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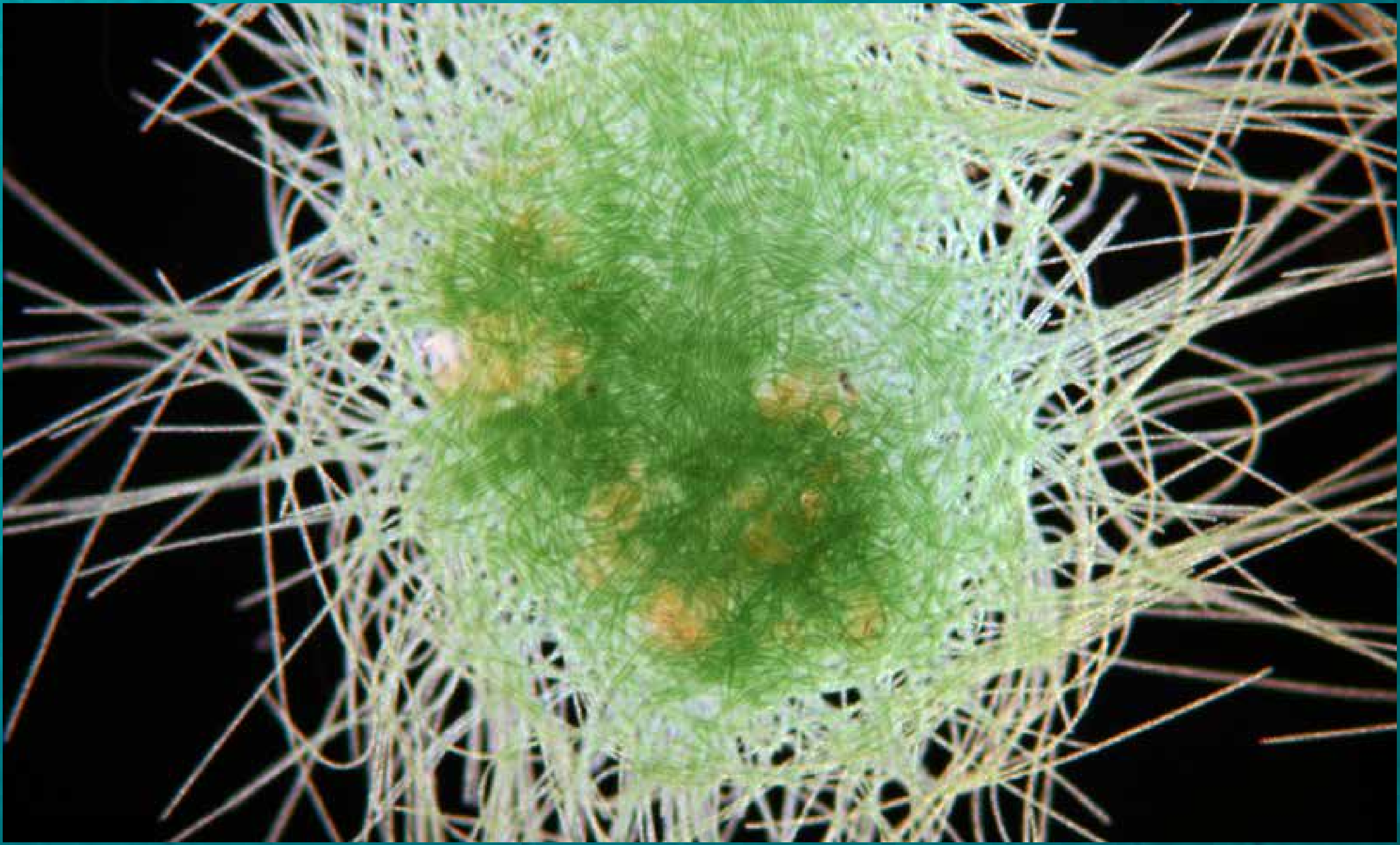
Comparative studies of chemical composition of commercial and native edible macroalgae from Mar del Plata (Buenos Aires, Argentina): Mineral Content, lipids, and toxic metals



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Comparative studies of chemical composition of commercial and native edible macroalgae from Mar del Plata (Buenos Aires, Argentina): Mineral Content, lipids, and toxic metals

Estudios comparativos de composición química de macroalgas comestibles comerciales y nativas de Mar del Plata (Buenos Aires, Argentina): Contenido de minerales, lípidos y metales tóxicos

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ABSTRACT

Macroalgae are recognized as a healthy food source due to their high content of minerals, lipids, and secondary metabolites. However, their ability to accumulate high concentrations of toxic metals, such as As, Cd, Cr, Hg, and Pb, among others, necessitates chemical studies to determine the benefits and risks associated with their consumption. The objective of this study was to analyze and compare the chemical composition of various macroalgae samples collected in Mar del Plata, Argentina, and commercial samples of *Undaria pinnatifida*. Mineral content was determined by ICP-MS, total polyphenols were measured using the Folin-Ciocalteu method in methanolic and aqueous extracts, and lipids were quantified gravimetrically. Significant differences were observed in the mineral composition between local samples of *Ulva lactuca* and *U. pinnatifida*. In *U. lactuca*, major metals included Ca, Fe, and Al, whereas Ca, Fe, and Sr predominated in *U. pinnatifida*. Notably, *U. pinnatifida* exhibited higher accumulation of Cr, As, and Pb. Commercial samples generally showed lower levels of toxic metals, with the exception of Cd and Hg. The Japanese *Undaria* sample presented elevated levels of As, Cd, and Pb, while the sample originating from China displayed high concentrations of Cr. Polyphenol extraction efficiency was greater with methanol. Lipid content was low (ranging from 3.4 % to 4.3 % of dry weight), with *U. lactuca* showing higher levels. These results highlight the chemical variability among macroalgae species and underscore the importance of conducting such studies to ensure safe consumption and promote the sustainable utilization of this resource.

Key words: algal resources, chemical content, food safety, seaweed.

RESUMEN

Las macroalgas son reconocidas como un alimento saludable por su alto contenido de minerales, lípidos y metabolitos secundarios. Sin embargo, su capacidad de acumular altas concentraciones de metales tóxicos, como el As, Cd, Cr, Hg y Pb, entre otros, plantea la necesidad de realizar estudios químicos para determinar beneficios y riesgos de su consumo. El objetivo fue analizar y comparar la composición química de distintas muestras de macroalgas recolectadas en Mar del Plata, Argentina y de muestras comerciales de *Undaria pinnatifida*. Se determinó el contenido mineral mediante ICP-MS, los polifenoles totales por el método de Folin-Ciocalteu en extractos metanólicos y acuosos, y lípidos gravimétricamente. La composición mineral de muestras locales de *Ulva lactuca* y *U. pinnatifida* mostró diferencias. Los metales mayoritarios en *U. lactuca* fueron Ca, Fe y Al, mientras que en *U. pinnatifida* predominaron Ca, Fe y Sr. *U. pinnatifida* mostró una mayor acumulación de Cr, As y Pb. Las muestras comerciales exhibieron menor contenido de metales tóxicos, a excepción de Cd y Hg. La muestra de *Undaria* japonesa mostró niveles elevados de As, Cd y Pb, mientras que la muestra proveniente de China exhibió altas concentraciones de Cr. La eficiencia de extracción de polifenoles fue mayor con metanol. El contenido lipídico fue bajo (entre 3.4 y 4.3 % del peso seco) mostrando *U. lactuca* niveles más elevados. Los resultados destacan la variabilidad química entre especies de macroalgas y resaltan la importancia de realizar estos estudios para garantizar el consumo seguro y promover el aprovechamiento de este recurso.

Palabras clave: algas marinas, contenido químico, recursos algales, seguridad alimentaria

INTRODUCTION

Marine macroalgae are considered a natural and healthy foodstuff due to their high protein, vitamin (notably vitamins A, C, and B^{-12}), lipid, natural fatty acids including omega-3, fibre, and mineral content with a particular focus on micronutrients such as iron, calcium, iodine, potassium, and selenium (Cofrades *et al.* 2019; Schmid *et al.* 2018; Skirzypczyk *et al.* 2019). For all these reasons, seaweeds are consumed either directly or as a dietary supplement in both human and animal feed (Cofrades *et al.* 2019; Ganesan *et al.* 2019; Losada *et al.* 2020; Mouritsen *et al.* 2018; Rebours *et al.* 2014; Taboada *et al.* 2013). Global consumption has grown in recent years (FAO 2024), influenced by changing eating habits, including plant-based diets and greater interest in gourmet food (Baroni *et al.* 2019). The principal cultivated species for human consumption include *Undaria pinnatifida*, *Pyropia* sp., *Porphyra* sp., *Ulva* sp. and *Gracilaria* sp., typically sold in dehydrated forms (such as rolls, chopped, minced, ground, flour) or as cooked or smoked products (Muñoz 2015).

The chemical composition of seaweed is highly variable, influenced by both environmental and biological factors. Variations in metal concentrations and bioaccumulation capacity in macroalgae have been attributed to seasonally fluctuating environmental conditions, such as water temperature, light intensity, and nutrient availability, as well as metabolic factors related to type of algae and species (Astorga *et al.* 2016; Balboa *et al.* 2015; Losada *et al.* 2020; Rodrigues *et al.* 2015). Macroalgae demonstrate a notable capacity to absorb and accumulate potentially harmful metals and metalloids from their surrounding environment, including arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) (Bonanno & Orlando-Bonaca 2018; Monteiro *et al.* 2019; Rubio *et al.* 2017; Salomone *et al.* 2017; Salomone & Riera 2019). This aspect is of particular concern in the context of edible seaweed, given the potential implications for human health. Numerous studies have addressed this issue, highlighting the relevance of evaluating metal content in edible seaweeds (Circuncisão *et al.* 2018; Ma *et al.* 2018; Marzocchi *et al.* 2016; Miedico *et al.* 2017; Paz *et al.* 2018; Paz *et al.* 2019; Taylor & Jackson 2016). Toxic elements such as Al, Pb, Hg, Cd, and As are of significant concern due to their potential impacts on both human health due to can cause harm even at low concentrations if exposure is prolonged (Khan *et al.* 2015). Some authors have even suggested that the intake of toxic metals through seaweed consumption may be non-negligible and warrants careful assessment (Amin *et al.* 2018; Taylor *et al.* 2017; García-Salgado & Quijano, 2014). Considering the world's growing population and increasing environmental challenges, seaweed is emerging as a sustainable solution to enhance food security and restore aquatic ecosystems (FAO 2024). Consequently, analysis of the elemental composition of edible marine macroalgae is imperative for the determination of their nutritional value and potential toxicity. However, it is crucial to highlight that the concentration of an element in a foodstuff does not necessarily indicate the amount that is absorbed by the human gastrointestinal tract. Therefore, it is essential to conduct simulated digestion experiments to estimate this value (Alves *et al.* 2018; García-Sartal *et al.* 2013).

Although the lipid content is low in macroalgae (1-5% of dry weight), they contain lipids with important functional compounds, such as omega-3 and omega-6 polyunsaturated fatty acids (PUFAs), carotenoids, chlorophylls, terpenoids and sterols. These compounds are associated with health benefits, including antioxidant, anti-tumor, anti-inflammatory, and neuroprotective effects (Susanto *et al.* 2019). Polyphenols derived from marine algae are distinguished by their structural diversity and powerful biological effects, particularly their antioxidant capacity. These substances have been demonstrated to contribute to the prevention of diseases associated with the ageing process, oxidative stress and neurodegenerative disorders. In addition, these compounds have been shown to possess anti-inflammatory properties, anti-cancer effects, and antibacterial, antiviral, anti-diabetic, and neuroprotective benefits. This positions them as promising candidates for therapeutic and nutraceutical applications (Cotas *et al.* 2020; Kumar *et al.* 2022).

Even though seaweed consumption remains relatively infrequent in Argentina, there is a growing body of research focused on the chemical composition of macroalgae, particularly regarding their content of metals, lipids, phenolic content, and photosynthetic pigments (Arijón *et al.* 2023; Dellatorre *et al.* 2020; Muse *et al.* 1999; Nagai *et al*. 2022; Pérez *et al.* 2007). Recent studies have also reported the presence of emerging pollutants, such as microplastics, in macroalgal tissues (Forero-López *et al.* 2024). Given Argentina's recognized potential for algal production within Latin America (Mendez *et al.* 2024), advancing research in this field is of strategic importance. The aim of this study is to evaluate the chemical composition of macroalgae from Mar del Plata (Buenos Aires, Argentina), with the goal of identifying their potential applications as food. The analysis focuses on polyphenols, total lipids, and mineral content, including potentially harmful elements such as arsenic (As), cadmium (Cd), and mercury (Hg). The results will be compared with those of commercially available edible seaweeds and previous studies on edible macroalgae.

MATERIALS AND METHODS

Chemical and standard solutions

All reagents employed in this experiment were of analytical grade. When required, solutions were prepared using distilled and ultrapure water. The ultrapure water required for solution preparation was obtained using a Heal Force PW VF 1.5-2 L purification system. The following reagents were used: methanol (Merck), gallic acid (Biopack), sodium carbonate (Na_2CO_3) (Sigma-Aldrich), Folin-Ciocalteu reagent (Anedra), chloroform (Biopack), and NaCl (Biopack). Ultrapure oxygen peroxide (Merck) was employed in its unmodified form. Additionally, nitric acid (Anedra, 65 %) was utilised, which had been purified through sub-boiling distillation. A stock solution of 0.1 g L^{-1} gallic acid was prepared and stored in a falcon tube in darkness for the quantification of total polyphenols. A solution of Folin-Ciocalteu reagent at a concentration of 2N was prepared. Furthermore, a 20 % sodium carbonate solution was prepared by dissolving the precise amount of reagent in distilled water.

Sample preparation and analytical determinations

Samples: Algae samples were collected from the coast of Mar del Plata, Buenos Aires Province, Argentina (latitude: 38°02' S and longitude: 057° 31´ W) in August 2018. The samples comprise native *Ulva lactuca* Linnaeus (Ulvophyceae) and the invasive *Undaria pinnatifida* (Harvey) Suringar (Phaeophyceae), both of which are edible macroalgae. However, in that location, they are not utilised for this purpose. One kilogram of each seaweed species was collected from Mar del Plata and subjected to a washing process with distilled water to remove sediment and epifauna. Thereafter, the seaweed was frozen and freeze-dried in the laboratory setting using a freeze-drying apparatus fabricated by LABCONCO. Finally, all samples were pulverised using a mortar to produce a fine and uniform powder, which was then stored in opaque plastic bags until analysis. To make a comparison, two commercial samples of *U. pinnatifida*, commonly known as wakame, purchased from a market in Buenos Aires, were subjected to analysis. The commercial samples were identified as follows: a) Trademark Wakou: 100 grams of dried seaweed of *U. pinnatifida* from Japan; b) Trademark Kinwaya: 100 grams of dried seaweed of *U. pinnatifida* from China.

For mineral content analysis two randomly selected sub-samples of each seaweed powder were subjected to acid digestion using a CEM-SPD-Discover Explorer microwave digester (MW). The operating conditions for MW digestion are presented in Table 1. A control sample without algae was prepared and processed in the same manner as the samples in each series. In summary, the digestion process entailed the transfer of 0.5 g of dried algae samples into the digestion vessel, followed by the addition of 1 mL of purified HNO_3 and 0.5 mL of ultrapure H_2O_2. Once the digestion process was completed, the vessel was allowed to cool, resulting in the formation of a transparent and homogeneous solution. These solutions were then diluted with ultrapure water to a final volume of 10 mL and filtered using a Whatman 0.45 µm nylon filter. Ultimately, the processed samples, along with their corresponding blanks, were placed in conical tubes and refrigerated at 4 °C until analysis by inductively coupled plasma mass spectrometry (ICP-MS) Agilent instrument model 7500cx with Octopole Reaction System collision/reaction cell and pure He as the inert collision gas. The elements determined were aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), strontium (Sr), uranium (U) and zinc (Zn). The method was validated by measuring BCR-279 *Ulva* sp. certified reference material in a previous study (Camurati *et al.* 2021).

Table 1. Conditions used for MW acid digestion of dried algal material.

Algae sample	0.5 g
Reagents	1 mL HNO3 + 0.5 mL H2O2
Final volume	10 mL
Temp (°C)	180
Ramp Time (min)	5
Rest time (min)	15
Pression (PSI)	300
Power (W)	300

Total polyphenol content: The first step involves extracting polyphenols from the algal matrix. According to the literature, two different moderate extraction solutions are used to maximize polyphenol yield without compromising their structural integrity:

-*Methanol extraction*: 0.1 grams of each dried seaweed sample were mixed with 10 milliliters of 80 % methanol solution in a conical tube, then placed in a preheated thermostatic bath (TESLAB) at 70 °C for 60 minutes. The tubes were then removed, cooled, and the thermostat was adjusted for the next extraction at 80 °C. The resulting extracts were diluted at a 1:10 ratio and stored for analysis (Machu *et al.* 2015).

-*Aqueous extraction*: 0.1 grams of each died seaweed sample were mixed with 10 milliliters of distilled water in a conical tube, then placed in a preheated thermostatic bath (TESLAB) to 80 °C for 10 minutes. The tubes were then removed, cooled, and stored until analysis (Machu *et al.* 2015).

The polyphenol content of the extracts was determined using the Folin-Ciocalteu method, with absorbance measurements taken at 760 nm using a UV-VIS spectrophotometer (Gutiérrez-Avella *et al.* 2008). To achieve this, 0.5 mL of 1N Foulin-Ciocalteu reagent, obtained by 1:2 dilution of the commercial reagent of 2N concentration, and 1mL of a 20 % Na_2CO_3 solution are added to 1 ml of algae extract, which may be in either methanol or water. The solutions were then vortexed and adjusted to a final volume of 4 mL with the addition of 1.5 mL of distilled water. Subsequently, the samples were stored in the dark for 90 minutes, after which the absorbance was measured at 760 nm using a Perkin Elmer UV-VIS spectrophotometer. The polyphenol content was quantified by measuring the gallic acid equivalents per gram of the dried sample. The calibration curve was prepared with gallic acid in the range of 0.25–5 mg/L.

Total lipids content: The gravimetric method for estimating total lipids, as described by Rougham (1985), comprises the extraction of lipids using a solution of methanol and chloroform in a 1:1 ratio. A gram of seaweed sample was introduced into a previously dried and weighed 100 mL beaker. Subsequently, 5 mL of a 1:1 methanol:chloroform solution was added, and the mixture was stirred with a magnetic stirrer (ITESTER) for a period of 10 minutes. After this, the solution was filtered. This process was repeated twice. Thereafter, the aqueous fraction of the solution was obtained by adding a few milliliters of 1 % NaCl solution to the extract. The lipid fraction was then obtained by drying the solution in an oven at 60 °C for 72 hours. The percentage of total lipids was obtained by the following calculation (Equation 1):

$$L = \frac{(W1 - W2)}{W_{\text{sample}}} \times 100 \qquad \text{Equation 1}$$

where L is the percentage of lipids in the sample (%), W1 is the initial weight of the beaker without extract (g), W_2 is the final weight of the beaker after evaporation of the extract (g), and W_{sample} is the mass of dry seaweed sample used (g).

Statistical analysis

Results are expressed as mean values ± standard deviation, significances between species were analysed using one-way analysis of variance (ANOVA), followed by post hoc Tukey testing if a significant difference was found (IBM SPSS Statistics). A significant level of $p < 0.05$ was accepted for all statistical analysis.

RESULTS AND DISCUSSION

Mineral content

Table 2 presents the mineral content of the algal samples collected in Mar del Plata and commercial seaweeds (Wakou and Kinwaya), expressed in $\mu g\ g^{-1}$ dry weight. The results show that there are notable variations in the mineral composition of the Mar del Plata algal species, despite their collection from the same site and at the same time. The relative abundance of elements in *U. lactuca* decreases in the following order: Ca, Fe, Al, Sr, Mn, Zn, Cu, As, Cr, Se, Ni, Pb and Ba; while in *U. pinnatifida* the order is: Ca, Sr, Fe, Zn, Al, Cr, As, Ba, Mn, Cu, Pb, Ni, U and Se. Furthermore, our findings indicate that *U. pinnatifida* from Mar del Plata, exhibits a notable accumulation of toxic elements such as, Cr (24.64 ± 1.85), As (14.0 ± 1.0), and Pb (2.0 ± 0.1) in comparison to *U. lactuca*. The difference in elemental content between *Ulva lactuca* and *Undaria pinnatifida* observed in this study, may be attributable to the fact that both species belong to distinctly different groups of algae. The three main taxonomic groups of macroalgae: (a) phylum Chlorophyta—green algae; (b) phylum Rhodophyta — red algae; (c) phylum Ochrophyta, class Phaeophyceae — brown algae (Pereira 2021). In addition to differences in pigmentation, these organisms exhibit variations in their chemical and structural cell wall compositions (Fabre *et al.* 2020). These characteristics are closely related to the ability to adsorb and absorb substances through different mechanisms. Brito *et al.* (2017) observed that, in general, samples from the green algal group exhibited a lower calcium concentration compared to the brown group, in accordance with the findings of the present study. In research conducted by Arisekar *et al.* (2021), it was found that brown algae have the highest potential for accumulating trace elements such as Cu

Table 2. Mean elemental composition of samples of *U. lactuca* and *U. pinnatifida* from Mar del Plata and commercial seaweed (*U. pinnatifida*). Results are expressed in micrograms per gram of dry weight ($\mu g\ g^{-1}$ dry weight). Not detected (ND).

	Mar del Plata samples	***Commercial samples***		
Element	***U. lactuca***	***U. pinnatifida***	***U. pinnatifida* (Wakou)**	***U. pinnatifida* (Kinwaya)**
Al	190.6 ± 17.1	27.1 ± 2.5	15.5 ± 1.5	36.2 ± 2.0
As	5.0 ± 0.4	14.0 ± 1.0	9.3 ± 0.8	6.7 ± 0.5
Ba	0.18 ± 0.01	14.0 ± 1.0	8.5 ± 0.7	8.5 ± 0.7
Ca	3502 ± 224	9186 ± 785	11.3 ± 1.1	10.4 ± 1.0
Cd	ND	ND	0.25 ± 0.01	0.14 ± 0.01
Cu	5.5 ± 0.4	5.0 ± 0.4	0.27 ± 0.02	0.39 ± 0.01
Cr	2.7 ± 0.2	24.6 ± 1.9	0.03 ± 0.01	0.07 ± 0.01
Fe	234.6 ± 3.6	137.0 ± 10.2	13.4 ± 1.0	22.7 ± 1.8
Hg	ND	ND	0.002 ± 0.001	0.002 ± 0.001
Mn	13.6 ± 1.1	8.8 ± 0.6	2.17 ± 0.18	2.7 ± 0.1
Ni	0.94 ± 0.08	0.96 ± 0.05	0.11 ± 0.02	0,16 ± 0.01
Pb	0.33 ± 0.01	2.0 ± 0.1	0.09 ± 0.01	0.06 ± 0.01
Se	2.5 ± 0.2	0.12 ± 0.01	0.07 ± 0.01	0.05 ± 0.01
Sr	38.2 ± 2.8	638.4 ± 5.6	123.0 ± 8.8	104.8 ± 10.0
U	ND	0.7 ± 0.1	0.06 ± 0.01	0.05 ± 0.01
Zn	7.9 ± 0.7	31.5 ± 2.7	4.2 ± 0.2	4.0 ± 0.2

and Zn. The concentration Cu and Zn is important in food due to their antifouling chemical properties (Nomura *et al.* 2023). Our findings are consistent with those previously documented in the published literature for Zn, yet not for Cu, where the content of both samples did not demonstrate significant differences. Similarly, Losada *et al.* (2020) discovered that brown algae species have a higher bioconcentration capacity for certain metals, such as As, U and Sr, in comparison to other groups. These findings reveal that *U. pinnatifida* accumulates higher levels of Cr, As, and Pb compared to *U. lactuca*. The concentration of toxic metals and metalloids in edible algae represents a crucial aspect that demands attention (Casas *et al.* 2010).

The analysis of commercially available samples of algae is of great importance. In this study, commercial samples of *Undaria pinnatifida* were analysed. *U. pinnatifida* is an invasive seaweed from Asia and one of the most important commercial seaweeds in the world (Arijón *et al.* 2023). Since its initial discovery in Argentina in 1992, research has been conducted into its potential applications, yet the market has not been sufficiently promoted (Camurati & Salomone 2019; Lobato *et al.* 2023; Nagai *et al.* 2022; Salcedo *et al.* 2020). Regarding toxic elements, the results indicated that the *U. pinnatifida* from Japan (Wakou) exhibited higher concentrations of As (9.3 ± 0.9), Cd (0.25 ± 0.01), and Pb (0.09 ± 0.01), whereas the same species of algae from China (Kinwaya) showed a higher content of Cr (0.07 ± 0.01). However, analysis of commercial samples revealed no significant differences in the other elements quantified, with the exception of Al and Fe content, which exhibited the highest levels in seaweed from China. The Argentine Food Code (AFC) recognises marine macroalgae as a foodstuff suitable for human consumption. However, no limits are specified about their mineral content. The AFC has only established maximum limits for As (1 µg g^{-1}), Cu (10 µg g^{-1}), Pb (2 µg g^{-1}) and Zn (100 µg g^{-1}) in solid food. The analysis revealed that all samples exhibited arsenic levels above the permitted maximum, while also complying with the established limits for Cu and Zn. Furthermore, the Pb content in *U. pinnatifida* approached the maximum permitted level. However, international regulations governing edible marine macroalgae have established specific maximum limits for metal levels. For example, French regulations stipulate that the maximum permissible levels of Cd, Hg, and Pb are 0.5 µg g^{-1}, 0.1 µg g^{-1}, and 5 µg g^{-1}, respectively (CEVA 2024). Furthermore, the European Regulation 1881/2006 for authorised supplements has established maximum levels for toxic contaminants in macroalgae-based supplements, as follows: 3.0 µg g^{-1} for Cd and Pb and 0.1 µg g^{-1} for Hg (Commission Regulation 2006). The concentrations of Cd, Hg, and Pb in the algal samples analysed in this study were found to be below the specified limits. It is noteworthy that the commercially available algae exhibited lower levels of toxic elements compared to the samples collected in Mar de Plata, with the exception of Cd and Hg, which were not detected in the local samples. Both samples complied with the current regulations regarding toxic element levels. In particular, arsenic content is often high in algae, and arsenic speciation studies are crucial in this context, where chemical form and toxicity are related (Camurati *et al.* 2021; Camurati & Salomone 2019).

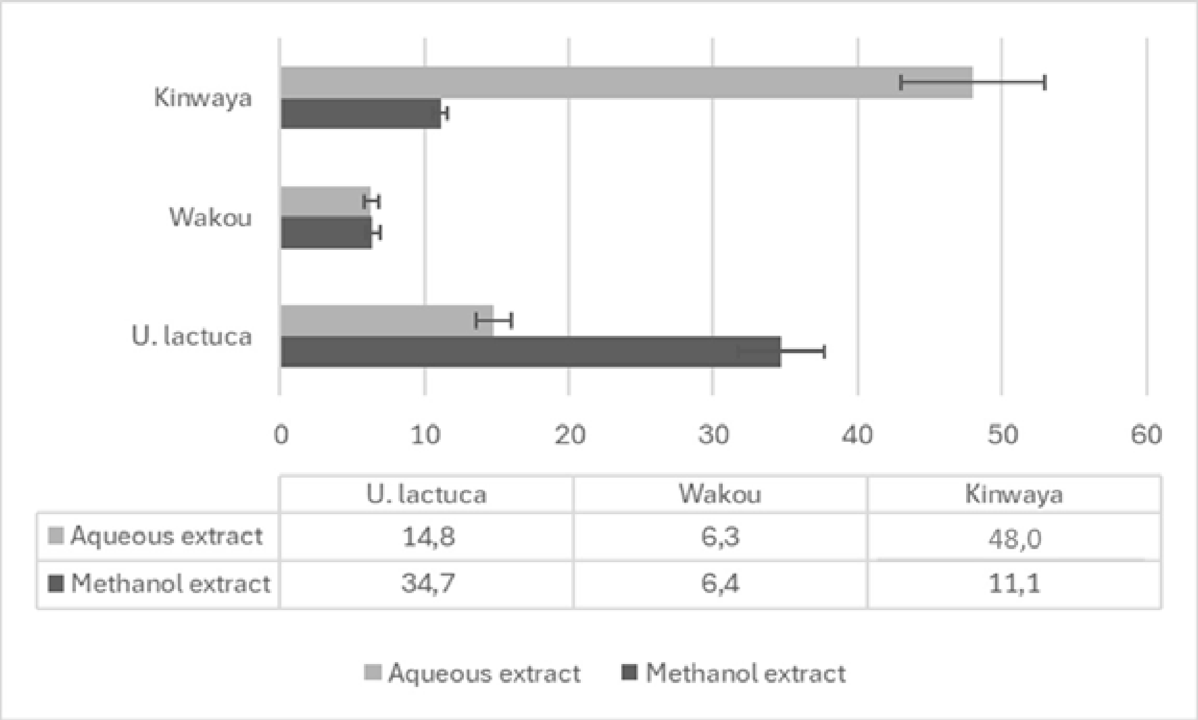
In comparison with our results, samples of *U. pinnatifida* from Nuevo Gulf and San José Gulf (Patagonia, Argentina) exhibited lower concentrations of certain elements than the samples from Mar del Plata, including Fe (86 and 17.3 mg Kg^{-1} dw), Zn (28.4 and 18.7 mg Kg^{-1} dw), Mn (5.0 and 2.0 mg Kg^{-1} dw), and Cu (1.0 and 0.7 mg Kg^{-1} dw); however, they showed a higher concentration of As (47.7 and 46.9 mg Kg^{-1} dw), Ni (1.8 mg Kg^{-1} dw), Cd (1.0 and 5.9 mg Kg^{-1} dw), and Hg (0.11 and 0.02 mg Kg^{-1} dw) (Casas *et al.* 2010; Gil *et al.* 2014). A further study of *U. pinnatifida* samples from San Jorge Gulf revealed notable discrepancies in the concentrations of certain potentially toxic elements (Salomone & Riera 2019). The concentration of arsenic was found to be higher in the algal samples obtained from San Jorge Gulf (17-33 mg Kg^{-1} dw), while the levels of Cu (1-2 mg Kg^{-1} dw) and Cr (0.8-2.6 mg Kg^{-1} dw) were observed to be higher in the samples from Mar del Plata. The research findings suggest that, in addition to the taxonomic factor of the species, the environment exerts a significant influence on the elemental composition of the samples analysed.

Studies on *U. lactuca* are also found in Argentina. This species is adaptable to a range of climates and can be used for various purposes (Areco *et al.* 2021). In a study conducted by Muse *et al.* (1999), the metal content of *U. lactuca* was analysed in two locations within San Jorge Gulf (Patagonia, Argentina). The levels of Cd (0.12 mg Kg^{-1} dw) and Pb (3.68 mg Kg^{-1} dw) at Punta Borja, a city with a high degree of human influence, were found to be higher than those observed in the Mar del Plata samples, which exhibited the highest levels of Cr (1.56 mg Kg^{-1} dw), and Zn (5.20 mg Kg^{-1} dw). In Punta Maqueda, a naturally protected area situated at a considerable distance from potential sources of contamination, significantly lower levels of toxic metals were observed (0.33, 0.55, 1.73 and 1.98 mg Kg^{-1} dw for Cr, Cd, Pb and Zn, respectively). Later, Muse *et al.* (2006) published findings regarding the Cd (0.28 and 1.70 mg Kg^{-1} dw) and Pb (3.55 and 1.65 mg Kg^{-1} dw) content of *U. lactuca* from Punta Borja and Punta Maqueda, which exhibited higher levels than those observed in the present study and previously reported. Another study examined the concentrations of As, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn in *Ulva sp.* from three locations in southern Argentina with varying levels of human activity exposure (Pérez *et al.* 2007). When we compared our results with those from Bahía Solano, a site in the San Jorge Gulf that is free from anthropogenic influence, we found that the concentrations of Cu (3.81 mg Kg^{-1} dw), As (2.98 mg Kg^{-1} dw), Cr (1.05 mg Kg^{-1} dw), and Se (0.75 mg Kg^{-1} dw) in *U. lactuca* samples from Mar del Plata were higher. In contrast, levels of Ca (10.53 mg g^{-1} dw), Fe (380 mg Kg^{-1} dw), Mn (51.4 mg Kg^{-1} dw), Zn (31.3 mg Kg^{-1} dw), Ni (4.11 mg Kg^{-1} dw), Pb (1.72 mg Kg^{-1} dw), and Cd (0.46 mg Kg^{-1} dw) were lower than those reported for Bahía Solano. Comparing Mar del Plata samples with those from Arroyo La Mata, an area impacted by industrial activities, showed that Ca (7.06 mg g^{-1}dw), Fe (532 mg Kg^{-1} dw), Zn (17.4 mg Kg^{-1} dw), Mn (15.1 mg Kg^{-1} dw), As (5.61 mg Kg^{-1} dw), Pb (1.33 mg Kg^{-1} dw), Ni (1.22 mg Kg^{-1} dw), and Cd (0.17 mg Kg^{-1} dw), concentrations were higher in Arroyo La Mata, while Cu (3.21 mg Kg^{-1} dw), Cr (1.14 mg Kg^{-1} dw), and Se (0.53 mg Kg^{-1} dw) levels were lower.

Total polyphenols

Figure 1 presents the total polyphenol content of the methanolic, and aqueous extracts obtained from all algal samples, except *U. pinnatifida* from Mar de Plata.

In accordance with the findings of other studies, the results of this investigation demonstrate that the polyphenol content is significantly influenced by the extraction method employed (Apumayta-Suárez 2019; Chakraborty *et al.* 2013; Chan-



	U. lactuca	Wakou	Kinwaya
▨ Aqueous extract	14,8	6,3	48,0
■ Methanol extract	34,7	6,4	11,1

Figure 1. Total polyphenols content in algal samples. Results expressed in mg equivalent of gallic acid 100 g^{-1} of dry weight.

dini *et al.* 2008; Cofrades *et al.* 2017; Córdova 2018; García-Casal *et al.* 2009; Gómez-Ordóñez 2013; Machu *et al.* 2015; Montero *et al.* 2018; Ortiz Viedma, 2011; Rodríguez *et al.* 2010; Sathya *et al.* 2017; Vidal *et al.* 2006, 2009). Except for the Kinwaya sample, methanolic extracts exhibited a higher polyphenol content than aqueous extracts. In the case of the commercial sample Wakou, the values observed in both extracts were found to be comparable. Despite the biological value of polyphenols and the high polyphenol content of marine macroalgae, there is a scarceness of studies on Argentinean marine algae (Dellatorre *et al.* 2020). The authors found that total phenolic content in seaweed powder (*Undaria* sp.) reached 1550 mg GAE/100g). The values obtained were significantly higher than those observed for our samples. Previous research has demonstrated that the polyphenol content of algae varies depending on the species, yet this is not the unique contributing factor. Brown algae have consistently been reported to contain substantial levels of phenolic compounds, which exhibit notably high biological activity. Compared to green and red algae, they tend to possess both higher concentrations of these compounds and greater antioxidant capacity (Melkinic *et al.* 2019). Machu *et al.* (2015) analysed the total polyphenol content of various seaweed species. In accordance with them, the aqueous extracts of *U. pinnatifida* (wakame) samples were found to contain elevated levels of total polyphenols. Furthermore, the study revealed that two species of red algae (*Palmaria palmata* and *Porphyra ternera*) and green algae (*Chlorella pyrenoidosa*) exhibited a similar trend. The results indicate that there is no correlation between the algal class and the polyphenol content. The polyphenol values obtained in this study are markedly lower than those reported in the literature for algae of the same division.

Total lipids

The lipid content was found to range from 3.4 % to 4.3 % of dry weight. Higher values, but without significant differences, were observed in the *U. lactuca* samples (4.3%), followed by the commercial *U. pinnatifida*, Wakou and Kinwaya (3.4 % and 3.7 %, respectively). In comparison with the results obtained by other authors for the same species, Dellatorre *et al.* (2020) analysed different species of algae from the Gulf Nuevo (Chubut, Argentina) and found lipids values for *Ulva* sp. of between 8 and 9 %, while for *U. pinnatifida*, about 6.3% were found, higher values than those reported in this study. Casas *et al.* (2010) obtained values of 3.1 % and 1.4 % in *U. pinnatifida* from Nuevo and San José gulfs (Chubut, Argentina), respectively. Sánchez-Machado *et al.* (2004) reported 1 % lipids in *U. pinnatifida*, lower values than those reported in this study. In the study conducted by Maehere *et al.* (2014), the lipid content of various seaweed samples was analysed, with reported values ranging from 1-3 % for *U. lactuca*. These values were found to vary according to the extraction solvent employed in the analysis. All previously reported studies agree that the lipid content of marine macroalgae typically does not exceed 6 % of the dry matter; however, they are of high quality (Cardoso *et al.* 2017; Quitral *et al.* 2012). Seaweeds are not typically considered a conventional source of energy, despite having a polyunsaturated fatty acid content that can be as high as that of vegetables (Mæhere *et al.* 2014; Sánchez-Machado *et al.* 2004; van Ginneken *et al.* 2011). Consequently, seaweeds represent promising natural sources of novel bioactive compounds with diverse biological functions, making them suitable candidates for use as functional ingredients in various industrial sectors, including the development of functional foods (Quitral *et al.* 2012). Further studies are required to determine the specific lipids present in algal extracts and to establish a reliable and reproducible procedure for their determination. The results may be significantly influenced by the method of algae treatment, particularly during the harvesting stage.

CONCLUSIONS

This study investigates the chemical and nutritional composition of selected macroalgal samples, including two species currently available on the market for human consumption. Assessing the chemical profile of macroalgae allows for the identification of both beneficial and potentially toxic elements, thus enabling an informed evaluation of their suitability as a food source for human or animal use. The analysis of metal concentrations revealed that marine macroalgae contain appreciable levels of essential minerals—such as calcium, iron, and zinc—when compared to other plant-based foods. However, these organisms also tend to bioaccumulate non-essential and potentially hazardous elements, including arsenic, lead, cadmium, and mercury. Regarding lipid content, the values obtained are consistent with those previously reported for other seaweed species. In contrast, polyphenol concentrations were comparatively lower than those documented in other studies. This discrepancy appears to be strongly influenced by sample preparation variables, including drying methods, storage conditions, and the type of extract used, which complicates direct comparisons. Overall, the chemical composition of macroalgae is highly variable and influenced by multiple factors, such as environmental element concentrations, life cycle stage, and seasonal variation. The findings of this study underscore the current gaps in knowledge, the methodological challenges inherent in macroalgal analysis, and the relevance of continued research to support their safe and sustainable use in food systems.

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