, 1.5, 1.2 g m^{-2}, respectively; root FW, DW, ash-free DW: 5.0, 1.5, 0.8 g m^{-2}, respectively) (Figure 6–3a; Supplementary Information, Figure S6–3). These values were significantly larger ($p < 0.05$) than those of the rest of treatments. Shoot and root biomass (FW, DW and ash-free DW) of treatments in which saline water was applied, followed similar trends (T5 > T3 > T4 = T2 = T6 = T1) for the three parameters measured and only those of DW are described below. Compared with the positive control (T1) (shoot DW of 0.31 g m^{-2}), significant increases ($p < 0.05$) in shoot DW were observed in treatments T3 (12% PU) , T4 (3% PU + 2% AL), and T5 (12% PU + 2% AL), these being of 145, 76, and 260%, respectively. Likewise, compared with treatment T1 (root DW of 0.17 g m^{-2}), significant increases ($p < 0.05$) in root DW were observed in treatments T3, T4, and T5, these being of 121, 76, and 239%. No significant effect of either treatment T2 (3% PU) or treatment T6 (2% AL) on plant shoot and root biomass was observed in the study compared with the positive control (T1). Consistent with the plant weight results, the relative growth rate (RGR), both on total DW basis and on ash-free DW basis (Figure 6–3b; Supplementary Information, Figure S6–3c) was highest in the negative control (T7) (72 mg kg^{-1} d^{-1}, DW basis), and significantly larger ($p < 0.05$) than the rest of treatments and, specifically, 36% larger than the positive control (T1). The RGR values of treatment T5 were 13% significantly larger ($p < 0.05$) than those of the positive control (T1) (DW basis). Likewise, similar patterns were observed in leaf dry matter content (LDMC) calculated on a trifoliate leaf basis (Figure 6–3c).

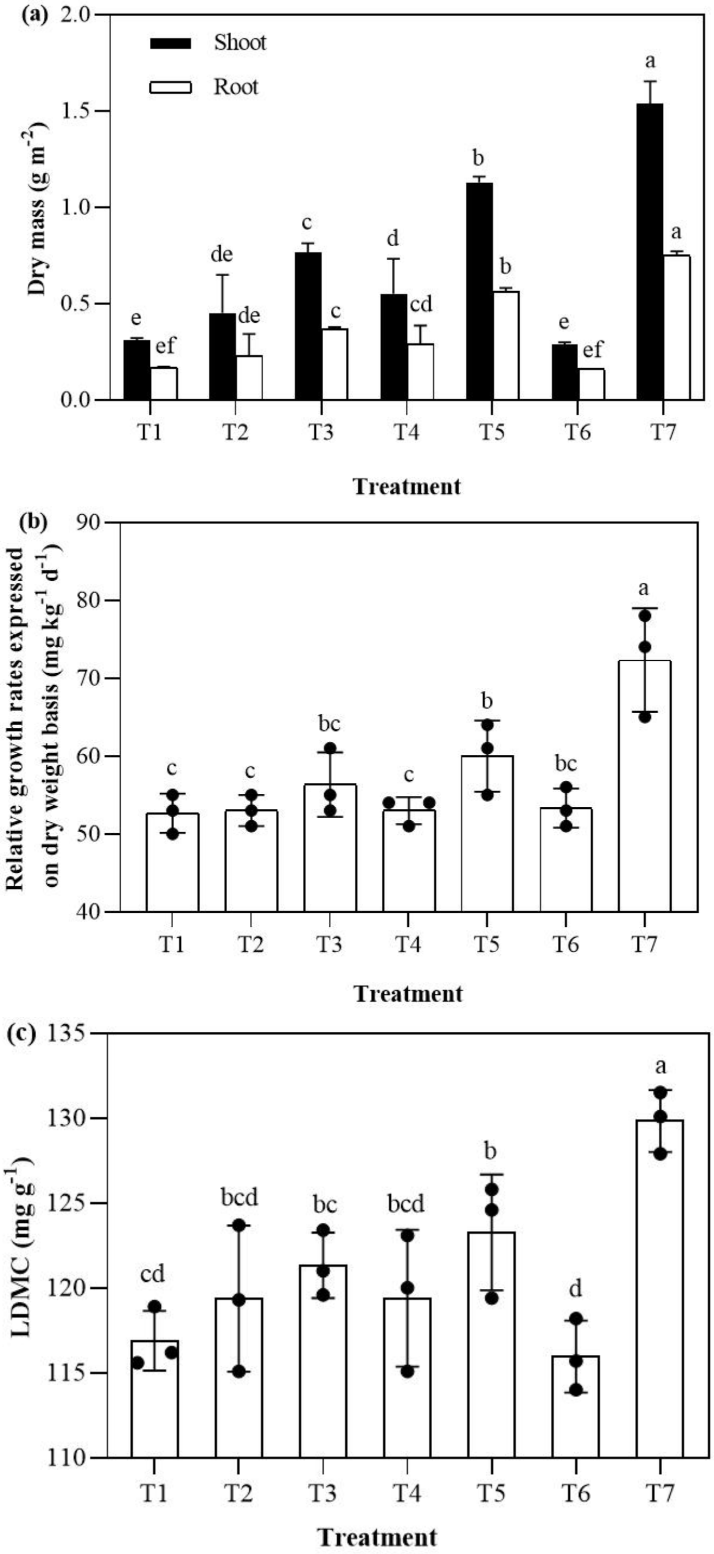

Figure 6-3 (a) Dry mass, (b) relative growth rate expressed on dry weight basis and (c) leaf dry matter content of lucerne (*Medicago sativa* L.) at final harvest. The study included (i) treatments to which saline water was applied: T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL), and (ii) a treatment, T7 (sand – negative control), to which deionised water was added. Values are mean ± S.E. of 3 replicates. Different letters in the same block indicate significant differences between the treatments according to Duncan's test ($p < 0.05$).

6.3.5 Retention of saline and non-saline water during 10 wetting and drying cycles

The amount of water (m/m, basis) able to permeate into pumice (1.5-cm Ø particle size) after each wetting and drying cycle of a sequence of 10 cycles (Figure 6–4) decreased over time under both deionised water and saline water treatments, but were only significant ($p < 0.05$) in the latter, and already evidenced after cycle 2. By the end of cycle 10, the permeability of saline water into pumice had dropped by 23.3% (significant at $p < 0.05$) compared with the deionised water treatment.

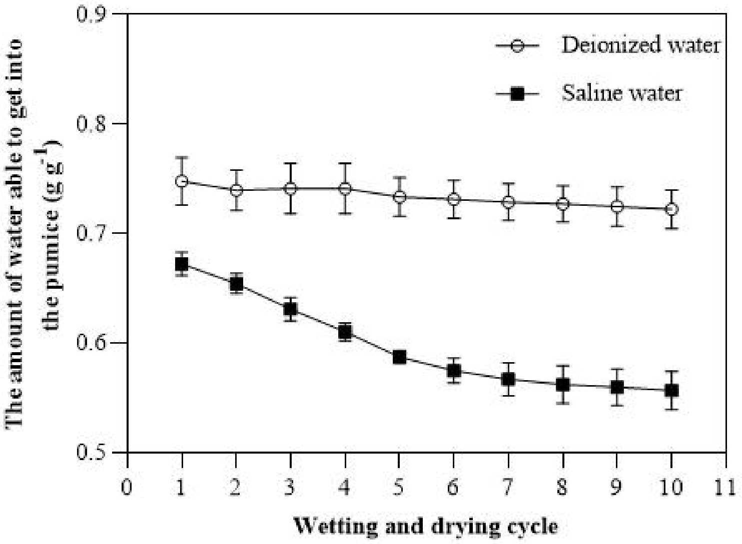

Figure 6-4 The amount of water (m/m, basis) able to get into the pumice (1.5 cm Ø particle size) under each wetting and drying cycle (by applying 10 wetting and drying cycles). Values are means of three replicates. Error bars represent the standard error.

6.4 Discussion

6.4.1 Effects of the amendments on the chemical properties of the residual sand after plant harvest

According to the Mass-Hoffman model, the threshold salinity value for alfalfa is 2 dS m^{-1} (Ayars et al., 2009) and, therefore, efforts should be made to maintain salinity levels below that limit. In this study, treatments that involved the presence of 12% PU (T3 and T5), were able to lower EC to below 2 dS m^{-1}, with the presence of algae (in T5) not contributing further to this reduction in soil salinity. The application of pumice at this volume ratio (12%) also showed the largest reduction in SAR to about 18 meq L^{-1}, which, according to the classification system developed by Sadashivaiah et al. (2008), corresponds to a “Good” class, as opposed to treatments T1-T4 and T6, which had SAR values considered as “Doubtful” based on the same classification system.

To date, there is still limited empirical evidence related to the application of pumice as a soil desalinisation material. Studies found in the literature often focus on the retention of metals within this material. In a previous study carried out by our team without plants (Kong et al., under review) using the same type of pumice, we showed that saturation index values of salts such as halite, KCl(s), mirabilite and thenardite increased inside the pumice’s pores, and this might help alleviate soil salinity and sodicity stress. Kraepiel et al. (1999) reported that metal adsorption on pumice could be described in terms of two mechanisms (i) inorganic cation exchange in the inter-layer, and (ii) specific adsorption resulting from surface complexation. Similar observations were also described by Mustafa et al. (2008), who reported that the mechanisms for cation (Cu^{2+} and Cr^{3+}) removal by pumice and polyacrylonitrile/pumice composite included sorption and complexation. However, values of CEC of the pumice were low (0.17 cmol (+) L^{-1}, w/w basis), as well as its surface charge (-10.39 mV) (Kong et al., under review), and therefore the chemical retention of ions at the surface of the pumice cannot explain the differences observed.

Based on our previous findings (Kong et al., under review) and the results obtained in this study, along with the findings of Doak (1972), the contribution of physical processes on the salinity patterns observed should not be disregarded. The slight decrease in the ability of pumice to allow the penetration of deionised water after several wetting and drying cycles observed here, could be explained by a breaking of the hydraulic connections within the water column, induced by the formation of entrapped air blocks in the pumice pores during desiccation (Doak, 1972). As well, in the presence of saline water, it is more likely that the presence of salt crusts may also impede the entrance of water. These would result in a significant volume of inaccessible solution (deionised water/saline water), becoming more concentrated in the centre of pumice particles with respect to soluble salts and water than the outside solution (Doak, 1972).

6.4.2 Effects of the amendments on the survival rate and growth of lucerne in sandy soils with saline or freshwater irrigation

Lucerne crops best thrive on deep, well-drained loam, silt loam, or clay loam soils with a pH between 6.2-7.5 (Undersander et al., 2011), adequate nutrient and moisture content, and a soil with an EC < 2 dS m^{-1} (Ayars et al., 2009). In terms of plant survival rate and growth at the end of P-II stage, the fact that the negative control (T7) had only a survival rate of 32% while the common survival germination rate in growth chambers under non-saline conditions is about 85% (Gao et al., 2011), reflects the water stress suffered by plants when undergoing the drying and wetting cycles. The existence of nutrient deficiency cannot be ruled out either, given that none of the treatments included fertilisation.

Irrigation with saline water (6.4 dS m^{-1}) had a clear detrimental effect on plant survival and growth, with survival rate being only about 8% for the positive control (T1), but this was ameliorated by the addition of 12% pumice (with and without 2% algae). The fact that the combined 12% PU + 2% AL treatment rendered a significantly larger survival rate and growth than the only 12% PU suggests that the addition of an organic amendment contributed to the retention of plant-available water, and/or the provision of limiting nutrients such as NPK in low amounts (Supplementary Information, Figure S6–1; Table 6–1). This is in agreement with Riley (2002), who observed enhanced plant-available water in a gravelly loam soil in Southern Norway after algal application. Also El-Shakweer et al. (2008), reported significant decreases in soil EC and SAR in an algae-amended sandy loam soil in Egypt, as well as Saadaoui et al. (2019), who obtained better plant growth after the incorporation of algae to a mixture of peat-moss and vermiculite (2:1, v/v basis). Algae have been reported to contain specific bioactive compounds, including polyphenols, vitamin C, vitamin E, amino acids, carotene xanthophyll, chlorophylls, phycobilins, fycocyanine, gibberellins, and auxins, and these may favour plant growth, through root development, hormonal and metabolic processes such as photosynthesis, transpiration, and stomatal conductance (Sabh and Shallan, 2008; Grzesik and Romanowska-Duda, 2015; Izabela and Katarzyna, 2015). Based on linear regression, for every 1% increase of pumice added to sandy soil this can improve the lucerne survival rate by 0.57% and in the presence of both amendments the increase was of 1.15%, reflecting the synergistic effect of the two amendments to help lucerne cope with salinity and water stress (Figure 6–5).

The benefits provided by the pumice could be related to three factors. Firstly, the retention/adsorption of ions, such as Na^+, Ca^{2+} and Cl^- could occur on the surface of the pumice surface, as well as salt entrapment and sequestration in the pumice's internal pores (Doak, 1972; Onar et al., 1996; Ashraf, 2011; Ashraf et al., 2012; Mohammad et al., 2013). Secondly, there was pumice-induced enhancement in soil water-retention capacity (in this study, significantly higher water retention at $p < 0.05$ were obtained with treatments T2, T3, T4 and T5, all involving the presence of pumice) – (Supplementary Information, Figure S6–1). This could help mitigate both water scarcity stress and salt-induced osmotic stress and ion toxicity to plants through its dilution (Verdonck, 1984; Sahin et al., 2006; Tunçez et al., 2007； Segura-Castruita et al., 2012; Ramasamy and Muralitharan, 2015). Thirdly, the retention of nutrients, could help regulate nutrient supply (Boyraz et al., 2015). Algae could further contribute to (1) and (2), and with the provision of organic matter (Sabh and Shallan, 2008), nutrients (Sayed et al., 2015; Chatterjee et al., 2017), and other organic substances to plants, which can in turn improve plant tolerance to salinity and water scarcity stresses (Lichner et al., 2013; Duarte et al., 2018).

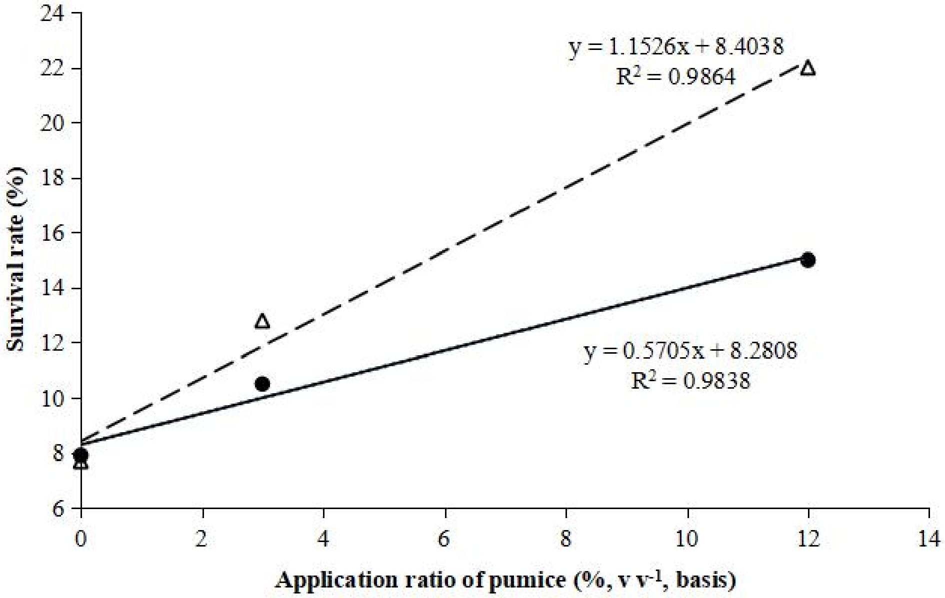

Figure 6-5 The linear regression relationships pumice application ratio and the survival rate of lucerne (*Medicago sativa* L.). The black trend line represents the absence of algae. The dotted trend line represents the presence of algae.

6.5 Conclusions

This is the first study that has shown the benefits of applying pumice (at a 12% v/v) to alleviate salinity and sodicity stress in plants. The benefits of pumice were amplified when this was added along with algae (at a 2% v/v), although our study did not discern whether this effect was due to either the addition of nutrients present in the algae or other factors. In a previous study carried out without plants (Kong et al., under review), we showed that the beneficial effect of pumice on soil salinity and sodicity was independent of its particle sizes tested, which were 1.5-, 3-, and 6-cm diameter. The use of pumice of large particle size could facilitate its removal from the field once it saturated with salts using technologies already available say the one currently used to harvest tubers. Salt-saturated pumice could also be desalinised for re-use, where feasible. Thus the use of pumice as an amendment to manage salt-affected soils seems promising. Overall, these results provide a strong incentive for further studies on salt adsorption/retention by pumice, and on its use (along with algae) in the formulation of the Technosols aimed to rehabilitating salt-affected soils in arid environments.

6.6 Acknowledgements

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Chapter 7

OVERALL SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

This chapter provides (i) a general summary of the main achievements of this study; (ii) the highlights of this research; and (iii) some recommendations for future research.

7.1 Overall summary

Given the ever-increasing demand in exploiting effective restoration techniques for alleviating salt- and plant-water stress this thesis posed the question “Can Technosols be specifically designed for reducing salinity and water stress of crops growing under arid environments?” After reviewing the literature (Chapter 2), the mechanisms through which potential ingredients (i.e. pumice, biochar, sand, organic material, and compounds rich in available silicon) for the production of Technosols might influence the above-mentioned limitations (i.e., salt stress, and plant-water stress) were identified: (i) an increase in water retention within either pumice and/or biochar pores associated with their porous structure may cause a dilution of soil salinity and a increase in soil moisture content; (ii) the addition of either pumice and/or biochar may cause a decrease in the soil bulk density and an increase in the soil hydraulic conductivity, which facilitates the leaching of salts when a leaching fraction is applied; (iii) the potential presence of diatoms within the pumice may contribute to nutrient supply in the form of silica, which increases plant’s resistance to salt and plant-water stress; (iv) the retention of salts within biochar through either adsorption on the biochar surfaces or physical entrapment within fine pores (e.g., precipitates that may block water movement) may contribute to alleviate salt stress; (v) the use of sand may help impair the capillary rise of the salty water; and (vi) the addition of organic materials may contribute to increase aggregation, moisture retention, and carbon and nutrients supply to soil microorganisms and plants.

7.1.1 Selection and application of a biochar to dryland soils

A meta-analysis of 40 studies published between 2013 and 2020 using pairwise comparisons was carried out to evaluate the short-term (≤ 1 year) effect of biochar on the salinity using EC as the proxy in soils under Mediterranean, arid, semi-arid climates, or under simulated dry and saline conditions in glasshouse/incubation chamber experiments (Chapter 3). The results clearly indicate that, when a moderate amount of soluble salts in biochar is added to a soil under a dry environment, and a leaching fraction is applied, in the risk of increasing soil EC is negligible. The results obtained in this study could be useful in the development of guidelines on the use of the biochar feedstock and its ash content, temperature of pyrolysis, initial EC of biochar, and the application rate in dry areas. A manuscript entitled “How to minimize the impact of biochar on the salinity of soils in dry regions: a meta-analysis” has been prepared and will be submitted to *Soil Use and Management*.

7.1.2 How the physical properties of pumice and biochar affected their mobile-immobile water when added to a sandy soil?

The influence of the porosity and pore-size distribution of amendments of a pumice (from New Zealand) and a biochar (produced from willow wood chips at a highest heating temperature of 350 °C) on the mobile-water content when added to a sandy soil was investigated (Chapter 4). Pumice and biochar (of 1.5-, 3-, and 6 cm Ø) were characterised using Scanning Electron Microscope (SEM) technology. The fraction of mobile-water present in these amendments, previously added to a sandy soil at different application rates and particle sizes, was determined using a tracer (Na^+) technique. The results emphasise a predominance of pores with a Ø < 30 µm and relatively high total porosity under the three given particle sizes of both materials, which are expected to contribute to water retention for some pumice/biochar−sandy soil combinations, and the dilution of salinity in salt-affected sandy soils. Yet, the contribution of biochar's ash to soil salinity cannot be disregarded. The overall larger contribution of pumice to the water mobility than that of biochar under near-saturated conditions might be to some extent related to its relatively higher levels of macro-scale plus meso-scale porosity, and this increased as the pumice particle size increased. The knowledge generated in this study provides an enhanced understanding of the relationship between the pore characteristics and mobile-water fractions of pumice and biochar, and their implications for potential use in saline environments. A manuscript based on this study (Chapter 4) has been submitted to *Soil Research*: Chao Kong, Marta Camps–Arbestain, Brent Clothier. Influence of the physical properties of pumice and biochar amendments on soil's mobile- and immobile-water: implications for use in saline environments.

7.1.3 Amelioration effects of pumice and biochar on soil salinity under arid conditions

In this part of study, pumice (from New Zealand) and biochar (made from willow at a highest heating temperature of 350 °C) of different particle sizes (1.5-, 3-, and 6-cm Ø) were separately added at different rates (3, 6, and 12%, v/v basis) to a sandy soil and their effects on soil salinity and water retention were evaluated over time. Soils were drip irrigated with an artificial saline water under non-draining conditions. Pebbles applied at identical rates and sizes as pumice and biochar, were used as positive controls, whereas no amendment was the negative control. Treatments underwent 10 wetting and drying cycles at 35 °C at the end of which, the residual sandy soil (RS) was separated from the amendments. The study confirmed that pumice (from the 1994–1995 Ruapehu eruption, New Zealand) has shown to be a promising amendment to alleviate salt- and water-stress under arid conditions. The slower salt mobilisation process with pumice-treated sandy soils compared with the other treatments tested during the miscible displacement experiment corroborates its strong salt-trapping capacity. We therefore propose the application of pumice of large particle size to salt-affected soils in arid and semi-arid regions. Its subsequent removal once it is saturated with salts using technologies already available, such as the one used to harvest tubers, as a promising tool that deserves further attention. A manuscript on this study (Chapter 5) – Chao Kong, Marta Camps–Arbestain, Brent Clothier, Peter Bishop, Felipe Macías Vázquez. Use of either pumice or willow-based biochar amendments to decrease soil salinity under arid conditions – has been submitted to the journal of *Environmental Technology and Innovation*.

7.1.4 Reclamation of salt-affected soils using pumice and algal amendments: impact on soil salinity and the growth of lucerne

Whether individual or combined additions of either pumice and/or algae to a sandy soil could alleviate the impact of irrigation with saline water on the growth of lucerne (*Medicago sativa* L.) under simulated semi-arid conditions was investigated (Chapter 6). This study included six treatments that received saline water (6.4 dS m^{-1}): T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% pumice), T4 (sand + 3% pumice + 2% algae), T5 (sand + 12% pumice + 2% algae), T6 (sand + 2% algae). A seventh treatment was T7 (sand – negative control), to which deionised water was added. All treatments underwent 14 cycles of irrigation wetting and drying events (at 27 ± 1 °C/ 16 ± 1 °C day/night). The results showed that there were benefits of applying pumice (at a 12% v/v) to alleviate salinity and sodicity stress in plants. The benefits of pumice were amplified when this was added along with algae (at a 2% v/v), although this study did not discern whether this effect was due to either the addition of nutrients present in the algae or other factors. In the previous study carried out without plants (Chapter 5), we showed that the beneficial effect of pumice on soil salinity and sodicity was independent of its particle sizes tested, which were 1.5-, 3-, and 6-cm diameter. The use of pumice of large particle size could facilitate its removal from the field once it saturated with salts using technologies already available say the one currently used to harvest tubers. Salt-saturated pumice could also be desalinised for re-use, where feasible. Thus, the use of pumice as an amendment to manage salt-affected soils seems promising. A manuscript based on this study (Chapter 6) has been submitted to the journal of *Environmental Technology and Innovation*: Chao Kong, Marta Camps–Arbestain, Brent Clothier, Peter Bishop, Felipe Macías Vázquez. Reclamation of salt-affected soils using pumice and algal amendments: impact on soil salinity and the growth of lucerne.

We concluded that pumice (from the 1994–1995 Ruapehu eruption, New Zealand) and algal residues (from the Whanganui estuary, Manawatu-Wanganui, New Zealand) is a suitable ingredient to use in a Technosol with reclamation values, and is therefore able to alleviate soil salinity and stimulate crops growing under arid conditions.

7.2 Highlights of the thesis

- Based on the meta-analysis carried out, the application of biochar to soil causes a 17% mean increase of soil EC (Chapter 3).
- Based on the meta-analysis carried out, the application of a biochar with a relatively low amount of soluble salts in the ash fraction (along with the application of a leaching fraction) to a soil under a dry environment, poses no risk of soil salinisation. Conversely, biochar made from high-ash material should not be applied to soils in dry regions (Chapter 3).
- Both pumice and biochar have a predominance of pores with a Ø < 30 μm and relatively high total porosity, which are expected to contribute to water retention when these amendments are used in sandy soil, and to the dilution of salinity in salt-affected sandy soils assuming a low ash biochar is used (Chapter 4).
- The overall larger contribution of pumice to the water mobility than that of biochar under near-saturated conditions could be related to its relatively higher levels of macro-scale plus meso-scale porosity, and this increased as the pumice particle size increased (Chapter 4).

- Pumice (from the 1994–1995 Ruapehu eruption, New Zealand) was shown to be a promising amendment to alleviate salt- and water-stresses under arid conditions. The slower salt mobilisation process in sandy soils amended with pumice (compared with those amended with biochar or no amended) during the miscible displacement experiment corroborated its strong salt-trapping capacity (Chapter 5).
- Pumice alleviated salinity and sodicity stress in lucerne, and this effect was amplified when pumice was added along with algae (at a 2% v/v) (Chapter 6).
- Pumice-induced salt trapping could be explained by a breaking of the hydraulic connections within the water column, induced by the formation of entrapped air blocks in the pores during desiccation (Chapter 6).

7.3 Future research recommendations

7.3.1 A more in-depth meta-analysis would be needed for future research

The major challenge when conducting a meta-analysis on the effect of biochar on soil salinity under dry environments has been the data limitation, which precluded the identification of the influence of production conditions without bias. A more in-depth analysis with additional data will be needed in future research.

We carried out a meta-analysis using MetaWin 2.0 software, which is affordable and easy to use, and helped draw general conclusions. Yet, when more data becomes available, the use of R software with *metafor* package would be needed as it can discern publication bias (Schmid et al., 2013).

7.3.2 Applying the technique of NMR to determine the pore size distribution of pumice and biochar

To determine the porosity and pore-size distribution of pumice and biochar, Scanning Electron Microscope (SEM) technology was used in our study. Yet the destruction effect of cutting process on the sample structure (SEM requires small particle size of samples) cannot be disregarded. An alternative method that could be used is Nuclear Magnetic Resonance (NMR) technology. This has been proven to be a non-destructive tool for characterisation of the pore size distribution of porous samples (Strange and Webber, 1997), and the results were in good agreement with SEM. The application of this method might help further validate the results from our study.

7.3.3 Field-based studies would be warranted for future research

Given that the use of pumice and algae as either ingredients of sandy

Technosols or as direct amendments to soil showed encouraging results, this aspect needs to be studied in the field and with various cropping patterns, under dry environments.

The impacts of pumice on soil salinity with and without plants were only based on pot experiments and short-term incubations under simulated dry and saline conditions. Field studies and over longer period of time would be required to further evaluate the feasibility of the use of these amendments in cropping systems.

7.3.4 The potential of pumice and biochar to mitigate salt-affected soils with a texture other than sandy

In this study, only a soil with a sandy texture was investigated. If the use of these amendments is to be widespread, soils with other textures would first need to be tested. Different textures have different porosities and thus influence water and salt movement differently, but a key consideration over and above texture is the hydraulic nature of flow in the soil. Texture will affect the mobile/less-mobile water fraction, yet the prime consideration will be the hydraulic pathways in the system. Differences would be attenuated under saturated conditions, but if undersaturated, the flow towards the pumice and the biochar pores would strongly depend on the flow of the water from the bulk soil towards the pores of the amendments and a higher water pressure head might be needed compared with a sandy soil. More research on the application of these amendments to other soil types is needed in order to up-scale this technology and use it widely.

7.3.5 A quantitative assessment on plant-water stress would be needed for future research

Given that the use of pumice and willow-based biochar as either ingredients of sandy Technosols or as direct amendments to soil showed encouraging results on soil water retention in the absence of salts, a quantitative assessment on the effect of these amendments on soil water availability needs to be studied in future research.

In this study, only the effect of soil water contents on plant-water stress (Chapter 6) or the effect of salts on EC as soil moisture decreases (Chapter 5) was investigated. Given that water scarcity and salt stress are interrelated as both result in osmotic stress to plants (Mahajan and Tuteja, 2005; Hui et al., 2014), more research on the interaction between direct 'water' stress, and the associated 'salt' stress due to the salt content of the water is needed in order to quantify the effect of pumice and biochar on plant-water stress.

Appendix

Appendix 1 Supplementary data of chapter 4

Methodology of the measurement of the mobile-water fraction in pumice and biochar (Clothier et al., 1992; Clothier et al., 1995)

The volumetric content of the tracer in the mobile and immobile water at any time is

$$\theta C = \theta_m C_m + \theta_{im} C_{im} \qquad [1]$$

Here θ_m and C_m are the volumetric water content and the resident fluid concentration of the mobile phase, respectively, and θ_{im} and C_{im} are the volumetric water content and the resident fluid concentration of the tracer in the immobile phase, respectively. Here we assume that, in the equilibrated region immediately under the sandy soil mixtures, the tracer concentration in the mobile phase will be that supplied by the wetting system, namely C_m. Furthermore, if the tracer is chosen so that none is present in the amendment under study beforehand, and if it is sufficiently small so that the immobile water remains essentially free of tracer at the time of sampling, then Eq. [1] will reduce to

$$\theta_m = \theta(C^*/C_m) \qquad [2]$$

This will allow easy determination of the mobile phase from measurements of θ and C^*, along with the known C_m.

Appendix 2 Supplementary data of chapter 5

Table 5-S1 Cumulative water loss in sandy soil with, or without, amendment (pumice, biochar, and pebble) additions. When averaging the water loss from the different treatments grouped by application rates, regardless of the particle size. When averaging the water loss from the different treatments grouped by particle sizes, regardless of the application rate.

Averaging the water loss from the different treatments grouped by application rates, regardless of the particles size	Mean value	Averaging the water loss from the different treatments grouped by particles sizes, regardless of the application rate	Mean value
S	593.2 ± 2.3	S	593.2 ± 2.3
3%Pu	570.0 ± 6.9a	Pu-1.5	547.0 ± 28.0a
6%Pu	547.8 ± 7.0b	Pu-3	545.7 ± 17.1a
12%Pu	542.3 ± 32.8ab	Pu-6	567.4 ± 15.7a
3%B	591.6 ± 14.2a	B-1.5	562.2 ± 13.5b
6%B	582.6 ± 22.4ab	B-3	573.7 ± 16.1ab
12%B	561.0 ± 15.5b	B-6	599.2 ± 15.8a
3%Pe	615.3 ± 9.4b	Pe-1.5	628.7 ± 18.1a

6%Pe	639.8 ± 8.8a	Pe-3	641.9 ± 21.3a
12%Pe	647.5 ± 16.9a	Pe-6	631.9 ± 14.1a

S, sandy soil; 3%Pu, pumice was added to the soil at an application rate of 3% (v/v); 6%Pu, pumice was added to the soil at an application rate of 6% (v/v); 12%Pu, pumice was added to the soil at an application rate of 12% (v/v); 3%B, biochar was added to the soil at an application rate of 3% (v/v); 6%B, biochar was added to the soil at an application rate of 6% (v/v); 12%B, biochar was added to the soil at an application rate of 12% (v/v); 3%Pe, pebble was added to the soil at an application rate of 3% (v/v); 6%Pe, pebble was added to the soil at an application rate of 6% (v/v); 12%Pe, pebble was added to the soil at an application rate of 12% (v/v); Pu-1.5, pumice with 1.5-cm diameter; Pu-3, pumice with 3-cm diameter; Pu-6, pumice with 6-cm diameter; B-1.5, biochar with 1.5-cm diameter; B-3, biochar with 3-cm diameter; B-6, biochar with 6-cm diameter; Pe-1.5, pebble with 1.5-cm diameter; Pe-3, pebble with 3-cm diameter; Pe-6, pebble with 6-cm diameter.

Table 5-S2 Saturation indices for salts - Visual MINTEQ.

Mineral	Sat. index																	
	3%Pu-1.5	6%Pu-1.5	12%Pu-1.5	3%Pu-3	6%Pu-3	12%Pu-3	3%Pu-6	6%Pu-6	12%Pu-6	3%B-1.5	6%B-1.5	12%B-1.5	3%B-3	6%B-3	12%B-3	3%B-6	6%B-6	12%B-6
Anhydrite	-0.32	-0.22	-0.25	-0.25	-0.14	-0.19	-0.32	-0.27	-0.27	-0.68	-0.64	-0.68	-0.71	-0.55	-0.68	-0.70	-0.86	-0.92
Brucite	-5.49	-5.47	-5.43	-5.48	-5.48	-5.53	-5.25	-5.52	-5.56	-5.45	-5.24	-5.34	-5.26	-5.12	-5.25	-5.18	-5.38	-5.10
$Ca_3(PO_4)_2$ (am1)	0.11	0.64	0.80	0.45	0.88	1.00	0.72	0.95	1.25	1.73	2.20	2.03	1.91	2.47	2.33	2.11	1.50	1.73
$Ca_3(PO_4)_2$ (am2)	2.86	3.39	3.55	3.20	3.63	3.75	3.47	3.70	4.00	4.48	4.95	4.78	4.66	5.22	5.08	4.86	4.25	4.48
$Ca_3(PO_4)_2$ (beta)	3.53	4.06	4.22	3.87	4.30	4.42	4.14	4.37	4.67	5.15	5.62	5.45	5.33	5.89	5.75	5.53	4.92	5.15
$Ca_4H(PO_4)_3{:}3H_2O(s)$	4.04	4.74	4.95	4.48	5.07	5.21	4.82	5.15	5.54	6.34	6.92	6.71	6.52	7.25	7.07	6.76	6.04	6.26
$CaHPO_4(s)$	0.81	0.98	1.02	0.90	1.07	1.08	0.99	1.09	1.18	1.45	1.56	1.52	1.45	1.62	1.59	1.49	1.38	1.38
$CaHPO_4{:}2H_2O(s)$	0.49	0.66	0.71	0.59	0.75	0.77	0.67	0.77	0.86	1.16	1.27	1.23	1.16	1.33	1.29	1.20	1.09	1.08
Epsomite	-2.58	-2.64	-2.72	-2.65	-2.64	-2.83	-2.59	-2.84	-3.01	-3.17	-3.17	-3.22	-3.19	-3.13	-3.29	-3.23	-3.19	-3.22
Gypsum	-0.11	-0.01	-0.03	-0.03	0.07	0.02	-0.11	-0.06	-0.06	-0.44	-0.40	-0.44	-0.47	-0.32	-0.44	-0.46	-0.62	-0.68
Halite	-1.83	-1.76	-1.88	-1.84	-1.69	-1.86	-1.69	-1.64	-1.73	-3.17	-3.11	-3.09	-3.13	-2.99	-3.03	-3.15	-3.13	-2.98
Hydroxyapatite	12.00	12.89	13.18	12.59	13.28	13.52	13.03	13.39	13.91	14.62	15.44	15.14	14.97	15.93	15.67	15.33	14.22	14.69
KCl(s)	-2.82	-2.85	-3.06	-2.93	-2.78	-3.02	-2.75	-2.87	-3.10	-3.30	-3.27	-3.30	-3.10	-3.20	-3.18	-3.19	-3.20	-3.13
Lime	-21.17	-20.99	-20.90	-21.02	-20.93	-20.83	-20.93	-20.91	-20.77	-20.83	-20.58	-20.66	-20.64	-20.42	-20.50	-20.52	-20.91	-20.68
$Mg(OH)_2$(active)	-7.18	-7.16	-7.13	-7.18	-7.18	-7.23	-6.94	-7.21	-7.26	-7.14	-6.93	-7.03	-6.95	-6.82	-6.94	-6.88	-7.07	-6.80
$Mg_2(OH)_3Cl{:}4H_2O(s)$	-9.71	-9.66	-9.72	-9.69	-9.64	-9.93	-9.19	-9.69	-9.94	-10.47	-10.10	-10.30	-10.18	-9.89	-10.10	-10.12	-10.30	-9.86
$Mg_3(PO_4)_2(s)$	-1.82	-1.77	-1.77	-1.91	-1.75	-2.09	-1.19	-1.86	-2.09	-1.13	-0.78	-1.01	-0.95	-0.64	-0.90	-0.87	-0.90	-0.56
$MgHPO_4{:}3H_2O(s)$	-0.25	-0.24	-0.25	-0.29	-0.22	-0.36	-0.07	-0.26	-0.35	0.12	0.19	0.13	0.12	0.20	0.13	0.12	0.21	0.24
Mirabilite	-2.08	-2.05	-2.12	-2.20	-2.02	-2.09	-2.16	-2.12	-2.10	-3.57	-3.58	-3.49	-3.53	-3.38	-3.57	-3.52	-3.64	-3.44
Periclase	-9.96	-9.93	-9.90	-9.95	-9.95	-10.00	-9.71	-9.99	-10.03	-9.92	-9.72	-9.82	-9.74	-9.60	-9.72	-9.66	-9.86	-9.58
Portlandite	-11.19	-11.01	-10.92	-11.04	-10.95	-10.85	-10.96	-10.93	-10.80	-10.84	-10.59	-10.67	-10.65	-10.43	-10.51	-10.53	-10.92	-10.69
Thenardite	-3.35	-3.31	-3.39	-3.46	-3.27	-3.36	-3.40	-3.36	-3.35	-4.96	-4.96	-4.87	-4.92	-4.75	-4.94	-4.90	-5.02	-4.82

Sat. index, saturation index; 3%Pu, pumice was added to the soil at an application rate of 3% (v/v); 6%Pu, pumice was added to the soil at an application rate of 6% (v/v); 12%Pu, pumice was added to the soil at an application rate of 12% (v/v); 3%B, biochar was added to the soil at an application rate of 3% (v/v); 6%B, biochar was added to the soil at an application rate of 6% (v/v); 12%B, biochar was added to the soil at an application rate of 12% (v/v); 3%Pe, pebble was added to the soil at an application rate of 3% (v/v); 6%Pe, pebble was added to the soil at an application rate of 6% (v/v); 12%Pe, pebble was added to the soil at an application rate of 12% (v/v); Pu-1.5, pumice with 1.5-cm diameter; Pu-3, pumice with 3-cm diameter; Pu-6, pumice with 6-cm diameter; B-1.5, biochar with 1.5-cm diameter; B-3, biochar with 3-cm diameter; B-6, biochar with 6-cm diameter.

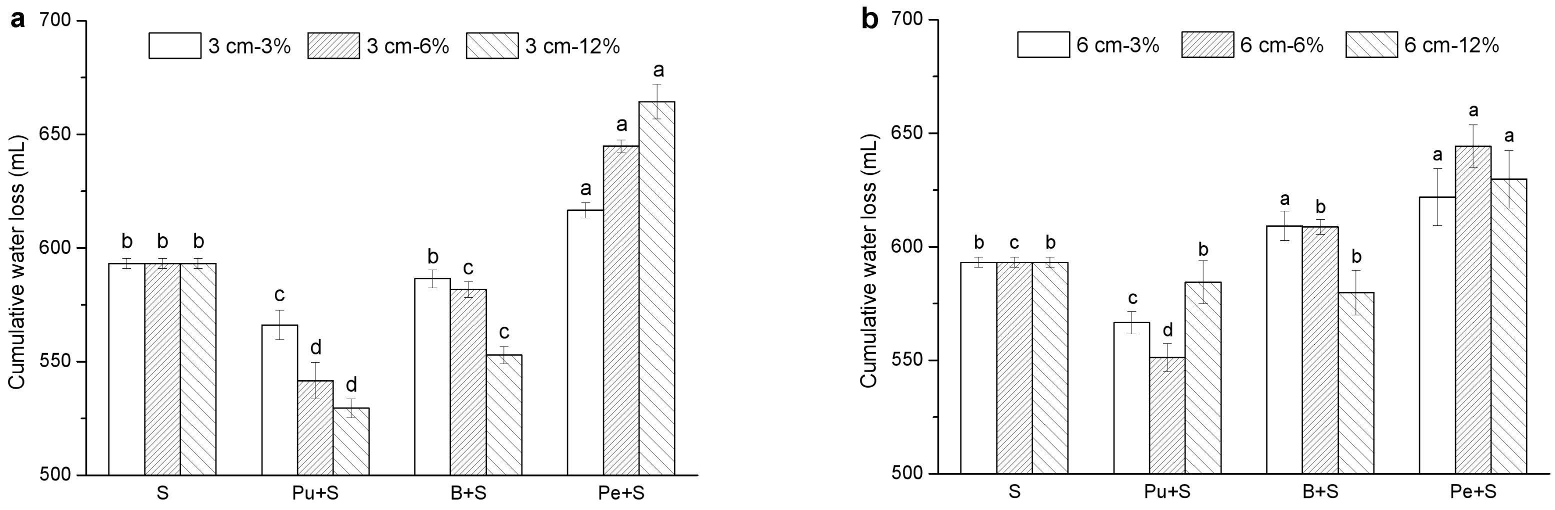


Figure 5-S1 Cumulative water loss in sandy soil with, or without, amendment (pumice, biochar, and pebble) additions. Bar charts showing: (a) the amendments with 3-cm diameter, (b) the amendments with 6-cm diameter. Different letters in columns with similar filling pattern indicate significant difference between treatments ($p < 0.05$). Values are means of four replicates. Error bars represent the standard error. S, sandy soil; Pu + S, pumice + sandy soil; B + S, biochar + sandy soil; Pe + S, pebble + sandy soil.

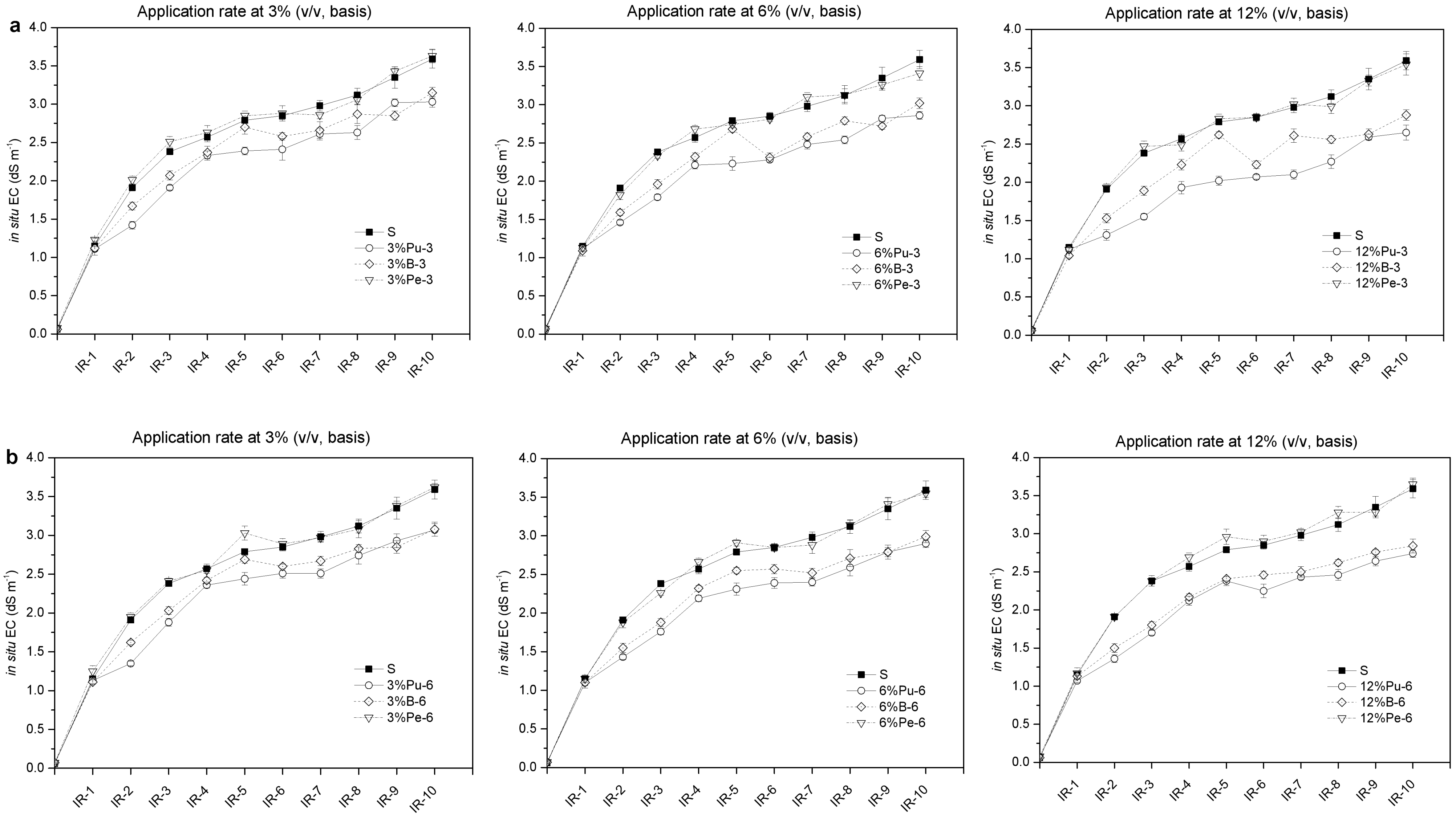

a
Application rate at 3% (v/v, basis)
Application rate at 6% (v/v, basis)
Application rate at 12% (v/v, basis)
in situ EC (dS m^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
IR-1
IR-2
IR-3
IR-4
IR-5
IR-6
IR-7
IR-8
IR-9
IR-10
S
3%Pu-3
3%B-3
3%Pe-3
6%Pu-3
6%B-3
6%Pe-3
12%Pu-3
12%B-3
12%Pe-3
b
3%Pu-6
3%B-6
3%Pe-6
6%Pu-6
6%B-6
6%Pe-6
12%Pu-6
12%B-6
12%Pe-6

Figure 5-S2 *In situ* EC in sandy soil with, or without, absorbent (pumice, biochar, and pebble) additions after each cycle of irrigation. Line charts showing: (a) the amendments with 3-cm diameter, (b) the amendments with 6-cm diameter. Values are means of four replicates. EC, electrical conductivity; S, sandy soil; Pu-3, pumice with 3-cm diameter; B-3, biochar with 3-cm diameter; Pe-3, pebble with 3-cm diameter; Pu-6, pumice with 6-cm diameter; B-6, biochar with 6-cm diameter; Pe-6, pebble with 6-cm diameter.

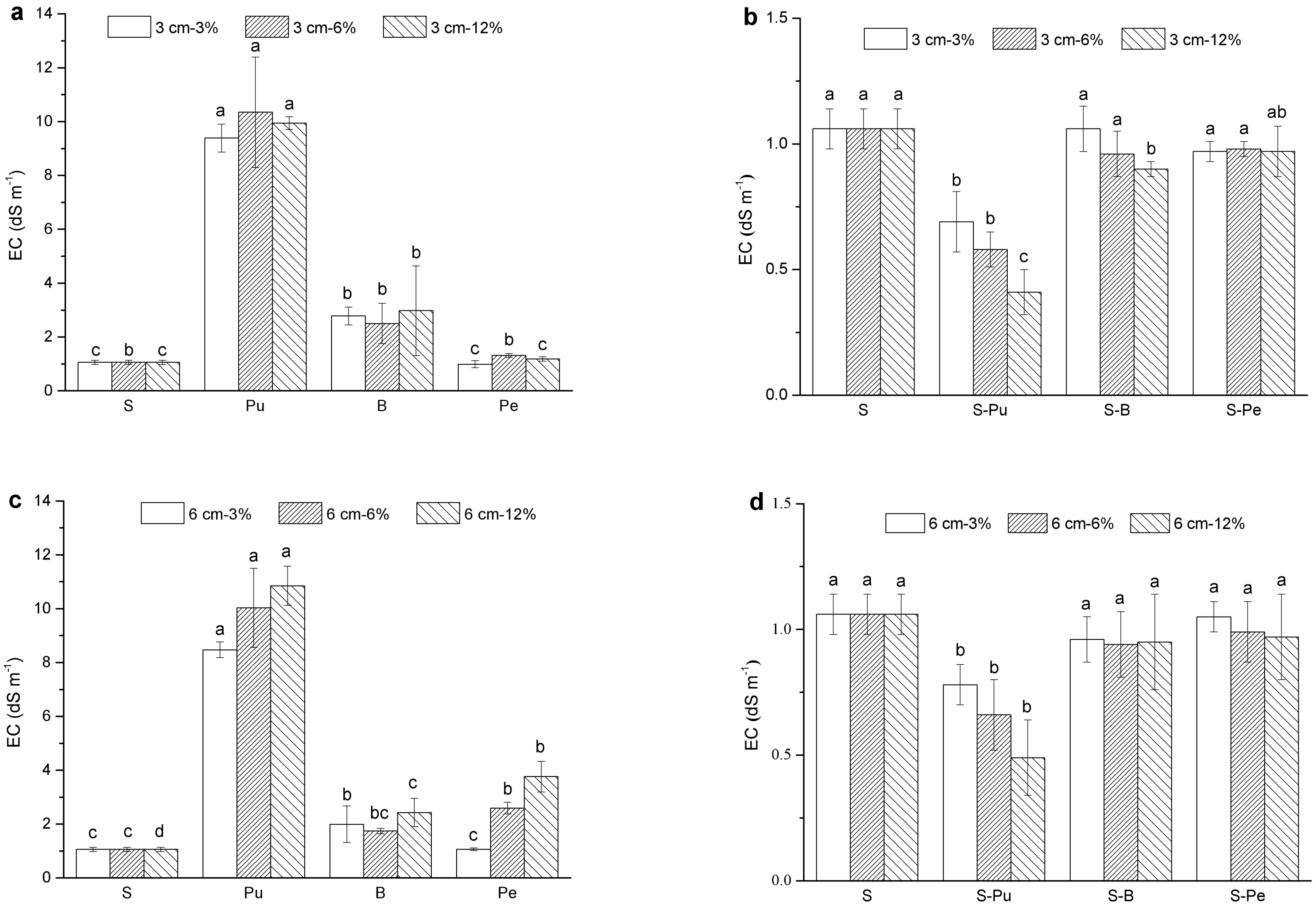

a
b
c
d
3 cm-3%
3 cm-6%
3 cm-12%
6 cm-3%
6 cm-6%
6 cm-12%
EC (dS m^{-1})
0
2
4
6
8
10
12
14
0.0
0.5
1.0
1.5
S
Pu
B
Pe
S-Pu
S-B
S-Pe
c b c
a a a
b b b
c b c
a a a
b b b
b a b
a a ab
c c d
a a a
b bc c
c b b
a a a
b b b
a a a
a a a

Figure 5-S3 The electrical conductivity (EC) of the amendments and sandy soil after the experiment (1:5 w/v ratio). Bar charts showing: (a) the amendments with 3-cm diameter, (b) sandy soil treated by the amendments with 3-cm diameter, (c) the amendments with 6-cm diameter, (d) sandy soil treated by the amendments with 6-cm diameter. Values are means of three replicates. Error bars represent the standard error. Different letters in columns with similar filling pattern indicate significant difference between treatments according to Duncan's test ($p < 0.05$). S, sandy soil; Pu, pumice; B, biochar; Pe, pebble; S-Pu, the residual sandy soil after the removal of pumice; S-B, the residual sandy soil after the removal of biochar; S-Pe, the residual sandy soil after the removal of pebble.

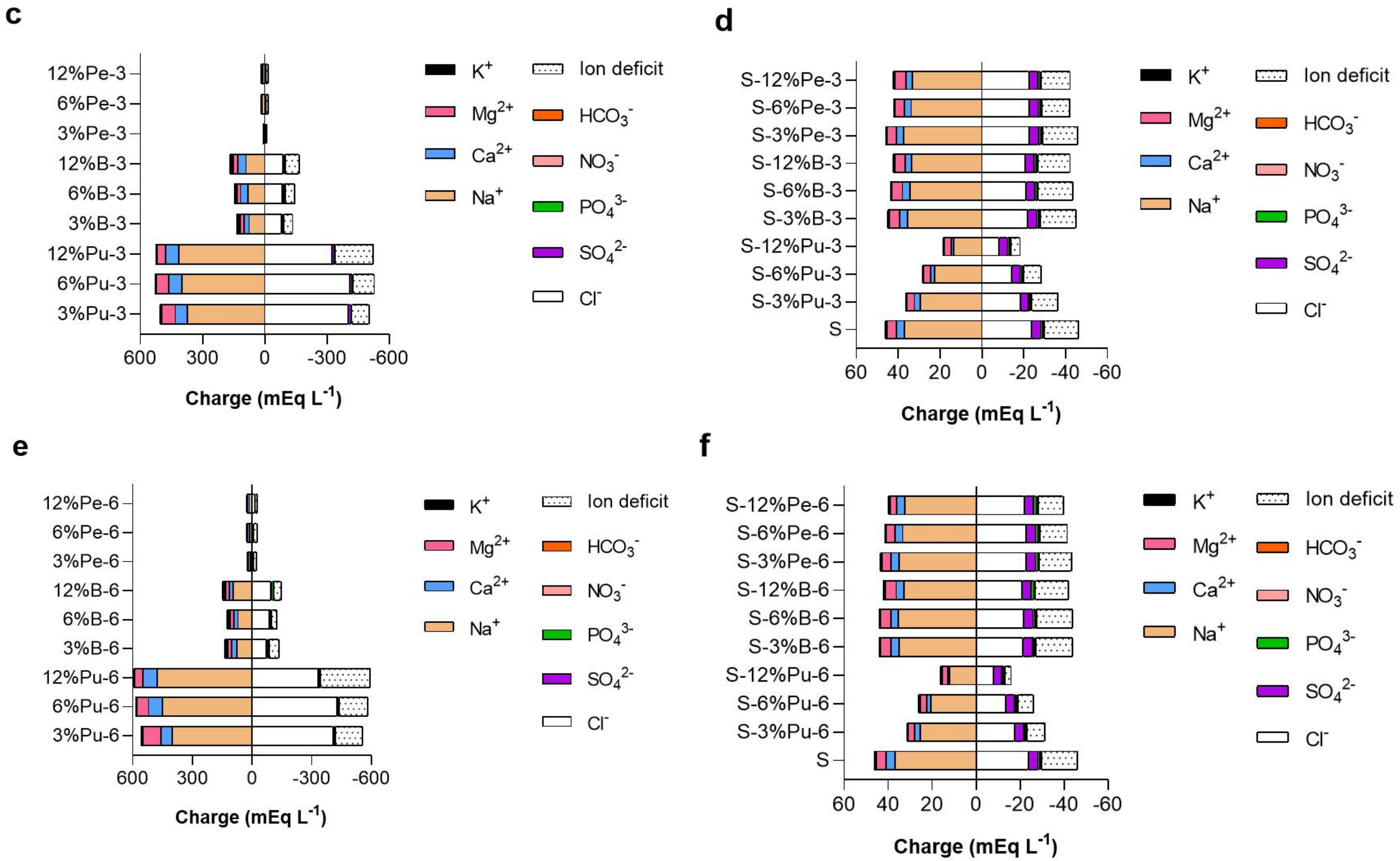

c
12%Pe-3
6%Pe-3
3%Pe-3
12%B-3
6%B-3
3%B-3
12%Pu-3
6%Pu-3
3%Pu-3
600
300
0
-300
-600
Charge (mEq L^{-1})
d
S-12%Pe-3
S-6%Pe-3
S-3%Pe-3
S-12%B-3
S-6%B-3
S-3%B-3
S-12%Pu-3
S-6%Pu-3
S-3%Pu-3
S
60
40
20
0
-20
-40
-60
Charge (mEq L^{-1})
e
12%Pe-6
6%Pe-6
3%Pe-6
12%B-6
6%B-6
3%B-6
12%Pu-6
6%Pu-6
3%Pu-6
600
300
0
-300
-600
Charge (mEq L^{-1})
f
S-12%Pe-6
S-6%Pe-6
S-3%Pe-6
S-12%B-6
S-6%B-6
S-3%B-6
S-12%Pu-6
S-6%Pu-6
S-3%Pu-6
S
60
40
20
0
-20
-40
-60
Charge (mEq L^{-1})
K^+
Mg^{2+}
Ca^{2+}
Na^+
Ion deficit
HCO_3^-
NO_3^-
PO_4^{3-}
SO_4^{2-}
Cl^-

Figure 5-S4 Charge balance (units in mEq L^{-1}) of the water extraction of (c & e) the amendments and (d & f) sandy soil after the experiment (1:5 w/v ratio). Values are means of three replicates. Pu-3, pumice with 3-cm diameter; Pu-6, pumice with 6-cm diameter; B-3, biochar with 3-cm diameter; B-6, biochar with 6-cm diameter; Pe-3, pebble with 3-cm diameter; Pe-6, pebble with 6-cm diameter; S, sandy soil; S-Pu, the residual sandy soil after the removal of pumice; S-B, the residual sandy soil after the removal of biochar; S-Pe, the residual sandy soil after the removal of pebble.

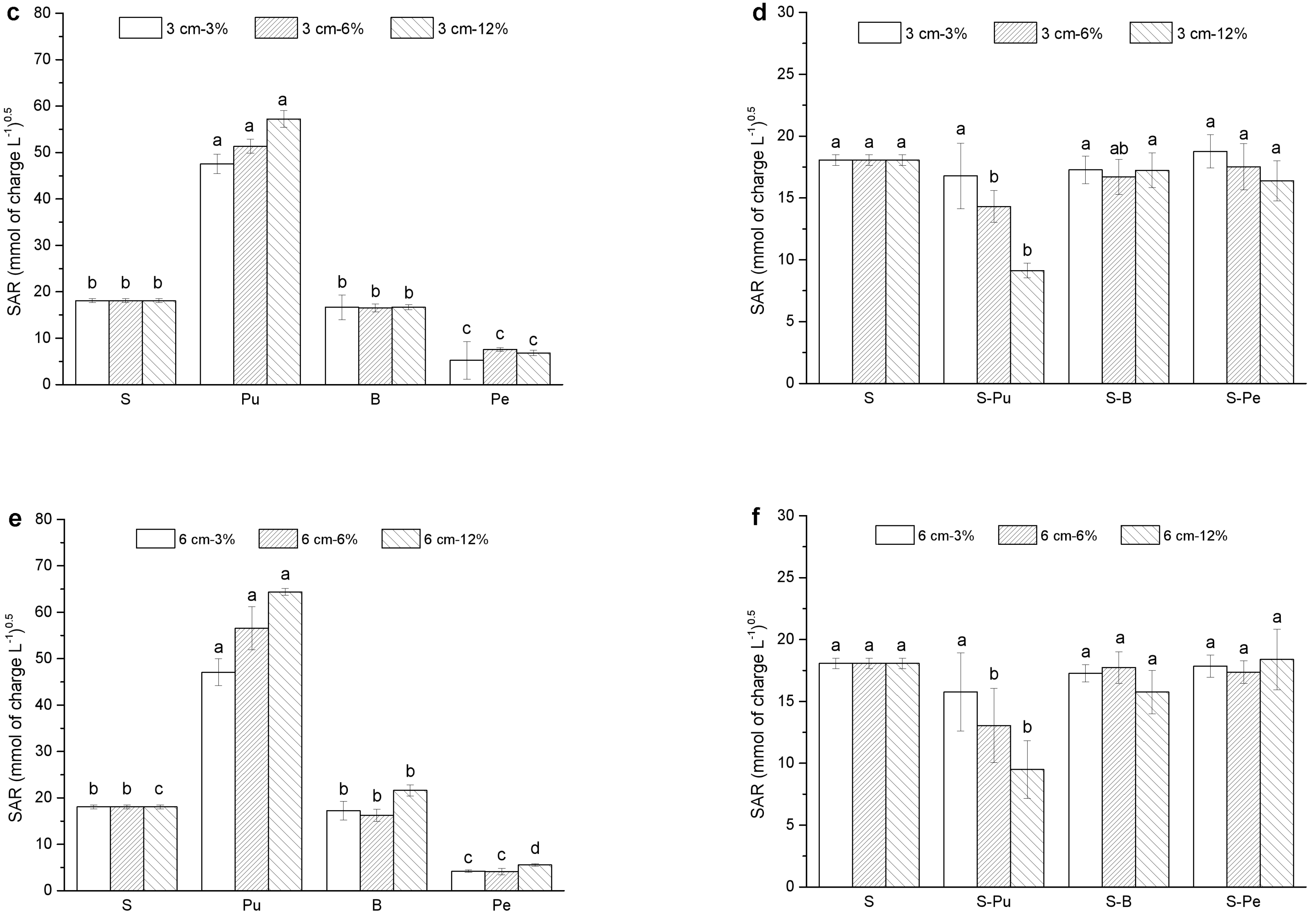

c
SAR (mmol of charge L^{-1})$^{0.5}$
3 cm-3%
3 cm-6%
3 cm-12%
S
Pu
B
Pe
0
10
20
30
40
50
60
70
80
b b b
a a a
b b b
c c c
d
SAR (mmol of charge L^{-1})$^{0.5}$
3 cm-3%
3 cm-6%
3 cm-12%
S
S-Pu
S-B
S-Pe
0
5
10
15
20
25
30
a a a
a b b
a ab a
a a a
e
SAR (mmol of charge L^{-1})$^{0.5}$
6 cm-3%
6 cm-6%
6 cm-12%
S
Pu
B
Pe
0
10
20
30
40
50
60
70
80
b b c
a a a
b b b
c c d
f
SAR (mmol of charge L^{-1})$^{0.5}$
6 cm-3%
6 cm-6%
6 cm-12%
S
S-Pu
S-B
S-Pe
0
5
10
15
20
25
30
a a a
a b b
a a a
a a a

Figure 5-S5 Sodium adsorption ratio (SAR) of the amendments and sandy soil after the experiment (1:5 w/v ratio). Bar charts showing: (c) the amendments with 3-cm diameter, (d) sandy soil treated by the amendments with 3-cm diameter, (e) the amendments with 6-cm diameter, (f) sandy soil treated by the amendments with 6-cm diameter. Values are means of three replicates. Error bars represent the standard error. Different letters in columns with similar filling pattern indicate significant difference between treatments according to Duncan's test ($p < 0.05$). S, sandy soil; Pu, pumice; B, biochar; Pe, pebble; S-Pu, the residual sandy soil after the removal of pumice; S-B, the residual sandy soil after the removal of biochar; S-Pe, the residual sandy soil after the removal of pebble.

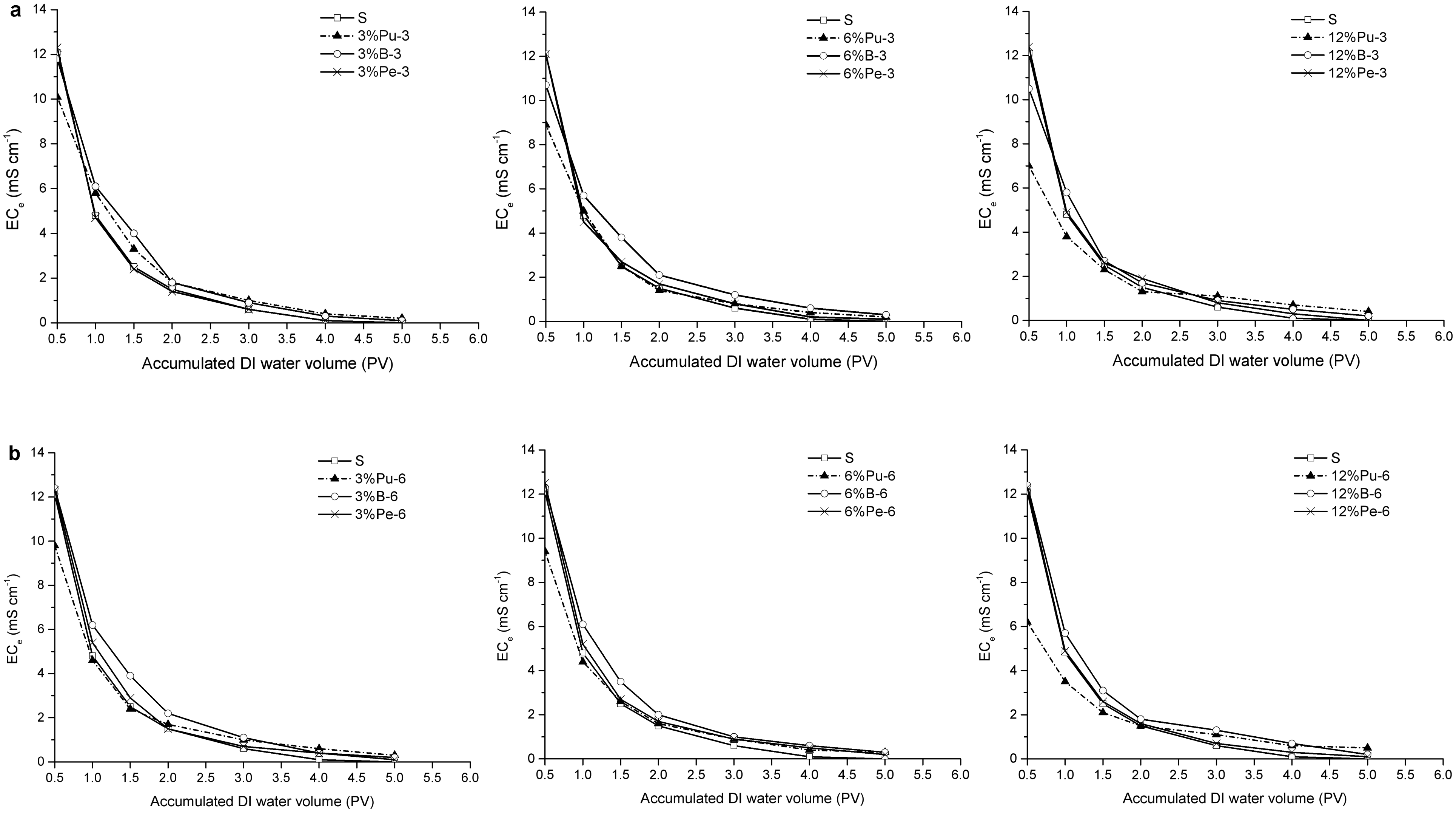

a
b
ECe (mS cm-1)
Accumulated DI water volume (PV)
0
2
4
6
8
10
12
14
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
S
3%Pu-3
3%B-3
3%Pe-3
6%Pu-3
6%B-3
6%Pe-3
12%Pu-3
12%B-3
12%Pe-3
3%Pu-6
3%B-6
3%Pe-6
6%Pu-6
6%B-6
6%Pe-6
12%Pu-6
12%B-6
12%Pe-6

Figure 5-S6 Graphical trend of electrical conductivity (EC) of the leachate to accumulated deionised water volume using pumice, biochar, and pebble as the amendments. Line charts showing: (a) the amendments with 3-cm diameter, (b) the amendments with 6-cm diameter. Here EC_e, electrical conductivity of the effluent; DI, deionised water; PV, pore volume; S, sandy soil; Pu-3, pumice with 3-cm diameter; B-3, biochar with 3-cm diameter; Pe-3, pebble with 3-cm diameter; Pu-6, pumice with 6-cm diameter; B-6, biochar with 6-cm diameter; Pe-6, pebble with 6-cm diameter.

Appendix 3 Supplementary data of chapter 6

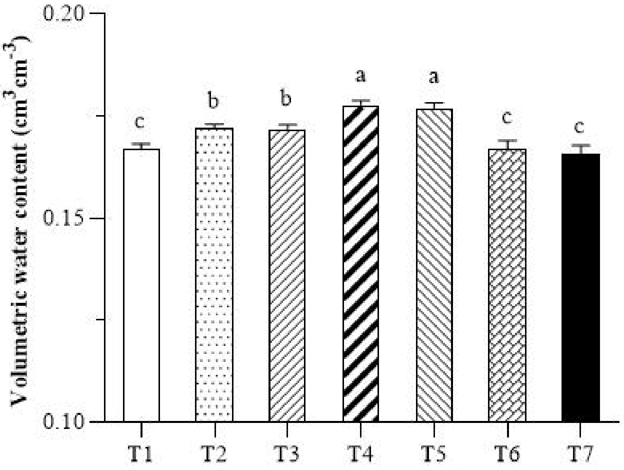
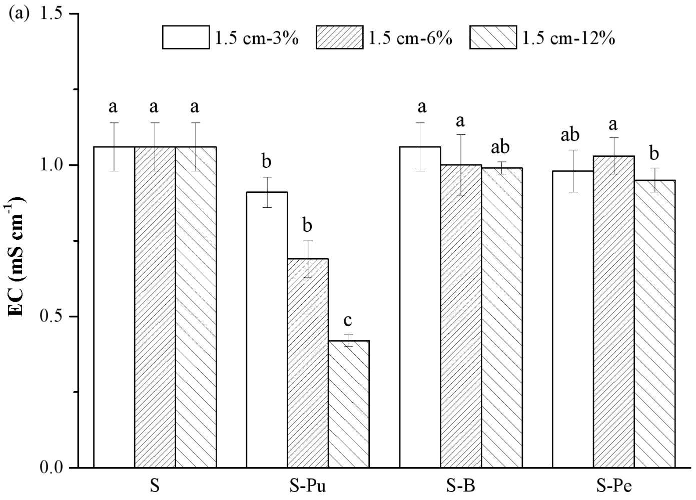
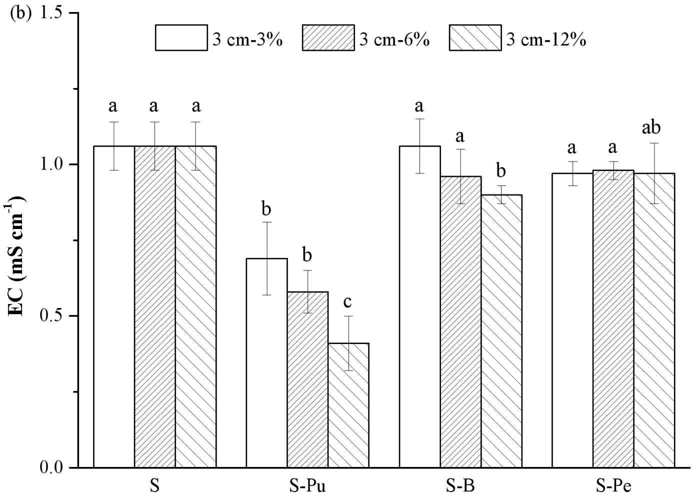


Figure 6-S1 Soil water content at the end of the experiment. Values are mean ± S.E. of 3 replicates. Different letters over the bar indicate significant differences between the treatments according to Duncan's test ($p < 0.05$).


(a)
1.5 cm-3%
1.5 cm-6%
1.5 cm-12%
EC (mS cm^{-1})
0.0
0.5
1.0
1.5
a a a
b b c
a a ab
ab a b
S
S-Pu
S-B
S-Pe


(b)
3 cm-3%
3 cm-6%
3 cm-12%
EC (mS cm^{-1})
0.0
0.5
1.0
1.5
a a a
b b c
a a b
a a ab
S
S-Pu
S-B
S-Pe

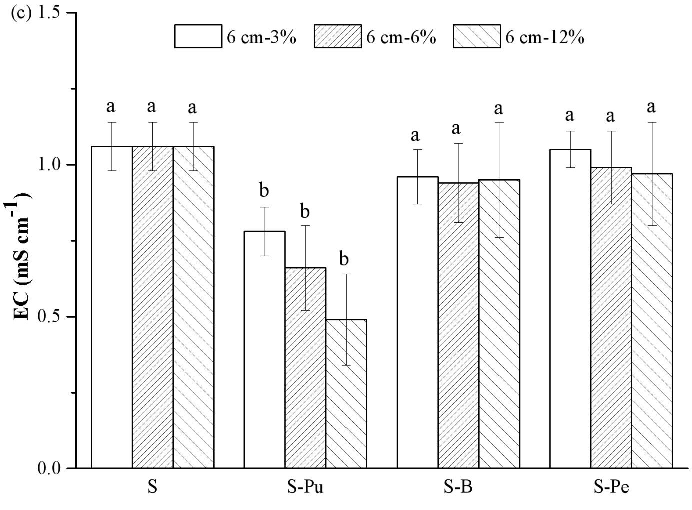

(c)
6 cm-3%
6 cm-6%
6 cm-12%
EC (mS cm^{-1})
0.0
0.5
1.0
1.5
a a a
b b b
a a a
a a a
S
S-Pu
S-B
S-Pe

Figure 6-S2 The electrical conductivity (EC) of sandy soil after the experiment (1:5 w/v ratio). Bar charts showing: (a) sandy soil treated by the amendments with 1.5-cm diameter, (b) sandy soil treated by the amendments with 3-cm diameter, and (c) sandy soil treated by the amendments with 6-cm diameter. Values are means of three replicates. Error bars represent the standard error. Different letters in columns with similar filling pattern indicate significant difference between treatments according to Duncan's test ($p < 0.05$). S, sandy soil; Pu, pumice; B, biochar; Pe, pebble; S-Pu, the residual sandy soil after the removal of pumice; S-B, the residual sandy soil after the removal of biochar; S-Pe, the residual sandy soil after the removal of pebble.

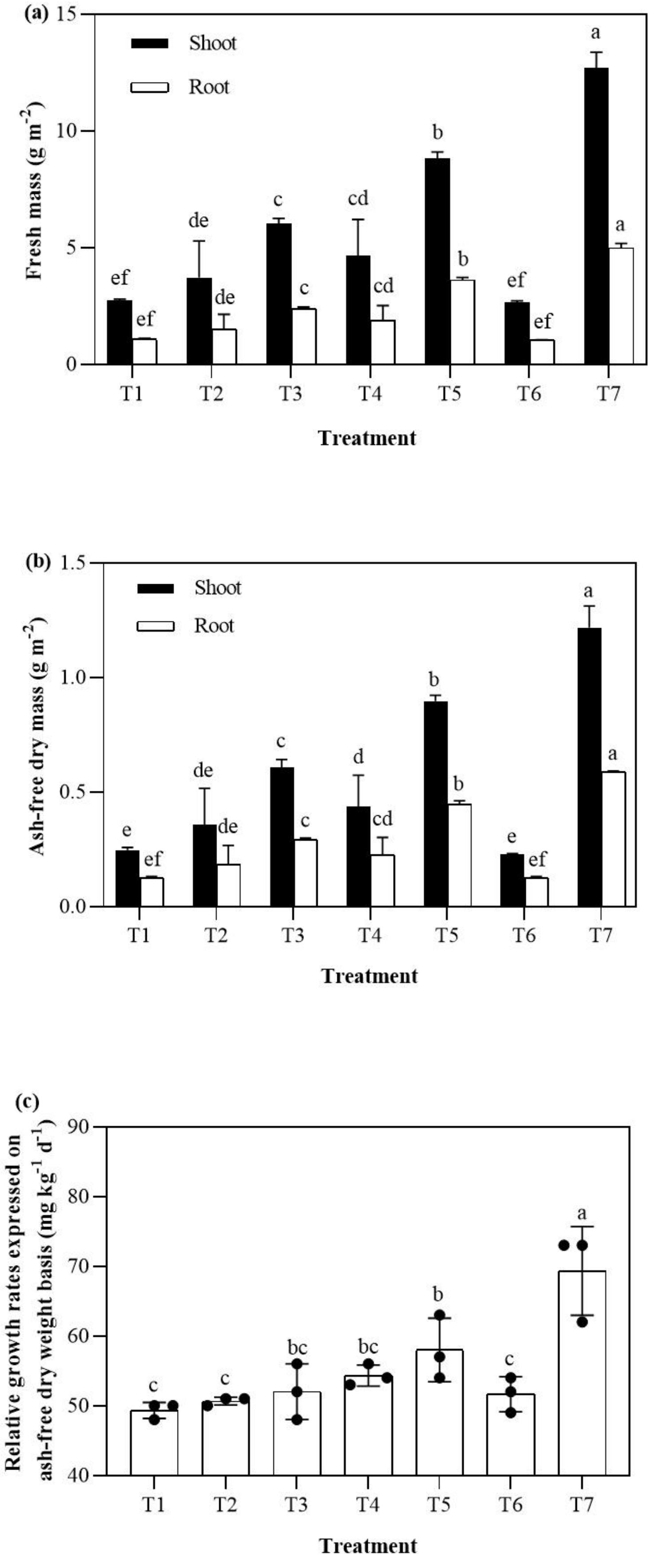

(a)
Fresh mass (g m^{-2})
0
5
10
15
Shoot
Root
ef
ef
de
de
c
c
cd
cd
b
b
ef
ef
a
a
T1
T2
T3
T4
T5
T6
T7
Treatment
(b)
Ash-free dry mass (g m^{-2})
0.0
0.5
1.0
1.5
Shoot
Root
e
ef
de
de
c
c
d
cd
b
b
e
ef
a
a
T1
T2
T3
T4
T5
T6
T7
Treatment
(c)
Relative growth rates expressed on ash-free dry weight basis (mg kg^{-1} d^{-1})
40
50
60
70
80
90
c
c
bc
bc
b
c
a
T1
T2
T3
T4
T5
T6
T7
Treatment

Figure 6-S3 (a) Fresh mass, (b) ash-free dry mass, and (c) relative growth rate expressed on ash-free dry weight basis of lucerne (*Medicago sativa* L.) at final harvest. The study included (i) treatments to which saline water was applied: T1 (sand – positive control), T2 (sand + 3% (v/v basis) PU), T3 (sand + 12% PU), T4 (sand + 3% PU + 2% AL), T5 (sand + 12% PU + 2% AL), T6 (sand + 2% AL), and (ii) a treatment, T7 (sand – negative control), to which deionised water was added. Values are mean ± S.E. of three replicates. Different letters in the same block indicate significant differences between the treatments according to Duncan's test ($p < 0.05$).

References

*Abbas, T., Rizwan, M., Ali, S., Adrees, M., Zia-ur-Rehman, M., Qayyum, M.F., Ok, Y.S., Murtaza, G., 2017a. Effect of biochar on alleviation of cadmium toxicity in wheat (*Triticum aestivum* L.) grown on Cd-contaminated saline soil. Environmental Science Pollution Research 25, 25668-25680.

*Abbas, T., Rizwan, M., Ali, S., Zia-ur-Rehman, M., Qayyum, M.F., Abbas, F., Hannan, F., Rinklebe, J., Ok, Y.S., 2017b. Effect of biochar on cadmium bioavailability and uptake in wheat (*Triticum aestivum* L.) grown in a soil with aged contamination. Ecotoxicology and Environmental Safety 140, 37-47.

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