Seaweed Biochar (Sourced from Marine Water Remediation Farms) for Soil Remediation: Towards an Integrated Approach of Terrestrial-Coastal Marine Water Remediation

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Biochar made from seaweed biomass of marine farms established for water pollutant remediation may be a promising amendment for soil remediation in the same coastal territory. The study aimed to assess the soil Cu-immobilizing, pH neutralizing, and nutrient improvement capabilities of a seaweed biochar when incorporated into degraded soil of the same coastal territory (Puchuncaví District, central Chile). Experimental design considered five treatments; degraded soil of Puchuncaví valley (C-), C- amended with either local seaweed biochar (B), vermicompost (V), or its mixture (BV), and a background soil (C+). Experimental soils were placed in pots and kept in a greenhouse (4 weeks). *Lolium perenne* was then sown and cultivated until week 11. Treatments amended with biochar (B and BV) significantly increased soil pH, available nitrogen and decreased Cu^{2+} ions. These treatments reached very high EC values but had no negative effect on plant yield. Regarding plant growth, V and BV significantly increased biomass, but V resulted in higher yield because of its higher nutritional status. It was concluded that seaweed biochar, made from local seaweed biomass of a coastal marine water pollutant remediation farm, may be an effective soil amendment for degraded soils of the same coastal territory, although its combination with an organic amendment should be considered.

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INTRODUCTION

Globally, coastal zones have long become active for urbanization and industrialization (Halpern *et al.* 2015; Ausili *et al.* 2020). As a result of historical and/or current industrial pollution, both terrestrial and marine ecosystems of many coastal territories have been significantly affected (He *et al.* 2014; Yanes *et al.* 2018; Zhai *et al.* 2020). Generally, remediation actions to reduce environmental risks in these territories are performed independently. For polluted coastal marine waters, passive processes for *in situ* pollutant uptake through biosorption methods have been implemented (de Freitas *et al.* 2019) and offer many advantages (*e.g.*, simple implementation, low operating cost, high efficiency, no additional nutrient requirements, and relatively low energy input) (Michalak *et al.* 2013; Bordoloi *et al.* 2017; Liu *et al.* 2019). In contrast, *in situ* remediation techniques for physicochemically degraded soils, based on the application of soil amendments, are widely implemented because of their fast, low-cost, and easy application (Palansooriya *et al.* 2020). Among other factors, the election of soil amendments depends on the type of pollutants present (*i.e.*, organic and/or inorganic), their bioavailable fraction, and the degree of other physical (*i.e.*, compaction or reduction of organic matter) and/or chemical (*i.e.*, acidification, salinization, nutrient loss) soil alterations (Palansooriya *et al.* 2020). Through delivering cost-effective remediation techniques and fulfilling green and sustainable remediation principles (because of their low life cycle environmental footprints), the use of proper bioadsorbents and soil amendments has been widely used for environmental remediation (Hou and Al-Tabbaa 2014).

Yet, the opportunity remains for an integrated approach of coastal marine water and terrestrial remediation in coastal territories. Specifically, some bioadsorbents generated from coastal marine water remediation could potentially be processed for pollutant removal and thus reused as amendments for soil remediation in the same territory. This approach may not only reduce waste disposal and secondary pollution (normally associated with the reuse of residues) (Shi *et al.* 2018) but may also reduce remediation costs and support socioeconomical development of local communities in the territory. Indeed, emerging post-sorption technologies now enable the manufacturing of value-added key adsorption products that can subsequently be used for/in (i) fertilizers, (ii) catalysis, (iii) carbonaceous metal nanoparticle synthesis, (iv) feed additives, and (v) biologically active compounds (Kumar Reddy *et al.* 2017). These new strategies ensure the sustainable valorization of post-sorption materials (with their ecological affability, biocompatibility, and widespread accessibility) as an economically viable alternative to the engineering of other green chemicals (Kumar Reddy *et al.* 2017; Tawfik *et al.* 2022).

The Puchuncaví District in central Chile serves as an example of a coastal territory where both land (Puchuncaví Valley) and marine (Quintero Bay) ecosystems have been heavily polluted and degraded because of historical and current industrial operations. In fact, this territory is considered an environmental sacrifice zone because of the broad range of industrial activities along its shoreline since the 1960s, which includes the settlement of a copper smelter and a thermoelectric plant (Hormazabal *et al.* 2019). A recent study reported high concentrations of heavy metals in the water column near Quintero bay (Cu: 28 to 741 $\mu g\ L^{-1}$, As: 9 to 348 $\mu g\ L^{-1}$, Cd: 0.091 to 0.243 $\mu g\ L^{-1}$, and Pb: 0.093 to 3.425 $\mu g\ L^{-1}$) with similar concentrations being reported for two sites 5 km (Caleta Horcón) and 19 km (Cachagua) north of the industrial park (Oyarzo-Miranda *et al.* 2020). Furthermore, soils of the Puchuncaví valley have been strongly degraded (both physically and chemically) and characterized as acidic, depleted in organic matter and nitrogen, and as being enriched with metals (*e.g.*, Cu, Zn, Pb, and Cd) and metalloids (*e.g.*, As) (Ginocchio 2000; Ginocchio *et al.* 2004; Neaman *et al.* 2009). As such, several research studies and local government efforts have been directed at coping with the environmental risks of pollutants and soil degradation. Remediation actions for land (Muena *et al.* 2010; Córdova *et al.* 2011; Neaman *et al.* 2012; Ulriksen *et al.* 2012; Pardo *et al.* 2018) as well as coastal marine waters and sediments (Parra *et al.* 2015; Oyarzo-Miranda *et al.* 2020; Latorre-Padilla *et al.* 2021a, 2021b) have been suggested as cost-effective alternatives.

In the last decade, an experimental brown algae (*Macrocystis pyrifera*) seaweed farm had been established at Quintero Bay to encourage *in situ* pollutant (organic and inorganic) remediation of its coastal marine waters. The project was funded by a regional Chilean grant (Fondo de Innovación para la Competitividad [Innovation Fund for Competitiveness], FIC Algas 2017, n° 30397482-0). The species of *M. pyrifera* was selected based on its ability to grow to considerable sizes in a wide range of environmental conditions, representing a great advantage in terms of biomass productivity (Schiel and Foster 2015). Moreover, compared to other brown seaweeds, *M. pyrifera* has a higher capacity to accumulate metals (Davis *et al.* 2003; Latorre-Padilla *et al.* 2021b), which renders its biomass a potentially effective bioadsorbent for *in situ* clean-up of coastal marine waters. Whilst seaweed biomass can normally be used as a raw product for the food, animal feed, cosmetics, and nutraceuticals industries (Rotter *et al.* 2020), pollutant-rich seaweed biomass must be discarded.

Several studies have demonstrated that seaweed biomass may be a promising raw material for the production of biochar (a carbon-rich product produced *via* thermal decomposition under oxygen-limited conditions and at relatively low temperatures) (Chen *et al.* 2015; Roberts *et al.* 2015a; 2015b; 2015c; Cha *et al.* 2016; Contreras-Porcia *et al.* 2018). In recent years, because of its potential use as a soil amendment, biochar has become a subject of important scientific and commercial interest (Guo *et al.* 2020). Several studies have shown that biochar can remediate the physical and chemical properties of degraded soils (Curaqueo *et al.* 2014; Obia *et al.* 2016; Amin *et al.* 2017), which in turn promotes plant development (Al-Wabel *et al.* 2013; Amin *et al.* 2017; Godlewska *et al.* 2017; De Sousa Lima *et al.* 2018). Biochar made from macroalgae biomass has low carbon content and relatively low cation exchange capacity, but high pH (8.0 to 10.1), nitrogen, and extractable phosphate contents (Bird *et al*. 2011). Macroalgal biochars present more similarities to those produced from poultry litter relative to those derived from ligno-cellulosic feedstocks (Bird *et al*. 2011). Due to these positive characteristics, macroalgal biochar has properties that may provide direct nutrient benefits to soils and may be particularly useful for application on acidic soils (Bird *et al*. 2011; Yu *et al*. 2017). However, electrical conductivity (15.3 to 61.2 mS cm^{-1}) and extractable Na (range 141 to 812 cmol(+) kg^{-1}) in biochars from saline macroalgal species is high, unlike freshwater species that have lower values (2.8 mS cm^{-1} and 24 cmol(+) kg^{-1}, respectively) (Bird *et al*. 2011), which may restrict their use as soil amendment. Few studies have assessed the pros and cons of the use of seaweed-derived biochar as a soil amendment for *in situ* soil remediation (Bird *et al.* 2011). Biochar produced from pollutant-rich seaweed biomass (obtained from the Quintero Bay seaweed farms) represents a promising opportunity to implement a low-cost local amendment for degraded soil remediation in the Puchuncaví valley using an integrated bioremediation approach for this coastal territory, as long as its salinity is not a restriction to plant growth.

The primary aim of the present study was to assess the Cu-immobilizing and neutralizing capabilities of seaweed-derived biochar when incorporated into the acidic and metal(loid)-enriched soils of the Puchuncaví valley, to assess improvement of the soil's nutritional content for plants and to assess any impact in soil salinity (based on the results from small-scale and short-term laboratory experiments). Because the organic matter content and nutritional status of the chemically degraded Los Maitenes soil had been very low, the secondary aim of the study was to assess another organic amendment (vermicompost) for soil remediation. The present study represents the first research step towards field site evaluations.

EXPERIMENTAL

Study Area and Soil Sample Collection

Soil samples were collected from the Puchuncaví valley, Valparaíso Region, a semiarid Mediterranean climate-type ecosystem located in the coastal area of central Chile (Fig. 1), with an historical average annual precipitation of 351 mm, mainly collected in winter (May and August) and an average annual temperature of 14.4 °C. Since 1964, soil in this area has been heavily degraded *via* the emission of sulfur dioxide (SO_2) and metal(loid)-rich particulate matter (such as copper, zinc, cadmium, and arsenic) from the Ventanas industrial complex. Whilst environmental regulations (established in the 1990s) achieved a considerable reduction in pollutant emissions, the cumulative effect of more than 35 years of industrial activity in this area resulted in heavily polluted and eroded soils (Ginocchio 2000; Ginocchio *et al.* 2004; Neaman *et. al.* 2009) as well as polluted coastal marine waters (Oyarzo-Miranda 2020).

Using a shovel, two composite topsoil batches (0 to 20 cm depth; n = 10 (totaling 60 kg)) were sampled for use in this study. The first batch (C-) represented chemically and physically degraded soils collected from Los Maitenes, an area located 2 km southeast of the Ventanas industrial complex, known for its soil acidification and high concentrations of Cu, Zn, As, and Cd (Neaman *et al.* 2009; Cárcamo *et al.* 2012; Rueda-Holgado *et al.* 2016). The second batch (C+) represented background soils collected from Maitencillo, a coastal area located 11 km north of Los Maitenes, where the soil has not been affected by atmospheric pollutants derived from the Ventanas industrial complex (Neaman *et al.* 2009; Muena *et al.* 2010). Composite soil samples from both areas were stored in closed polyethylene containers before being transferred to the laboratory where respective samples were sieved to < 2 mm with a nylon mesh and oven-dried at 60 °C for 24 h. Thereafter, samples were manually homogenized, and a batch of each soil type was sent to the Soil Analysis Laboratory of the Pontificia Universidad Católica de Valparaíso, Quillota, Chile for physicochemical determinations. The obtained results are summarized in Table 1.

Table 1. Physicochemical Characteristics of Chemically Degraded Topsoil from Los Maitenes (C-) and Background Topsoil from Maitencillo (C+)

Soil Characteristics	Los Maitenes (C-)	Maitencillo (C+)
Texture	Sandy	Sandy loam
pH	4.1	5.8
EC (dS m^{-1})	0.18	1.00
CEC (cmol kg^{-1})	5.36	6.15
OM (%)	0.73	1.05
N available (mg kg^{-1})	12.9	9.5
P available (mg kg^{-1})	17.7	33.2
K exchangeable (mg kg^{-1})	169	179
Total Cu (mg kg^{-1})	354	27.6
Total Zn (mg kg^{-1})	81.2	174
Total Cd (mg kg^{-1})	<0.004	1.24
Total As (mg kg^{-1})	6.75	16.1

EC, electric conductivity; CEC, cation exchange capacity; OM, organic matter

Fig. 1. Satellite image (Google Earth) and Chilean map showing the Puchuncaví District in central Chile that includes Quintero Bay and the Puchuncaví valley (dotted circle). Seaweed biomass for biochar production was obtained from coastal marine cultivation areas located along Quintero Bay (experimental remediation farm, FIC Algas project). Soil collection areas in the valley included Los Maitenes (degraded soil) and Maitencillo (background soil) sites. The Ventanas industrial complex, established in the 1960s, is indicated by a red box.

Characteristics of Study Soil Amendments: Seaweed Biochar and Vermicompost

The seaweed biochar used in the present study was produced from air-dry *M. pyrifera* biomass. The latter was harvested from individuals that had been cultivated for 120 days in coastal waters of the experimental remediation farm in Quintero Bay (FIC Algas 2017, project n° 30397482-0) and which had been exposed to pollutant (organic and inorganic) emissions from the Ventanas industrial complex (Parra *et al.* 2015). Dried *Macrocystis* biomass was transferred to the Waste and Bioenergy Management Center of Universidad de la Frontera and subjected to a slow pyrolysis process in a specialized furnace with a stainless-steel reactor and two thermocouples. A constant N_2 flow (0.5 L min^{-1}) was used for air displacement. Starting at room temperature, constant biomass heating at a rate of 20 to 50 °C h^{-1} was implemented until a final temperature of 450 °C was reached (Araya *et al.* 2021). A biochar yield of 53.3% was obtained, with an ash content of 69.9%. General characteristics of produced biochar can be found in Araya *et al.* (2021).

Due to the absence of an intensive washing pretreatment of the seaweed biomass or deashing post-treatment, given the prioritization of productivity for commercial purposes (Araya *et al.* 2021), the elevated ash and EC values of biochar obtained in this study had been considerably higher than that of other types of biochar (Tag *et al.* 2016). This is to be expected, since the algae came from a saline environment (Bird *et al*. 2011), finding concentrations of sodium in seaweed biomass between 27 and 55 g kg^{-1} (Neveux *et al*. 2014). However, washing of seaweed biomass results in a reduction of the sodium concentration by approximately 95% (Neveux *et al.* 2014).

Metal(loid) contents of seaweed biochar and other characteristics are shown in Table 2. Noteworthy was the observation that even though seaweed biomass used for biochar production in the present study came from a highly contaminated environmental matrix (Oyarzo-Miranda *et al.* 2020), metals adsorbed in the seaweed biomass subsequently remained in the tars of the pyrolysis process (Araya *et al.* 2021).

In the present study, to better cope with low levels of OM and nutrient soil deficiency of degraded Los Maitenes soil (C-), commercial vermicompost (ANASAC) was used as a secondary soil amendment. The selected vermicompost had a pH of 7.7, EC of 6.53 dS m^{-1}, OM content of 14%, and an N-nitrate content of 118 mg kg^{-1} as stated in the label.

Table 2. Chemical Characteristics of Seaweed Biochar

Seaweed Biochar Characteristics	Seaweed Biochar
pH	11
EC (dS m^{-1})	27.4
CEC (cmol kg^{-1})	40.2
OM (%)	29.5
N (%)	2
Cu (mg kg^{-1})	11
Zn (mg kg^{-1})	21
Cd (mg kg^{-1})	10.6
Ni (mg kg^{-1})	8
Pb (mg kg^{-1})	4.4
As (mg kg^{-1})	1.03

EC, electric conductivity; CEC, cation exchange capacity; OM, organic matter

Experimental Design

A total of five soil treatments were assessed in the present study, the background soil of Maitencillo (C+), the physicochemical degraded soil of Los Maitenes (C-), and three experimentally amended conditions for the C- soil (Table 3). The latter was designated as B (seaweed biochar), V (vermicompost), and BV (seaweed biochar and vermicompost). The treatments consisted of six replications each and thus totaled 30 experimental units. To assess the effect of biochar and/or vermicompost in the physico-chemical properties of C- soil, experimental soil mixtures using single and combined amendments were prepared (as shown in Table 3). Batches of C- soil were mixed with 1% seaweed biochar and/or 3% vermicompost (dry weight basis, dw), which had been equivalent to doses of 22.3 ton ha^{-1} and 67.05 ton ha^{-1}, respectively. The biochar dosage was determined *via* laboratory assays, aimed at neutralizing the C- soil (up to pH 6.5), while the vermicompost dosage was defined based on previous area-related studies (Goecke *et al.* 2011; Cárcamo *et al.* 2012; Neaman *et al.* 2012). A fifth treatment, combining both amendments at their respective doses, was also incorporated (Table 3).

Table 3. Soil Treatments Used to Assess the Effects of Seaweed Biochar and Vermicompost on the Remediation of Chemically Degraded Los Maitenes Soil (C-)

Treatment	Biochar (%)	Vermicompost (%)
C-	0	0
C+	0	0
B	1	0
V	0	3
BV	1	3

Single and combined treatments of B and V were based on dry weight percentages and background soil from Maitencillo (C+) was included for comparison

Batches (6 kg, dry weight) of each experimental soil were prepared by adding the substrates in 10-L polyethylene bottles and mixing the components in an automatic roller (Tecco YGR) at 11 rpm for 20 min. The gravimetric water content at 100% field capacity of all experimental soils (amended and not amended) was estimated according to the method by Klute (1986) to define irrigation regimes for weight loss. Thereafter, the soil from each experimental soil was poured into six 1-L plastic pots (800 g of soil per pot) with holes for drainage. Pots with experimental soils (total of 30 experimental units) were randomly placed on benches in a greenhouse under a controlled temperature (26 ± 2 °C) and natural light and photoperiod (spring period). Positioning of pots was randomized once a week to avoid edge effects, and they were watered at 70% of field capacity every other day over 11 weeks. As suggested in the literature, soil chemical equilibration was supported during an initial 4-week period (España *et al.* 2019). Then, at the beginning of the fifth week, 0.6 g of *Lolium perenne* var. Belinda seeds (a species commonly used for assessing soil acidity and metal toxicity) were sown in every pot (Arienzo *et al.* 2004).

During the 1st, 4th, and 11th weeks of the assay, following the methodology described by Vulkan *et al.* (2000), 5 to 7 mL aliquots of soil pore water had been collected from all pots using Rhizon® pore water samplers (Rhizosphere Research Products, Wageningen, Netherlands). These samples were stored in acid-washed polyethylene vials and were analyzed for pH (combined pH electrode, Sensorex 120C), electrical conductivity (EC) (conductivity-meter, Schott Gerate CG858), and ionic copper (Cu^{2+}) (selective Cu ion electrode, Orion, model 9629 BN; calibrated using a diamino acetic acid solution) (Rachou *et al.* 2007). pCu^{2+} (Cu activity) was calculated from the obtained Cu^{2+} values (according to Eq. 1):

$$pCu^{2+} = -\log [Cu^{2+}] \qquad (1)$$

By week 11, the root and shoot biomass of *L. perenne* in each pot had been harvested. Aerial biomass was washed with deionized water and blotted dry with absorbent paper prior to fresh biomass determination. Roots were separated from soils by spraying tap water (at a low pressure) onto the roots over a fine-mesh sieve (allowing for the removal of soil while retaining thin roots). Root and aerial biomass were oven-dried to a constant weight (dried at 45 °C in an air-forced cabinet for 72 h) before determining dry weight biomass.

Statistical Analysis

A two-way analysis of variance (ANOVA) was performed (with a Tukey HSD *posteriori* test) to compare differences in chemical properties of pore water among treatments and time. A one-way ANOVA was used to contrast the root and shoot biomass of *L. perenne* among treatments. When data did not meet conditions to perform parametric tests, logarithmic transformations, as described in Zar (1984), were performed. All data processing was performed using the SPSS 23 (IBM, Armonk, NY, USA) and Infostat (UNC, 2020p, Córdoba, Argentina) statistical programs.

RESULTS AND DISCUSSION

Experimental Soils: Physicochemical Characteristics

As expected, the most successful neutralization of C- soil was obtained after biochar incorporation (with or without vermicompost) (Table 4). At the tested doses of the present study (Table 3), incorporation of vermicompost also reduced soil acidity, although less efficiently than seaweed biochar. Indeed, incorporation of biochar increased the pH of C- soil by 2.4 units (up to pH 6.6) followed by incorporation of vermicompost by 2.0 units (up to pH 6.1) (Table 4). This was unsurprising because biochar is known for its neutralization effects that may be attributed to its alkalinity (Ding *et al.* 2017; Yu *et al.* 2017; Moore *et al.* 2018). Soil neutralization *via* these soil amendments could furthermore be associated with the presence of phenolic, carboxyl, and hydroxyl functional groups in both vermicompost and biochar (which react with soil H^+ and thereby reduce H^+ concentrations and increase the pH level) (Ding *et al.* 2017; Oliveira *et al.* 2017; Yu *et al.* 2017; Araya *et al.* 2021).

Due to the high salinity of the seaweed biochar (27.4 dS m^{-1}; Table 2) of the present study, it was not surprising that biochar amended C- soils showed high EC soil values (with or without vermicompost) (Table 4), even at the low (1%) dose applied to C- soil. Incorporation of vermicompost did not affect EC values (Table 4). The CEC of amended soils (B, V, and BV) was lower than that of C- soil (with values ranging from 3.22 to 4.11 cmol kg^{-1}). Due to the dilution effect of adding amendments (particularly in the case of vermicompost), the total metal(loid) concentrations of amended soils were slightly reduced (Table 4).

Table 4. Initial Physicochemical Parameters of Experimental Soils

Treatment*	pH	EC	CEC	OM	Available Nutrients (mg kg^{-1})			Total Metal(loid) (mg kg^{-1})		
		(dS m^{-1})	(cmol kg^{-1})	(%)	N	P	K	Cu	Zn	As
C-	4.1	0.18	5.36	0.73	9.5	33.2	179	354	174	16.1
C+	5.7	1.0	6.15	1.05	12.9	17.7	169	27.6	81.2	6.8
B	6.6	21.2	3.61	0.73	15.9	62.4	1994	315	142	13.3
V	6.1	0.88	3.22	1.21	20.7	51.2	556	283	133	11.2
BV	6.6	20.4	4.11	1.21	17.5	73.6	1606	323	146	13.6

* Codes explained in Table 3
EC, electric conductivity; CEC, cation exchange capacity; OM, organic matter

Lastly, incorporation of biochar or vermicompost improved nutritional content of C- soil, but only vermicompost improved OM content (1.7-fold) of C- soil (to even higher values than that of the C+ soil) (Table 4). Specifically, available N, P, and K levels in C- soil increased 1.7-, 1.9-, and 11.1-fold after incorporation of biochar and 2.2-, 1.5-, and 3.1-fold after incorporation of vermicompost (Table 4). Therefore, available N increased much more (2.2-fold) after vermicompost incorporation than with biochar incorporation alone (1.7-fold). Findings from the present study agreed with previously described results regarding selected soil amendments (Amoah-Antwi *et al.* 2020; Kheir *et al.* 2021).

Experimental Soils: Pore Water Chemistry

Soil neutralization was rapidly achieved after the application of both amendments and significantly increased with the progression of time as shown by soil pore water values (Table 5). Specifically, B and BV treatments reached the highest pH values, with only slight variation detected throughout the 11 weeks. The pH value in vermicompost treatments (V and BV) also increased (up to pH 6.51 by week 11), although it should be noted that the initial pH of 5.7 had been nearly one unit higher than that of C- soil (Table 5). Whilst a gradual pH increase over time was observed in the pore water for all treatments, the magnitude of this increase varied among the treatments and the different sampling dates (Table 5). The C- soil showed the lowest pH values throughout the experiment and little variation was found throughout subsequent weeks. It is known that several factors may influence long-term soil pH changes (*e.g.*, the microbial decomposition of OM and the nitrification process) (Cárcamo *et al.* 2012), as observed in soil pore waters of the present study.

Table 5. Variation of pH, EC, and pCu^{2+} in Experimental Soils over Time (during weeks 1, 4, and 11)

Treatment / Week	pH			pCu^{2+}			EC (mS cm^{-1})		
	1	4	11	1	4	11	1	4	11
C-	4.6 ± 0.3	4.7 ± 0.2	5.1 ± 0.3	5.7 ± 1.1	5.4 ± 0.6	2.6 ± 0.2	0.5 ± 0.1	0.5 ± 0.1	0.3 ± 0.1
C+	5.8 ± 0.5	6.2 ± 0.2	7.0 ± 0.3	9.6 ± 1.9	9.2 ± 0.9	8.2 ± 0.4	1.3 ± 0.2	1.7 ± 0.1	0.3 ± 0.3
B	7.2 ± 0.1	7.3 ± 0.1	7.4 ± 0.2	20.2 ± 1.3	20.7 ± 1.1	14.0 ± 2.0	> 20	> 20	14.9 ± 2.4
V	5.7 ± 0.5	5.9 ± 0.4	6.5 ± 0.5	8.7 ± 1.5	7.8 ± 1.7	6.1 ± 0.9	1.2 ± 0.5	1.3 ± 0.4	0.4 ± 0.2
BV	7.3 ± 0.2	7.3 ± 0.1	7.6 ± 0.2	17.4 ± 0.4	16.9 ± 1.1	11.7 ± 0.6	> 20	16.9 ± 1.6	14.6 ± 2.9

Source of Variation	F	P	F	P
Treatment	375.78	< 0.001	748.8	< 0.001
Week	46.92	< 0.001	191.16	< 0.001
Interaction	3.87	< 0.001	8.85	< 0.001

Data are presented as means with standard deviation. Electrical conductivity (EC) that exceeded the measurement capacity of the conductivimeter is expressed as > 20. F and P values of two-way ANOVA for pH and pCu^{2+} levels are provided.

Biochar amended C- soil (B and BV) reached very high EC values (> 20 mS cm^{-1}), resulting in saline pore water values (particularly at the onset of the assay) (Table 5). While these EC values tended to decrease with time (in all treatments), EC values of the B and BV treatments were still higher than 14 mS cm^{-1} by week 11 (indicating high salt concentrations) (Table 5). Generally, the high EC values of biochar can be explained by its high ash content, high surface-area-to-volume ratio (Ullah *et al.* 2020), and a particularly high Na concentration when of marine origin (Bird *et al.* 2012). All three characteristics were true for the seaweed biochar used in the present study. Therefore, the increase of EC in biochar-amended soils could be explained by either the high contribution of ionic nutrients (that can promote plant growth) or the presence of cationic and anionic salts (that can cause toxicity symptoms in plants), which suggests that the present´s study increase in pore water EC rather reflects the increase in nutrient ions (such as K, Mg, or Ca). However, to test this hypothesis, analyses to quantify seaweed biochar salt concentrations and to assess its potential toxicity to plants are needed.

Copper activity (pCu^{2+}) values significantly increased after the incorporation of amendments (B, V, and BV), which suggests an important decrease in soluble Cu concentrations in C- soil (Table 5). As expected, the incorporation of biochar had been more effective in decreasing soluble Cu levels (3.8-fold) than that of vermicompost alone (1.4-fold). However, pCu^{2+} values also significantly decreased for all treatments over time, indicating an overall increase in Cu solubility over time irrespective of treatment (Table 5). Yet, the biggest changes were detected for B and BV treatments, where pCu^{2+} decreased from 20.24 to 13.95 and from 17.41 to 11.73, respectively (Table 5). The magnitude of this decrease was 3 to 5 times higher than that of the C- soil (which only decreased from 5.71 (week 1) to 2.64 (week 11), suggesting that the incorporation of biochar significantly decreased Cu solubility in the chemically degraded soil, at least for the duration of this assay. The effect of biochar on metal availability depends on its original feedstock and its processing temperature (Wu *et al.* 2017; Araya *et al.* 2021). As such and because of contrasting results, the potential of biochar to modify soil metal availability has been widely discussed. Some authors have found that biochar reduces the mobility and bioavailability of metals (mainly ascribed to its liming effect) (Jones *et al.* 2016; Wu *et al.* 2017; O'Connor *et al.* 2018), whereas others have found that metal(loid) concentrations in pore water of biochar amended soils may increase. For example, Beesley *et al.* (2010) found that Cu and As concentrations in pore water of biochar amended soils increased more than 30-fold, which could be explained by a significant increase of Dissolved Organic Carbon (DOC). In general, biochar produced at < 500 °C has a high DOC content that could, in turn, promote the solubilization and mobilization of Cu into soil pore water, due to the formation of Cu-DOC complexes (Ahmad *et al.* 2014; Hameed *et al.* 2019). Yet, in the present study, Cu activity significantly decreased in soil pore water after incorporation of seaweed biochar with C- soil (the biochar having been produced at < 500 °C). Moreover, this effect lasted 11 weeks after biochar application.

Plant Growth Parameters

Shoot biomass (dry weight basis, dw) of ryegrass plants that had been cultivated in experimental soils varied significantly among the treatments ($P < 0.001$) (with the lowest value recorded for C- soil (0.75 g) and the highest value recorded for V treatment (2.52 g) (Fig. 2a). All amended C- soils (B, V, and BV) showed significantly higher shoot biomass than that of C- soil, although, unexpectedly, B and BV treatments were not statistically different to the C+ soil (as was seen for V treatment) (Fig. 2a). Similar to shoot biomass, all amendments significantly increased root biomass (dw) compared to that of the C- soil ($P < 0.001$) (Fig. 2b), although none were statistically different from C+ soil (Fig. 2b). Pearson single correlations among plant biomass and soil pore water parameters (pH, EC, and pCu) showed positive and statistically significant correlations among root biomass and pH ($r = 0.53$) as well as shoot biomass and EC ($r = 0.43$). No single correlation of significance had been detected among pCu and *L. perenne* shoot or root biomass.

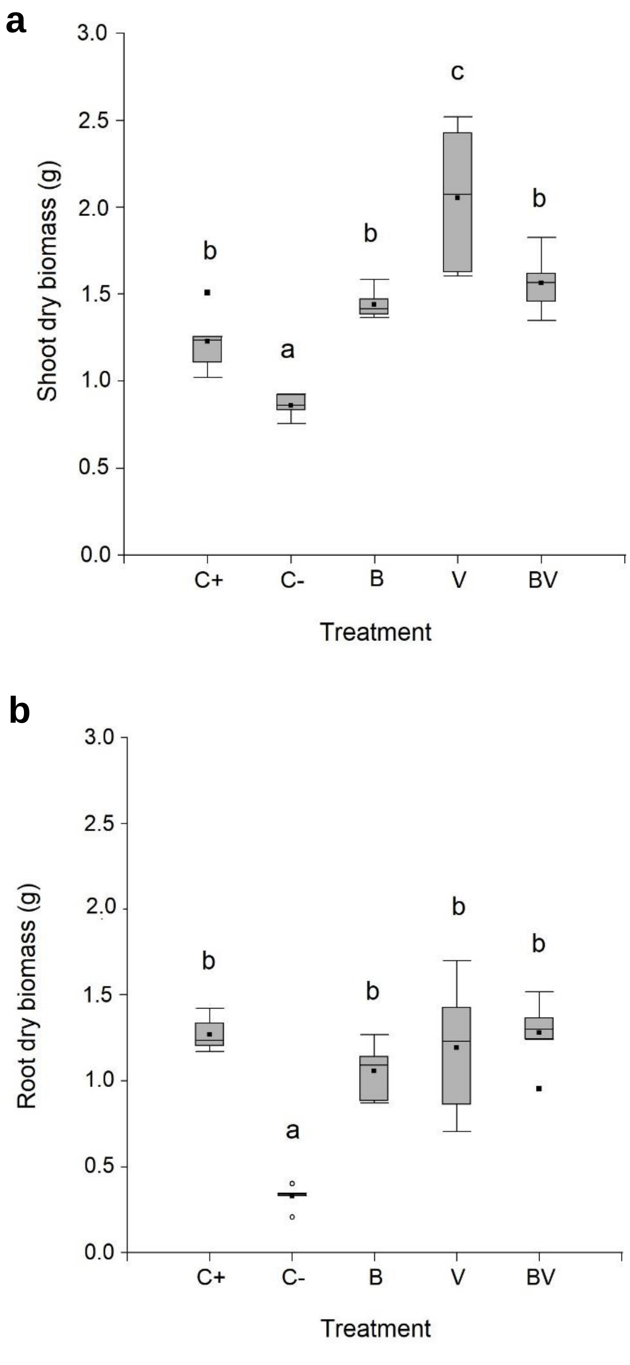

Fig. 2. Variation of shoot (a) and root (b) dry biomass of *Lolium perenne* plants grown in C- and C+ soils and amended C- soils (B, V, and BV) (n = 6). Letters indicate significant differences among treatments according to a Tukey HSD test ($P < 0.05$).

Seaweed biochar and/or vermicompost incorporation to C- soil resulted in a positive and significant response for dry biomass of *L. perenne*, with similar (B and BV) or even higher (V) yields than the C+ (background) soil. These results suggest that, at the experimental dosage tested, the use of both soil amendments had been effective to restore the soil chemistry of C- soils (discussed above) and to sustain normal growth of the indicator plant. For vermicompost (V) incorporation, shoot yield was even higher than that of the background soil. These results agreed with previous findings that biochar (Abd El-Azeem *et al.* 2013; Roberts *et al.* 2015b, 2015c; Godlewska *et al.* 2017) and vermicompost (Kheir *et al.* 2021) may be used as soil amendments for the remediation of chemically degraded soils. Changes in metal and nutrient availability are mainly governed by changes in soil pH (González *et al.* 2015). Because biochar tends to alkalize soils, it can reduce metal availability. In addition, nutrient availability could be reduced if the amendment changed the soil pH beyond its optimal range (5.5 to 6.8) (Lehmann *et al.* 2015). For example, N, K, Ca, and Mg deficiencies can occur when the pH goes below the optimal range, whereas the solubility of Fe, P, Mn, Zn, and Cu can decrease when the pH goes above the optimal range (Cortés-D *et al.* 2013). In this study, soil pH in the optimum range was achieved by incorporating vermicompost with acidified soils. However, biochar application then increased soil pore water pH above 6.8, which might explain its lesser effect on plant dry biomass.

Some studies have suggested that, while biochar promotes metal immobilization, it may also decrease the availability of macro and micro-nutrients (resulting in nutrient deficiencies for the plant). For example, a study by Rees *et al.* (2015) on the cultivation of *L. perenne* and *Noccaea caerulescens* illustrated that biochar incorporation with acidic soils improved the nutritional condition of the soil and decreased metal solubility. Yet biochar incorporation with soils of a higher pH decreased nutrient availability (mainly due to soil alkalization and changes in negative exchange sites for metal cations and nutrients) (Rees *et al.* 2015). The relationship between pH and biochar exchange sites was also studied by Gang *et al.* (2019), who found that there are pH ranges in which the nutrients provided by the biochar may become more/less available. For example, when the pH of an acidified soil increases, the adsorption of NH_4^+ also increases (due to the increase of negative charges on the substrate). In contrast, when soil pH increases above 8, NO_3^- adsorption decreases (because the negative charge of OH^- binds to the positive charges on the surface of the biochar) (Gang *et al.* 2019). As a result, the combined use of biochar with other amendments has been recommended to achieve the reduction of metal availability whilst contributing to soil fertility and favoring plant growth (Wu *et al.* 2017; Xu *et al.* 2017). For example, a study by Wang *et al.* (2016) found that the combination of compost and biochar resulted in significantly greater benefits than single biochar when it came to fresh root and shoot biomass of mung bean (*Vigna radiata*) plants. Yet, in the present work, the combined incorporation of seaweed biochar and vermicompost (BV) did not induce a better plant response (at least not with the tested doses).

It is also important to note that elevated EC values of B and BV treatments had no relevant effects on plant yield. It is well known that potential plant toxicity, based on high EC soil values, depends on several factors related to salt concentration and composition (*e.g.*, having high cation (K, Mg, Na), anion (NO_3, SO_4, Cl), or other ion (Mo, Al, and B) concentrations) (Wallender and Tanji 2011). In this study, the high macronutrient contribution of biochar suggests that its cationic component may be contributing to its high EC, which would thus not be toxic to the organisms growing in the soil. Generally, the high EC values of biochar can be explained by its high ash content, a high surface-area-to-volume ratio (Ullah *et al.* 2020), and a particularly high Na concentration when of marine origin (Bird *et al.* 2012). All three characteristics were true for the seaweed biochar used in the present study. Therefore, the increase of EC in biochar amended soils could be explained by either the high contribution of ionic nutrients (that can promote plant growth) or the presence of cationic and anionic salts (that can cause toxicity symptoms in plants), which suggests that the present study's increase in pore water EC rather reflects the increase in nutrient ions (such as K, Mg, or Ca). However, to test this hypothesis, analyses to quantify seaweed biochar salt concentrations and to assess its potential toxicity to plants are needed.

Incorporation of selected seaweed biochar and/or vermicompost with degraded soil of Los Maitenes (C-) proved to be effective for the improvement of relevant physical (OM) and/or chemical soil parameters (pH, Cu availability, and macronutrient availability), and subsequently allowed for proper *L. perenne* growth (at least over the short term of 11 weeks). Findings from the present study thus agreed with previously described results regarding soil amendments (Amoah-Antwi *et al.* 2020; Kheir *et al.* 2021). The findings furthermore suggested that the use of seaweed biochar as a soil amendment might be more effective than vermicompost for potential *in situ* and large-scale soil remediation in the Puchuncaví valley (inducing chemical improvements at a third of the application dosage). Indeed, while incorporated at a lower dose than vermicompost, seaweed biochar resulted in significantly higher soil neutralization and reduced free Cu^{2+} ions in soil pore water (even 11 weeks after its application). Whilst the present study represents a promising step toward field site evaluations, lower doses of vermicompost or other locally available organic amendment candidates must first be considered in similar laboratory-scaled experiments.

CONCLUSIONS

1. Seaweed biochar, produced at a slow pyrolysis temperature (450 °C) from *M. pyrifera* macroalgae biomass (grown at an experimental remediation farm in Quintero Bay), proved to be an effective amendment for remediation of degraded soils from the Puchuncaví valley under laboratory controlled conditions. At a low application dose (1%), it effectively increases pH, neutralizes the soil, and immobilizes its Cu ions, whilst improving macronutrient levels over the short-term period of 11 weeks. These achieved soil improvements were able to restore indicator plant (*L. perenne*) yield levels to that of the background soil (irrespective of the soil salinization detected after biochar incorporation).
2. Although seaweed biochar was effective in increasing soil pH and, therefore, reducing both soil acidity and Cu solubility in degraded soil of Los Maitenes, the authors recommend the combined use with vermicompost, or another organic amended, to better contribute to restore the soil OM levels and soil fertility and thereby favor plant growth. This approach could be particularly useful if aided phytostabilization with native plants is the preferred technique to encourage *in situ* soil remediation.
3. The positive experimental results obtained under laboratory-controlled conditions in the present study show the potential of an integrated terrestrial-coastal marine water remediation approach for the Puchuncaví District. However, further remediation studies under field conditions are needed as well as project evaluations and assessments of economic feasibility.

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