Mineral Composition of Subcritical Water Extracts of Saccorhiza Polyschides, a Brown Seaweed Used as Fertilizer in the North of Portugal

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Abstract: The present work aimed at studying Saccorhiza polyschides extracts obtained by subcritical water extraction as a potential source of essential macro and trace elements, aiming for its potential application as a biofertilizer. The mineral composition, as well as sulfate, chlorine and iodine, total organic matter, and total nitrogen content, were determined on the extracts obtained from seaweeds harvested during low tide at the northern Portuguese coast. The selected parameters are important for a biofertilizer. Among the macronutrients, the most abundant was K (15.7 ± 0.2 g/L), followed by Na (5.46 ± 0.11 g/L), S (1.52 ± 0.06 g/L), Ca (1.09 ± 0.11 g/L), and Mg (1.02 ± 0.08 g/L). Several important micronutrients (Zn, B, Cl, P, Mo, V, Se, and I) have also been found in the extracts. The total organic matter was 34.1 ± 0.3 g/L. The extracts present low levels of toxic compounds such as Ni, Cd, and Pb. Considering the composition of the obtained extracts, these can find application in the development of fertilization products. The composition of subcritical water extracts of S. polyschides suggests that they may have important characteristics as a biofertilizer and can be an option in biofortification experiments with essential nutrients. The method can be easily scaled up which makes it attractive for agricultural applications.

Keywords: Saccorhiza polyschides; Subcritical water extraction; macronutrients; micronutrients; biofertilizer; micronization

1. Introduction

Seaweeds are currently used in many coastal countries as human food, in animal feed formulation, and as fertilizer in agriculture [1–3].

The use of seaweeds as plants’ source of organic matter and nutrients is related to earlier seed germination, improved crop performance and yield, increased resistance to biotic and abiotic stress, and enhanced postharvest shelf-life of perishable products [4–6]. Seaweeds can be either directly...
applied in the soil or used as compost to improve soil fertility and the productivity of crops [2,4,7], but potential negative impacts related to salinity, sand, and heavy metal content must be taken into account [8]. A potentially advantageous alternative is the use of seaweed extracts as fertilizers [4,5,9]. Seaweed extracts are known to contain enriched minerals and trace element mixtures in a soluble form, very convenient for soil or foliar application, and present superior performance when compared to conventional chemical fertilizers [3,4,10]. The mechanism by which these extracts affect cellular metabolism of plants is based in the presence of macro and micronutrients, amino acids, vitamins, and other substances, including an eventual synergistic action of the different components [3,11].

It is well known that macro and microminerals are essential to soil fertility and plant development [12]. Seaweed extracts can be a rich source of N, K, and P, as well as trace elements like Zn, Mn, Mg, or Fe [13]. Saravana et al. [10] studied the chemical composition of aqueous extracts of *Saccharina japonica* obtained with pressurized hot water and determined the extraction yield, total organic content, mineral composition, and other nutrients’ content. The authors found Ca, Mg, P, K, and Na as the main macrominerals, and Fe, I, Mn, Zn, and Al as the principal microminerals. Uthirapandi et al. [14] treated brown and green seaweeds with boiling water for 1 hour, and the obtained extracts were characterized regarding Na, Mg, K, Fe, Mo, and N content. K and Na were the main minerals present in all samples. Godlewksa et al. prepared seaweeds extracts using an aqueous solution with different pH [15], at room or boiling temperature [16] and compared its Ca, K, Mg, Na, P, S, B, Cu, Fe, Mn, Mo, Si, and Zn content. In all extracts, Na, K, and Mg were the minerals present at higher concentrations, and the higher amounts were present when using water at pH 7 and higher temperatures. Michalak et al. [17] used microwave-assisted extraction at different temperatures for preparing a seaweed extract with “biostimulant” properties and also determined its Ca, K, Mg, Na, P, S, B, Co, Cu, Fe, Mn, Mo, Ni, Si, and Zn content. In all the extracts, Na, K, and Ca were the minerals present at higher concentrations. Generally, these studies show that increasing the extraction temperature leads to higher mineral concentration in the final extract [15–17]. Another conclusion is that seaweed extracts have in common higher levels of Na, K, P, Ca, and Mg, and its levels are related to the raw material and the extraction method [15–17]. Lotze et al. [18] determined the nutrient composition of three commercial seaweed biostimulants. The macrominerals present at higher concentrations were P, K, and Na. The method of preparation of these biostimulants was not discussed. A biostimulant can be described as any biological ingredient that aids plant growth, such as humic acids, biochemical materials, microbial inoculants, fulvic acids, amino acids, and seaweed extracts [4,5]. Seaweed extracts are being used widely as plant-biostimulants in horticultural crops since they impart abiotic stress tolerance and improve yield and shelf-life of produce [5].

Currently, the main issue in seaweed extracts manufacturing is the development of efficient, solvent-free methods, using mild processing conditions to prevent biologically active compounds from degradation [13,19]. Seaweed extracts to be used as fertilizer can be obtained through different techniques, such as ultrasound-assisted, microwave-assisted, enzymatic, supercritical fluid, and subcritical water extraction [6,9,13,16,17]. Supercritical water extraction (SWE) has been increasingly used and improved [20,21], being considered a green technique concerning energy spending and the use of organic solvents. The obtained extracts have advantages in terms of safety, without the need for a solvent removal step, and are highly compatible with both the soil and plants. SWE is a micronization technique, usually performed at temperatures lower than 220 °C to avoid degradation of compounds [22]. It improves the disruption of cell membranes’ rate and release of compounds from the biological matrices when compared with traditional milling, thermal recrystallization, spray drying, recrystallization using solvent evaporation, and supercritical antisolvent (precipitation) techniques [23].

*Saccorhiza polyschides*, a brown seaweed, is a fast-growing, annual, and opportunistic species commonly found in European coastlines, and one of the most abundant seaweeds in the Portuguese northwest seashore [24]. The large sporophytes are located on the rocks from May until late summer, when they start to decay, leaving behind the bulbous holdfast [25,26].
In Portugal, the use of seaweeds as fertilizer is most common in the northern area. In August and September, seaweeds are harvested during low tide, stacked in piles, and placed to dry under the sun [3,27,28]. This procedure, however, takes too much time, requires large areas of exposure under the sun, and causes fly infestations in the surrounding area during the full bathing season.

There are already several commercially available seaweed extracts for use in agriculture [9], but none are produced from *S. polyschides* or prepared using SWE. This work aimed at the application of SWE to prepare *S. polyschides* extracts and the study of its composition regarding the macro and microminerals, total organic matter, nitrogen, sulfur, chloride, and iodine concentrations in order to assess its potential application as a biofertilizer.

2. Materials and Methods

2.1. Reagents

Sodium sulfate anhydrous 99.99% and nitric acid 65%, both Suprapur®, were from Merck (Darmstad, Germany). Potassium nitrate 99.0% and tetra-ammonium cerium (IV) nitrate 98.0% were acquired from Sigma-Aldrich (Darmstad, Germany). Potassium iodide and orthophosphoric acid 85%, both for analysis grade, were from Pronalab (Tlalnepantla, Mexico) and Panreac (Barcelona, Spain), respectively. Other reagents used were silver nitrate 99.8%, from Fluka (Seelze, Germany) and arsenic trioxide 99.5%, from Riedel-de Haën (Seez, Germany). For Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis, a multi-elemental standard solution was acquired from Merck (Darmstadt, Germany). An additional standard solution of P was obtained from Reagecon (Shannon, Ireland). Calibration standards for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis were prepared from a 10 mg/L multi-element standard solution (PlasmaCAL SCP-33-MS), from SCP Science (Baie-D’Urfé, Canada). The internal standard solution was prepared by appropriate dilution of AccuTrace® ICP-MS-200.8-IS-1 solution (100 mg/L of Sc, Y, In, Tb, and Bi), obtained from AccuStandard® (New Haven, CT). All aqueous solutions were prepared using ultrapure water (resistivity >18.2 MΩ cm at 25 °C) obtained from a Millipore (Burlington, MA, USA) Simplicity 185 system.

2.2. Seaweeds Collection and Preparation

*S. polyschides* seaweeds were collected in August from Atlantic Ocean coastal waters, at Angeiras, NW region of Portugal (41°16’03.8”N 8°43’37.3”W), during low tide. At the laboratory, seaweeds were washed with abundant tap water. After drying at 60 °C until constant weight (approximately 96 h), the material was ground and sieved to less than 2 mm and kept in a dry and dark environment until further processing. The seaweeds presented a water content of 89.5% ± 1.2%.

2.3. Subcritical Water Extraction

SWE was performed in a homemade extractor with an internal volume of 1.7 L according to the optimized procedures (solvent/sample ratio, temperature, pressure, and extraction time) and apparatus previously described [21]. A screening to assess the best extraction condition was made analyzing Na, K, Mg, and Ca (data not shown). The extracts that presented the higher amount of these compounds were prepared with solvent to sample ratio 1/100, pressure 30 bar, temperature 180 °C, and extraction time of 30 min to obtain high extraction efficiency [22]. In the experiments, 10 g of sample was mixed with 100 mL of distilled water, and the extraction vessel was pressurized with nitrogen to prevent possible oxidation. The agitation frequency was set at 3 Hz. Then, the extraction vessels were cooled and depressurized, and the obtained extracts were filtrated and stored in a dark place at 4 °C until analysis. The extraction procedure was performed in duplicate for each specimen.
2.4. Dry Residue

The dry residue of the extract was determined in an oven at 105 °C. The determination was performed in duplicate. The dry residue of the extract was 5.27% ± 0.05%.

2.5. Organic Content

The determination of organic content was performed in the dry residue, according to Bragança et al. [29]. Briefly, a dry oxidative combustion procedure in a Shimadzu (Kyoto, Japan) total organic carbon (TOC) analyzer (model VCSN), equipped with a solid sample module (SSM-5000A) was used. The CO\textsubscript{2} released during the assay was carried by synthetic airflow to the non-dispersive infrared (NDIR) gas analyzer for detection. For total carbon (TC) determination, the sample was heated to 900 °C in the presence of oxygen. For inorganic carbon (IC) determination, the samples were previously acidified with 0.250 mL of orthophosphoric acid (85% m/m), and the analyses were performed at 200 °C. TOC was calculated as the difference between TC and IC. All determinations were made in triplicate. The determination of total organic matter (TOM) was based on the work of Jiménez and García [30], who proposed an empirical predictive equation: TOM = 1.135 + 1.803 TOC, to calculate the organic content of organic wastes.

2.6. Chloride and pH Determination

Potentiometric measurements were performed using a Crison (Barcelona, Spain) micro pH 2002 at 20 °C. The pH was determined with a Crison combined glass electrode. A potentiometric titration using a combined silver electrode (Ag-Titrode, Metrohm, Herisau, Switzerland) and a 0.1 mol/L AgNO\textsubscript{3} standard solution was performed to determine the chloride content [31]. To prepare the sample, 30 mL of 0.1 mol/L KNO\textsubscript{3}, acidified to pH 2, 100 µL of SWE water extract (0.1 mg/mL) was added. The determinations were carried out in duplicate.

2.7. Iodine Determination

The total iodine content of the extracts was determined through a modification of the Sandell–Kolthoff reaction according to Haap et al. [32] using a Synergy HT W/TRF Multimode Microplate Reader (BioTek Instruments, Winooski, VT, USA). Iodine was obtained from absorbance measurements at 405 nm, after the reduction of yellow tetra-ammonium cerium (IV) nitrate to the colorless cerous (III) form by arsenite, catalyzed by the presence of iodine. Blanks (extract plus reagents, except arsenite solution) were prepared to discount the extract’s intrinsic coloration. Measurements were performed in triplicate.

2.8. Nitrogen Content

The ammoniacal nitrogen content expressed as N – NH\textsubscript{4}\textsuperscript{+}, was determined by the Kjeldahl method [33]. Nitrate (N – NO\textsubscript{3}\textsuperscript{−}) was determined by a cadmium reduction spectrophotometric method (method 8039, Hach, Loveland, CO) [34]. The total nitrogen content of the extracts was assumed as the sum of N – NH\textsubscript{4}\textsuperscript{+} and N – NO\textsubscript{3}\textsuperscript{−}. The determinations were performed in duplicate.

2.9. Sulfur Determination

Sulfur determinations were based on the sulfate turbidimetric method, as described by Kolmert et al. [35]. The calibration curve was fitted to a third-degree polynomial curve over the range of 0.4 to 2.0 mmol/L. Wolfram Mathematica software was used to process the data [36]. The determination was performed in triplicate.

2.10. Determination of Minerals and Trace Elements

The determination of minerals’ and trace elements’ concentration was performed on the acid digestion solutions obtained from 1 mL of extract mixed with 9 mL of 65% nitric acid [37]. After 24 h
at room temperature, the solutions were transferred to a volumetric flask, adjusted to 100 mL with ultrapure water, and filtered before analysis. The determinations were performed by ICP-OES and ICP-MS. An Arcos FHE12 (Spectro, Kleve, Germany) ICP-OES instrument was used to quantify B, Ba, Bi, Ca, In, K, Li, Mg, Na, P, Sr, and Zn, according to the manufacturer’s recommended conditions. The instrumental conditions and determination parameters for ICP-OES are presented as Supplementary Material in Tables S1 and S2, respectively. The carrier gas was Ultra High-Purity Grade argon 5.0 (Praxair, Danbury, CT). An iCAP Q (Thermo Fisher Scientific, Waltham, MA) ICP-MS instrument was used for the quantification of Ag, Al, As, Be, Cd, Ce, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Ti, Tl, U, and V, according to Cabrita et al. [38]. The calibration curve parameters for ICP-MS are presented as Supplementary Material in Table S3. The determinations were performed in triplicate.

3. Results

According to the criteria proposed by Arnon and Stout [39,40], plant nutrients can be classified taking into account their importance and quantities necessary to plants as main macronutrients: N, P, K (indispensable to plants in high quantities being necessary its addition through fertilization), secondary macronutrients: Ca, Mg, S (necessary to plants in high quantities but usually available in the soil), micronutrients: Fe, Mn, Zn, Cu, Ni, B, Mo, Cl (vital to plants in low quantities and usually toxic in high concentrations), beneficial minerals: Na, Si, Co, Al, V, Ni, Se, As, F, Br, I, Cd, Cr, Pb (essential to some plants), and potentially toxic elements: Cd, Cr, Pb, Hg, Ni, Se, As (sometimes phytotoxic to some plants but mainly toxic to humans and animals). A table compiling brief information about the importance of macro and micronutrients for plant metabolism, their bioavailable chemical form for plants, and potential toxicity, is presented as Supplementary Material (Table S4).

The *S. polyschides* extracts prepared by subcritical water extraction showed a low pH (mean value of 4.61 ± 0.03) and dry solid content of 5.3% ± 0.1% (m/m). These values are comparable to those reported by Saravana et al. [10] for the seaweed *Saccarina japonica* SWE extracts. The parameters determined in the extracts are presented in Table 1. Iodine can be classified as a beneficial nutrient considering recent reports [12,41]. All extracts presented levels of IC, Al, Be, Ce, Tl, and U lower than the limit of detection (LOD), and these parameters were excluded from the tables.
Table 1. Mineral composition of subcritical water extracts of *S. polyschides*. Results presented per liter of extract.

| Element                  | Concentration Units Per Extract |
|--------------------------|---------------------------------|
| **Main Macronutrients**  |                                 |
| TOM                      | 34.1 ± 0.3 g/L                  |
| TOC = TC – IC \(^1\)     | 12.7 ± 0.2 g/L                  |
| K                        | 15.7 ± 0.2 g/L                  |
| N—total                  | 80.9 ± 2.1 mg/L                 |
| N—NH\(_4^+\)             | 52.0 ± 1.3 mg/L                 |
| N—NO\(_3^-\)             | 28.9 ± 1.7 mg/L                 |
| P                        | 363 ± 20 mg/L                   |
| **Secondary macronutrients**|                                 |
| S—SO\(_4^{2-}\)          | 1.52 ± 0.06 g/L                 |
| Ca                       | 1.09 ± 0.11 g/L                 |
| Mg                       | 1.02 ± 0.08 g/L                 |
| **Micronutrients**       |                                 |
| Cl                       | 17.4 ± 0.2 g/L                  |
| Zn                       | 21.0 ± 0.9 mg/L                 |
| Fe                       | 10.2 ± 0.3 mg/L                 |
| B                        | 6.02 ± 0.11 mg/L                |
| Ni                       | 2.11 ± 0.08 mg/L                |
| Mn                       | 1.12 ± 0.01 mg/L                |
| Mo                       | 0.533 ± 0.027 mg/L              |
| Cu                       | 0.368 ± 0.007 mg/L              |
| **Beneficial nutrients** |                                 |
| Na                       | 5.46 ± 0.11 g/L                 |
| Bi                       | 36.0 ± 0.2 mg/L                 |
| Ba                       | 30.0 ± 0.2 mg/L                 |
| In                       | 18.0 ± 3.0 mg/L                 |
| Rb                       | 6.7 ± 0.29 mg/L                 |
| Sr                       | 5.00 ± 0.90 mg/L                |
| Li                       | 4.00 ± 0.90 mg/L                |
| Cr                       | 1.76 ± 0.02 mg/L                |
| As                       | 1.32 ± 0.07 mg/L                |
| Se                       | 973 ± 39 µg/L                   |
| Pb                       | 533 ± 30 µg/L                   |
| Ti                       | 288 ± 10 µg/L                   |
| V                        | 243 ± 9 µg/L                    |
| I                        | 203 ± 19 µg/L                   |
| Cd                       | 74.6 ± 5.9 µg/L                 |
| Ag                       | 60.6 ± 5.6 µg/L                 |
| Sn                       | 27.8 ± 1.5 µg/L                 |
| Co                       | 11.3 ± 0.2 µg/L                 |
| Sb                       | 9.40 ± 0.50 µg/L                |

\(^1\) The Inorganic Carbon (IC) value was lower than the limit of detection (LOD) for all samples, and a zero value was used to calculate total organic carbon (TOC).

4. Discussion

The nutritional composition of seaweeds used as manure in Portugal has already been described by Santos [41] after the analysis of 17 samples (mixtures of seaweeds) collected in Póvoa do Varzim and Ria de Aveiro. However, no reports are available in the literature for the aqueous extracts obtained by SWE of this seaweed. Saravana et al. [10] evaluated the chemical composition of SWE extracts of the brown seaweed *S. japonica*. The authors studied different temperatures (from 180 to 240 °C) and pressures (13 to 520 bar), but used a single period of 5 min for extraction.
In this work, the SWE extracts of S. polyschides presented a TOC of 12.7 ± 0.2 g/L corresponding to 34.1 ± 0.3 g/L for TOM, both determined in the dry extract dissolved in water (1 mg/mL). Saravana et al. [10] presented a TOC value for S. japonica dry extracts of 18.1–22.2 mg/L. The total N content in the SWE extracts was 80.9 ± 2.1 mg/L. This element was not reported in any other study.

The most abundant micronutrient in the SWE extracts was Cl (17.4 ± 0.2 g/L), which agrees with previous studies made in the dry seaweed [31]. Chloride is classified as a micronutrient, considering the nutritional needs of higher plants for their metabolic processes. It participates in photosynthesis and is significantly concentrated in chloroplasts [42].

The I content in the SWE extracts was 203 ± 19 µg/L. Saravana et al. [10] also quantified I in their hydrolysates, reporting values between 0.01 to 0.09 µg/g DW depending on the extraction conditions. Iodine is present in soils as iodide, iodate, and iodine organic compounds. In most soils, I is associated with organic matter and usually is not phytoavailable [12,42]. Iodine is essential for animals, and recent studies suggest that small amounts of iodine are also involved in plant physiological and biochemical processes acting as a biostimulant [42,43]. These findings suggest that these extracts could be used in biofortification experiments. Iodine biofortification has been a strategy to fight iodine deficiency disorders [43]. The use of seaweed manure as a strategy for iodine biofortification has been successfully applied to yield more nutritious crops [43].

Seaweeds are known for their high content of macronutrients, such as K, Ca, Na, and Mg, and seaweed extracts are known to maintain an enriched trace element content, valuable for fertilization applications [4]. After Cl, the elements with the highest concentration, in decreasing order, were K, Na, S, Ca, and Mg, ranging from K with 15.7 ± 0.2 g/L to 1.02 ± 0.08 g/L (Mg). The P content was 363 ± 20 mg/L. The extracts also presented significant concentrations of Fe (10.2 ± 0.3 mg/L), Mn (1.12 ± 0.01 mg/L), Cu (0.368 ± 0.007 mg/L), and Ni (2.11 ± 0.08 mg/L), all these nutrients being necessary for soil fertility and plant growth. Zn is also an essential micronutrient for plants due to its crucial role in several enzymatic systems and as a precursor of essential vegetable hormones like indoleacetic acid [41]. In SWE extracts, the mean concentration of Zn was 21.0 ± 0.9 mg/L. A mean B concentration of 6.02 ± 0.11 mg/L was also found in the extract. In plants, B is essential for the metabolic pathways of carbohydrates synthesis [42]. The Se concentration found was 973 ± 39 µg/L. The physiological role of Se in plants is still not fully known, but it may be involved in specific metabolic processes, especially in plants that are Se accumulators [42]. Several compounds of Se, mainly with cysteine and methionine, were found in such plants. Selenium-containing plants can be a significant source of this element for animals, where it plays an essential role in the body’s antioxidant system [44]. Selenium enters the food chain through plants, which take it up from the soil and fertilizers [45]. The concentrations of the other trace elements analyzed in the SWE extracts (presented in Table 1) were in the range of 9.40 ± 0.50 µg/L for Sb to 36.0 ± 0.2 µg/L for Bi. The importance of these elements is not clear, and its potential functions in plants can be consulted in Supplementary Table S4.

Saravana et al. [10] also reported that the most abundant element in the S. japonica hydrolysate was K (4.92–9.18 µg/g DW) followed by Na (1.34–3.14 µg/g DW). These authors also found other minerals like Ca, Mg, and P (0.32 to 0.89 µg/g DW) but in significantly lower levels than the ones reported in this work for S. polyschides SWE extracts. The same authors also reported trace levels of Fe, I, Mn, and Zn, with contents ranging from 0.01 to 0.03 µg/g DW. Arsenic was the most abundant toxic element in their extracts (3.25 ± 0.01 µg/g DW). The macro and microminerals’ concentrations found in the present study were much higher than the values reported by Saravana et al. [10]. This difference can be justified by the different seaweed species studied and by the different extraction times used. One possibility is that the extraction time of 5 min used by Saravana et al. [10] was not enough to disrupt cell membranes, increasing the liberation of compounds when compared with the 30 min extraction time described in this work.

Some elements found in the extracts, such as Cd, Cr, Pb, Ni, Se, and As, although exhibiting potentially beneficial properties, can also be toxic to plants when present in higher quantities. Phytotoxicity levels of crops for Cd and Ni were reported to be 5 to 10 mg/L (DW), 5 to 60 mg/L (DW)
for Cr, for Se 4 mg/L (DW), and above 2 mg/L for As [41,42]. As for Pb, this element has a little effect on plant metabolism, but its bioaccumulation in edible plant tissues poses critical health concerns for humans and animals [41]. All potentially toxic elements (Cd, Cr, Pb, Ni, Se, and As) found in SWE extracts are in concentrations below those described as the toxicity limit for plants.

It is necessary to consider that the use of fertilizer depends mainly on the necessities of soil. Fertility assessment can be performed based on land and plant analysis and experimental testing [41]. Plant analysis, and observation of crop appearance, can give an idea of the deficiencies of nutrients in the soil and the needs of correctives and fertilizers [41]. Nowadays, fertilizers are used with the main or even sole objective of intervening in plant feeding, products that may not have main macronutrients (N, P, and K), but secondary macronutrients, micronutrients, growth regulators, among others, for a specific crop [41]. In biofertilizer technology, it is also necessary to consider the presence of microorganisms present in the soil. Microorganisms are considered an important tool in overcoming problems associated with the excessive use of chemical fertilizers and pesticides. It is widely accepted that plant-beneficial microorganisms play a crucial role in increasing the availability of minerals that otherwise are inaccessible to plants [46].

The results reported in this study suggest that the extracts of S. polyschides obtained by SWE can be used in agronomic strategies currently used to biofortify food crops with the mineral elements most commonly lacking in human diets (Fe, Zn, Cu, Ca, Mg, I, and Se), due to the presence of all these elements in the extracts [43,45]. The quantity of these elements necessary to plants is dependent on the particularities of the cultures, their presence in soils, and concentration in water [41,42]. The seaweed used in this study is available only for 3 or 4 months per year, but its huge quantity in the shores provides enough material to produce the extract [25,28]. After sun-drying, the seaweeds can be stored dried, and the extracts lyophilized. The possibility of the liquid storage of this extract must also be assessed. As future work, the extract will be tested in the field as soil and foliar fertilizer considering all the players related to soil fertility (soil, water, plants, and microorganisms) and compared with commercial fertilizers available in the market.

5. Conclusions

In the present work, S. polyschides seaweeds were extracted with subcritical water to evaluate the potential of the obtained extracts to be used as fertilizer instead of the macroalgae dried under the sun on the beach for an extended period during the bathing season. The extract was characterized in terms of TOM (34.1 ± 0.3 g/L), N (80.9 ± 2.1 mg/L), S (1.52 ± 0.06 g/L), Cl (17.4 ± 0.2 g/L), I (203 ± 19 µg/L), macrominerals, and trace elements. Macrominerals were present in the following decreasing order: K (15.7 ± 0.2 g/L), Na (5.46 ± 0.11 g/L), S (1.52 ± 0.06 g/L), Ca (10.9 ± 1.1 mg/g DW), and Mg (10.2 ± 0.8 mg/g DW). Within the trace elements, Bi (360 ± 2 µg/g DW) was present in a higher concentration, followed by Ba (300 ± 2 µg/g DW), Zn (210 ± 9 µg/g DW), In (180 ± 2 µg/g DW), Se (210 ± 6 µg/g DW), Sb (200 ± 4 µg/g DW), and Fe (102 ± 3 µg/g DW). Other minerals were present with levels ranging from 67.0 ± 2.9 µg/g DW for Rb to 0.94 ± 0.005 µg/g DW for Sb. These elements are essential for plant growth, and their presence in the SWE is significant. The potentially toxic elements Cd, Cr, Pb, Ni, Se, and As, although present in the extract, show a concentration smaller than the reported lowest limit of phytotoxicity.

Considering the safety and cost of the raw material and the extraction technique used, S. polyschides subcritical water extracts can find application in the development of fertilization products with the easy possibility of scaling up. The composition of subcritical water extracts of S. polyschides suggests that they may have interesting characteristics as a biofertilizer and can be an option in biofortification experiments with essential nutrients.

Supplementary Materials: The following are available online at http://www.mdpi.com/2077-1312/8/4/244/s1: Table S1: ICP-OES operating parameters, Table S2: Calibration parameters for ICP-OES analysis, Table S3: Calibration parameters for ICP-MS analysis. Calibration standards concentrations for all elements ranged between 0.500 µg/L to 100 µg/L. Table S4: Bioavailable chemical forms of the elements to plants, functions in plant metabolism, presence in specific organs or molecules in plants, and its potentially toxic effects due to element deficiency and/or excess.
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