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Review

Atomic Spectroscopy-Based Analysis of Heavy Metals in Seaweed Species

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Abstract: This review compiles different analytical methods reported by the researchers studying heavy metal contents in seaweed samples from a variety of natural and commercial sources. Heavy metals in seaweed affect environmental health and human health due to seaweed's role in the aquatic food chain and human consumption. The potential for heavy metal presence in seaweed is due to industrial pollution and other human activities. There is an ongoing demand for evaluation of the presence of nutritional as well as hazardous metals in raw and processed seaweeds. This review article will look at the importance and usage of seaweed, the importance of measuring heavy metals in seaweed, seaweed's ability to absorb heavy metals, the health risks of consuming seaweed, and reported atomic spectroscopy-based heavy metal analysis methods in research on seaweed.

Keywords: seaweed; atomic spectroscopy; heavy metal

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1. Introduction

1.1. The Importance and Commercial Usage of Seaweed

Seaweed has a long history of consumption in cultures around the world, both utilized as human food and animal feed due to the variety of nutrients that some seaweed species possess [1,2]. These include vitamin B_{12}; polyunsaturated fatty acids omega-3 and -6; minerals, such as selenium, sulfur, zinc, copper, manganese, and iron; amino acids; dietary fibers; carbohydrates; essential elements, including iodine, nitrogen, phosphorus, potassium, calcium, and magnesium; and antioxidants, such as fucoxanthin [3–6]. Having higher concentrations of essential elements compared to land vegetables, seaweed is also used as a daily nutritional supplement for a healthy diet [7,8].

Interest in seaweed as a health food has been an important factor in its widespread use, as it is low in fat and calories in proportion to its high nutritional value, boosting its image as a superfood and/or health food [3]. In recent decades, especially in Europe, a health-food trend occurring in the West has increased the extent to which seaweed is used and eaten in modern society [6]. Seaweed is a source of antibacterial, antifungal, and antiviral compounds helpful to the human body in fighting health issues [9,10]. In addition, due to its high iodine concentrations, eating seaweed has been linked to the suppression of tumors in the body [5]. Due to a growing interest in sustainable food practices, seaweed as a vegan protein source is being used in a variety of dishes in Europe, from bread to drinks [3,4].

Seaweed can be used in more applications than as part of the human diet. Seaweed has been historically used as and continues to be a sustainable source of livestock feed, requiring no land to be farmed, with high crop yields and reduced livestock methane emissions compared to land-based plants. Furthermore, seaweed is being used not only as feed but also as fertilizer for soil, showing the broad range of its applications in agricultural production. Given seaweed's contents, it has been historically used as medicine in Asian countries, and in a contemporary role it is being used by pharmaceutical companies for drug development [11].

The Food and Agriculture Organization of the United Nations (FAO) referred to seaweed production as an important economic activity for many countries, with worldwide production of farmed seaweeds increasing from 10.6 million tons in 2000 to 27.3 million tons in 2014, and further to 32.4 million tons in 2018. Commonly farmed species are carrageenan seaweeds, such as *Kappaphycus alvarezii* and *Eucheuma* spp., which are used in gelling and thickening applications. Japanese kelp (*Saccharina/Laminaria japonica*) is also farmed as a widely eaten seaweed in East Asian countries [12,13].

1.2. Seaweed's Ability to Absorb Heavy Metals

Compared to lower-level organisms in the aquatic food chain, it is said that seaweeds can contain heavy metal concentrations that are "thousands of times higher" [14]. Studies have shown that metal concentrations in seaweed species were higher than the concentrations in ambient sea water [15]. Seaweeds' unique qualities in their cell walls allow for the biochemical process of retaining particulate metals. Polysaccharides and proteins in the cell wall contain anionic carboxyl, sulfate, and phosphate groups, which act as binding sites to absorb heavy metal particles. Thus, the makeup of the cell walls is the reason why seaweed contains both concentrations of trace minerals essential for the human diet and has a significant absorption capacity for heavy metals several times higher than those found in surrounding seawater [16].

While many materials have biosorption capabilities, seaweed is unique in its high heavy metal absorption capacity due to its inability to regulate how many trace metals it absorbs [17–21]. Heavy metal concentrations in seaweed also do not undergo short-term fluctuations, which is useful in reliably monitoring ecosystem health. Compared to green species, brown seaweed species are considered better at absorbing heavy metals [22].

1.3. Health Risks Associated with Seaweed Consumption

Due to the toxicity of even trace amounts of heavy metals and other elements, eating large amounts of seaweeds that absorb pollutants may pose a health risk. High biosorption results in potentially harmful amounts of lead, mercury, inorganic arsenic, nickel, cadmium, and also toxic levels of the essential elements iodine, copper, and zinc [23–25]. Even if measurements of heavy metals in seawater or sediment seem not to be at levels sufficient to raise any concern, measurements in seaweed can possibly be thousands of times higher in the same environment [4,5,26]. The nonessential elements lead, cadmium, arsenic, and mercury have been specifically studied and are said to pose a carcinogenic risk [4]. Arsenic can be found in either organic or inorganic forms, with the latter being more toxic and dangerous to health. The similarity in the chemical structure of phosphate, an essential building block for DNA, and arsenate, which can interrupt DNA synthesis, causes both to be absorbed equally into seaweed, explaining why seaweed can also contain high levels of arsenic [23,24]. Based on human toxicity data, local guidelines as well as international standards have been set for permissible levels of heavy metals in food and drinking water. Table 1 lists the permissible levels for the four heavy metals that are most hazardous to human health [27–35].

Creating risk assessments based on regular surveys of heavy metal concentrations in commercially available seaweed is suggested to protect consumers and maintain food safety [36–38]. While the negative health effects of heavy metals on the body have been studied thoroughly, many studies have pointed out the need for more research on heavy metals or metalloids in seaweed, especially species-specific studies [23–25]. Lack of data on the distribution of metal contamination in waters and pre-/post-market seaweed in specific geographic areas, such as Europe and Malaysia, leaves the safety of consuming seaweed in question [3].

Table 1. Permissible limits (ppm) for heavy metals in food and drinking water according to international and local standards. Note that the US Food and Drug Administration has not established regulatory limits for trace metals in finished food products other than bottled water.

Matrices	Area of Application	Arsenic (As)	Cadmium (Cd)	Mercury (Hg)	Lead (Pb)
Food	International	0.1–0.2	0.05–2	0.5–1	0.01–3
	European Union	0.1–0.2	0.05–3	0.1–1	0.02–3
	USA	NA	NA	NA	NA
	China	0.5	0.05	0.01	0.2
Drinking water	International	0.01	0.003	0.001	0.01
	European Union	0.01	0.005	0.01	0.001
	USA	0.01	0.005	0.002	0.015
	China	0.01	0.005	0.001	0.01

The European Union has taken action to collect data and to potentially establish maximum allowable levels of elements in seaweed to prevent high exposure to toxins within the population [3,24]. The European Union has also published a recommendation on monitoring specific trace elements in seaweeds that are intended for consumption [23].

A study suggests limiting the consumption of seaweed and changing dietary habits due to the exposure risk of unhealthy trace metal levels [7]. More research on both the beneficial qualities and potentially harmful elements in specific seaweed species is needed to differentiate between environmental contamination and acceptable element levels [6,24,39]. One study focused on the species *Sargassum fusiforme*, also known as hijiki, a commonly eaten seaweed in Japan. While it is a popular seaweed to be eaten, if exposed to pollution, it is said to be likely to contain excessive amounts of heavy metals which are dangerous to the consumer. Even the essential elements copper, chromium, and zinc were found to be concentrated at toxic levels. Thus, detection models for specific elements in *Sargassum fusiforme* are needed for quality assurance in the case of this popular product [25]. Several studies found that levels of nonessential elements found in seaweed were greater than acceptable concentration limits. Limits set by European regulations were exceeded by the lead concentrations of multiple seaweed species from a collecting site in the Mediterranean Sea, and the combined risk of nonessential element amounts in seaweed exceeded the United States Environmental Protection Agency reference limit of 10^{-4}, showing evidence of carcinogenic risk [1,4]. The presence of antimony (a metalloid that can impair cellular metabolism), cobalt, and vanadium in seaweed has also been reported [39].

1.4. Seaweed and Environmental Health

Ocean water remediation of heavy metals has become a necessary action due to multiple industrial sources of heavy metal and trace metal contamination, such as mining and petroleum industries, affecting water systems. The accumulation of trace metals in marine ecosystems becomes metabolized by the organisms living in the water [26]. The side effects of urbanization and urban waste are also to blame for increasing heavy metal levels in aquatic ecosystems. Water pollution affects both wild seaweed and cultivated seaweed; therefore, it is a direct threat to food supplies and quality [1].

Seaweed has been used in environmental conservation as a bioindicator, especially in monitoring water pollution [40–42]. Bioindicators are organisms that reflect the overall health of an ecosystem [43]. A study assessing the biomonitoring potential of seaweed collected off the Indian coast reported that “seaweeds are considered as the best bioindicator of heavy metals pollution” [22]. There is research that tests seaweed’s absorption levels of toxic heavy metal cations, this absorption occurring in a process called biosorption, which removes heavy metals from surrounding water. Biosorption occurs when positively charged metal ions are absorbed through a solid biological surface into the cellular structure of the biomass. Since it does not have to involve a living organism, biosorption can occur with any biological material. Therefore, dead seaweed has also been used in biosorption. The use of seaweed is a natural way of managing environmental clean-ups and has a promising future as a renewable resource that is biodegradable and widespread in its distribution across the globe [23].

2. Atomic Spectroscopy-Based Heavy Metal Analysis Methods for Seaweed

Atomic spectroscopy comprises several analytical techniques allowing elemental quantitative analysis of a target sample. Since the determination of levels of various metals is essential in medicinal, food, environmental, and a wide range of manufacturing sectors, this method is widely applied for metal analysis. Depending on the measured parameter, atomic spectroscopy techniques can be divided into three basic types based on light absorption, emission, or fluorescence. Although atomic fluorescence can provide lower detection limits for some metal ions, the method is less commonly used in the food industry. Therefore, our discussion in this review emphasizes the application of atomic absorption and emission technologies in seaweed metal analysis.

Atomic spectroscopy is based on the quantized changes in atomic energy upon the absorption or emission of light. In absorption, the energy of an atom increases when an electron transitions from an orbital of lower energy in the ground state to one of higher energy in the excited state. Atomic emission is the reverse of the absorption process, where atoms in the excited state emit light upon the transition of an electron back to the lower energy ground state. Since the atomic orbitals are discrete and few in number, atomic spectra contain very narrow transition bands at single wavelengths corresponding to the various transitional energy values between the atomic orbitals specific to each metal.

Analytical techniques are often categorized according to the atomization/ionization source (flame, furnace, or plasma) or the type of spectroscopy used (absorption, emission, fluorescence, or mass). Combinations of these give rise to numerous analytical techniques with different performance characteristics [44].

Heavy metals can be enriched in seaweed species and seriously endanger human health due to the growing interest of people around the globe in the consumption of seaweed-based food. The wide range of metal concentrations present in seaweed, ranging from ng/g levels to percent levels, combined with the analyte and matrix specificity of atomic spectroscopy methods introduces challenges in the selection of a specific technique for metal analysis. In the food industry, the most common electromagnetic techniques are based on atomic absorption and atomic emission spectrometry. This review summarizes atomic spectroscopy-based technologies that have been used for heavy metal determination in various seaweed species at different geographical locations. The applicability of each technique is discussed by providing study cases reported by the scientists in the field.

2.1. Sample Preparation

Proper selection and treatment of seaweed samples are crucial since the complexity and homogeneity of a sample will dictate the subsequent steps that are needed to ensure accurate analysis. The use of titanium or high-purity glass knives and mixing blades and polyethylene and polypropylene containers along with the adoption of good laboratory practices can minimize trace element contamination. Containers made of quartz of borosilicate glass are less desirable. During sample preparation, glassware can be silanized to minimize the likelihood of contamination [45]. Conceivable sources of contamination include but are not limited to the analyst's skin, clothing, and gloves; sample containers; and metallic heating blocks and furnaces.

Samples are commonly introduced into atomic spectrometers as solutions. Several procedures can be used to obtain seaweed samples in solution. The choice of digestion method is made upon considering the efficiency of sample decomposition, the level of contamination of samples, possible reagent-related interferences and matrix effects, the instrument and detection limit requirements, and safety aspects.

Sample mineralization by an acid or a mixture of acids (wet ashing) on a heating plate under ambient pressure in a pressurized digestion vessel (digestion bomb) with open- and closed-vessel MW-assisted digestion or with ultrasound (US)-assisted extraction are among the most common sample preparations in food metal analysis.

HNO_3 is the most suitable acid for spectrometric analysis since no significant analytical problems or minimal interferences are observed when it is used at concentrations up to

10%. Due to the low oxidation potential of nitric acid, for optimum digestion, some materials require the addition of other types of acids despite the problems related to their use at high temperatures and pressures. To maintain a higher temperature under certain pressure limits and reduce the carbon contents in the digestates, often H_2O_2 is added to mineralization samples without introducing any major analytical difficulties. Nevertheless, H_2O_2's impurities limit the determination of some elements at low levels. Moreover, the use of HCl for GFAAS sample preparation may be challenging due to the formation of volatile and indissociable analyte chlorides that will lead to interferences. It is recommended to avoid the use of H_2SO_4 (due to its high viscosity) in sample preparation procedures for analytical instruments that use nebulizers for sample introduction. In addition, H_2SO_4 can sparingly form soluble sulfates that can precipitate from solution. Small amounts of other strong acids can be added for special analytical purposes, such as the addition of HF for the solubilization of Si-bound elements in food samples containing high amounts of Si [46]. Although $HClO_4$ and H_2SO_4 are also used as oxidants, their production of a number of spectral interferences and their being potential sources of contamination and increased danger do not make them good choices for digesting agents.

Open-vessel wet ashing digestion procedures for the determination of metals suffer from disadvantages, such as being time-consuming, the high possibility of analyte contamination and loss, and their not being vigorous enough for the complete mineralization of some matrices. To overcome these drawbacks, high-temperature and/or high-pressure methods are considered as alternative digestion methods. Microwave (MW)-assisted sample digestion is reported as a widespread technology in the field of food sample preparation [47]. Most often, small amounts of food samples are digested with HNO_3; a mixture of HNO_3 and $HClO_4$; or a mixture of H_2O_2, HNO_3, and $HClO_4$. In the MW heating process, the energy is generated within the digestion mixture and not transferred by conduction (as with hot plates), leading to a more effective heating.

Pressurized closed-vessel MW systems are preferred to open-focused systems that work under atmospheric pressure because of their reduced risk of sample contamination and loss of volatile elements. Employing tetrafluorometoxil polymer digestion vessels (TFM/PTFE) can accommodate higher temperatures (350 °C) and pressures (up to 160 bar), which results in more complete destruction of organic matrix constituents using only HNO_3 as the digestion medium [48].

Although the use of MW-assisted mineralization processes allows shorter digestion times than wet ashing techniques, the long cooling times required before opening the vessels remain as the main limitation. Ultrasound (US)-assisted digestions are reported to be a promising alternative to MW-assisted techniques in the search for faster sample preparation procedures [49]. Other advantages of US-assisted digestion methods include improved safety since the method involves neither high pressure nor high temperature, lower reagent consumption, reduced acid waste generation, and lesser risk of contamination due to the lower number of analytical steps involved. In a study by Costas et al., the procedural detection limits for rare earth elements in the case of the developed US-assisted digestion procedure were found to be five-fold better than those obtained with the MW-assisted digestion method [50].

When no standard method exists for digestion conditions of a certain type of sample matrix, modification of regulatory or standard methods may become necessary. The accuracy of an optimized procedure can be evaluated by the analysis of standards. Several individual digestion methods have already been validated in the field of food analysis, but only a little comparative information is available to help the analyst select the most appropriate method for a specific group of elements [51]. The choice of digestion method has a major influence on the precision and accuracy of a measurement with atomic spectroscopy techniques for a given element.

2.2. Atomic Absorption Spectrometry (AAS) Techniques

Atomic absorption techniques rely on the fact that every element absorbs light at a characteristic wavelength, and the amount of light energy absorbed is proportional to the number of analyte atoms in the light path. AAS methods are relatively inexpensive and convenient for uncomplicated elemental analysis in food. Other general advantages include the high precision and accuracy obtained by the calibration curves and the low interelement interferences in absorption signals. Typically, a hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL) is used as the source of light which is characteristic of each target element. Owing to this limitation, in most cases these techniques are limited to single element detection [52,53]. Another disadvantage is the limited application of AAS techniques, as only about 70 elements, excluding earth metals and non-metals, have been detected by these methods.

2.2.1. Flame Atomic Absorption Spectrometry

Flame atomic absorption spectrometry (FAAS), where a flame is used to atomize the elements, is widely accepted in many industries, which continue to utilize the unique and specific benefits of this technology. FAAS is simple, robust, and inexpensive for analysis of a wide range of elements. On account of the maturity of the technique, relatively well-established FAAS methods are available in the analytical literature. Calibration with aqueous standards can typically be accomplished using 3- to 5-point calibration curves. Conversely, FAAS has the limitation of transient and relatively diffuse atom density in the flame, which results in poor sensitivity when compared to other techniques. Typical detection limits are in the high ppb to ppm range [53,54]. Thermospray flame furnace atomic absorption spectrometry (TS-FF/AAS), as a relatively new technique, considerably increases the sample-introduction efficiency compared to traditional settings. The increased residence time of the sample in the flame results in better sensitivity, which can improve the DLs for a number of elements [55].

Among the elements of interest in the food industry, selenium (Se) measurement by traditional FAAS suffers from a relatively poor detection limit (DL) of around 1 µg/mL; however, the application of hydride generation (HG) sample introduction lowers the DLs to sub-parts per billion for Se [56]. Several examples of heavy metal analysis in seaweeds using AAS are given in the following sections, and the measured concentrations are presented in Table 2.

Table 2. Concentration of the heavy metals in seaweed species at different geographical locations measured by AAS. All values are in µg/g dry weight. The following data show the range of minimum and maximum values where applicable.

	Persian Gulf and the Gulf of Oman [37]	**Southern Thailand Provinces [8]**	**Bay of Bengal [34]**	**Coastal Areas of Rameshwaram, Tamil Nadu, India [22]**	**Coastline of Hormuzgan Province, Iran [18]**	**Coastal Areas of Karachi, Arabian Sea [40]**	**Coastal Sites of Northeast England [41]**
Cr		1.43–2.80	ND *			0.004–4	0.8–5.0
Mn		557.05–746.75	0.543–3.615	-	-	0.006–1.57	18.8–778.4
Fe	196.08	172.95–841.23		1104–2872	4438–14,867	0.011–12.6	65.0–1208.9
Co						0.003–0.20	
Ni	12.89	6.03–8.26			21.5–90.8	0.003–0.43	0.3–70.5
Cu	11.17	1.65–2.91	ND *	90–107	6.4–16.9	0.002–0.8	4.8–50.6
Zn	19.67	30.15–36.60	0.203	108–137	54.93	0.008–0.632	12.9–1015.5
Ag							0.9–4.2
Cd	4.8	0.08–0.13	0.092–0.121	27–42.2	2.1–7.0	0.002–0.42	0.02–10.03
Pb	7.41	4.79–6.60	0.429–0.933	19–37	13.1–30.5	0.006–1.1	0.1–12.1

* ND stands for "not detected".

Daryaii et al. analyzed green, brown, and red seaweed species from different intertidal regions of the Persian Gulf and the Gulf of Oman for the determination of Cu, Zn, Pb, Ni, Fe, and Cd concentrations [57]. Samples (1 g each) were digested in polytetrafluoroethylene digestion vessels with 5 mL concentrated HNO_3 at ambient temperature for 2 h followed by heating for 5 h at 100 °C until 1 mL of the acid remained. Filtered cool solutions were diluted to 50 mL in polypropylene volumetric tubes and analyzed. Trifan et al.'s method was used for blank preparation [58]. The results showed that Fe, Ni, Zn, Pb, Cu, and Cd were found in all the studied seaweed species. It was also found that the contamination levels in seaweeds were related to collection sites, seaweed species, and environmental factors, such as salinity, pH, and light intensity.

Another research group used method 975.03 of AOAC 2000 to analyze heavy metal contents in warm-water seaweeds (*Gracilaria fisheri*) cultivated in Southern Thailand provinces [8,59]. A quantity of 1 g of dried sample was soaked in 10 mL HNO_3 followed by the addition of 3 mL 60% $HC1O_4$. The mixture was heated slowly on a hot plate until frothing ceased and the HNO_3 had almost evaporated. After cooling, 10 mL HCl was added, mixture-filtered through a microfiber filter, and volume-adjusted to 50 mL prior to analysis. The researchers found that Mn and Fe were the main microelements in the studied seaweed species, while Ni and Pb were the dominant heavy metals. The study suggested that the daily consumption of the studied seaweed should be in the range of 38–52 g daily value (DV).

Karthick et al. digested seaweed samples from the Bay of Bengal using aqua regia (0.5 g in 5 mL) gently heated and diluted to 50 mL with deionized water (DI) [43]. In the reported investigation, the heavy metal accumulation of seaweeds was in the following order Mn > Pb > Cd in the six studied seaweed species. Zn was observed only in free-floating brown seaweed *S. swartzi*, whereas Cu and Cr were not detected in any of the samples. The study concluded that the variability of metal accumulation could be the result of competition between the metals to bind with polysaccharides to different extents and also depended on the color of the seaweed.

In another reported study, selected brown (*Sargassum* sp.) and green (*Ulva* sp.) seaweeds from coastal areas of Rameshwaram, Tamil Nadu, India, were digested using various concentration of acids: a 5:1 mixture of HNO_3: $HClO_4$, a 3:1 mixture of HNO_3: $HClO_4$, and a mixture of 5:1:0.5 of HNO_3: $HClO_4$: H_2SO_4 [22]. In the two studied seaweed types, metal content sequences were observed to follow the trend Fe > Zn > Cu > Cd, and Pb was not detected. This study found that some local seaweeds may be used as potential biomonitors as well as absorbents of cadmium from industrial effluent.

In the investigation by Sohrab et al., eleven seaweed species from the coastline of Hormuzgan Province in Iran were analyzed using a flame atomic absorption spectrometer with a deuterium background corrector [18]. The accuracy of the analysis was certified by the inclusion of DORM-3 (Fish protein) (National Research Council of Canada) reference material. In this study, the concentrations of heavy metals in eleven seaweed species from thirteen locations decreased in the following order: Fe > Zn > Pb > Ni > Cu > Cd. The researchers showed that variation in the accumulation of metals in seaweeds depends on the type of polysaccharides present in the cell walls as well as the different electronegativities of the elements. They observed more uptake of the metals with higher electronegativity values (e.g., Fe, Ni, and Cu) compared to the other metals with lower values (e.g., Cd). The study validated the use of seaweed for biomonitoring of polluted marine environments.

Red seaweeds belonging to twenty-six genera from coastal areas of Karachi, Arabian Sea, were collected over a period of three years by Qari et al. [60]. Quantities of 1 g of each sample were digested in a mixture of HNO_3 (4 mL) and $HClO_4$ (2 mL) in Teflon vessels at 80 °C on a hot plate. After digestion and evaporation of the acids, the samples were redissolved in 100 mL of DI. The accumulation of heavy metals in the 40 studied seaweed species showed great variation with respect to the sampling sites, seasons, and types of species. The study elucidated that the studied seaweeds had the ability to uptake Fe, Mn, Ni, Cu, Cr, and Pb more than the other metals and did not accumulate Co and Cd to a great extent.

2.2.2. Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Graphite furnace atomic absorption spectrometry (GFAAS), in which a graphite furnace atomizes a sample, is a conventional technology for measuring elements at the sub-ppb concentration range utilizing microliter-sized sample volumes. Traditionally, samples are fed into the graphite furnace as solutions; however, direct solid and slurry sampling are now possible. Most often, calibration (even for slurry samples) is established with aqueous standards.

The programmable temperature-control feature of GFAAS instruments allows the solvent and matrix to be separated from the analyte as a function of boiling point. The stabilized temperature platform furnace in GFAAS atomizes the analyte isothermally, which results in matrix modification for analyte stabilization and rapid furnace heating. Although this technique is a versatile and highly sensitive tool for the analysis of a wide range of sample types, it measures fewer analytes than FAAS and is much slower [35,36].

Vaporization of a large amount of solid in the graphite tube can lead to matrix effects. The presence of uncharred organic material may affect the volatility of some elements, increase background levels, and build up carbonaceous material in the furnace. To improve these problems, the application of chemical modifiers can stabilize volatile elements in heated furnaces. In addition, background correction methods, such as the Zeeman or Smith–Hieftje methods, should be considered. The use of an oxygen or air ashing step in the furnace program or the addition of H_2O_2 to the slurry diluent have been found to be effective in removing carbonaceous material [61–64].

A methodology was developed by Boucetta et al. in which a flame atomic absorption spectrometer (FAAS) was used to measure Cu and Zn, while graphite furnace atomic absorption spectroscopy (GFAAS) was utilized for the analysis of Cd, Cr, and Pb [14]. Seaweed specimens of 0.7 g of *U. lactuca (Sea Lettuce*) from the eastern coasts of Algeria were mineralized in a microwave oven with HNO_3 (6 mL) and H_2O_2 (2 mL). Phosphate monoammonium $NH_4H_2PO_4$ (10%), the phosphate PO_4 (0.2 mg), and magnesium nitrates $Mg(NO_3)_2$ were used as matrix modifiers for Cd, Pb, and Cr determination, respectively. Certified reference materials, CRM 279 (sea lettuce) and ERM CE 278 (muscle tissue), were used to validate the accuracy of the analytical procedure. Depending on the heavy metals, collection sites, and sampling seasons, significant correlations were determined for the different species studied. The accumulation sequence at all sites was found to be Zn > Cr > Cu, and the lowest concentration was observed for Pb. The authors observed that the accumulation of elements in seaweeds was closely related to thallus morphology and growth strategy. Filamentous and sheet-like macroalgae, exhibiting a higher surface area for element absorption, accumulated higher contents of elements than coarsely branched and thick-leathery macroalgae. The study confirmed that seaweeds are good biomonitoring tools of trace metal contamination in Mediterranean marine areas.

Quantities of 5 g of ashed brown seaweed (*Fucus vesiculosus*) from coastal sites of Northeast England were mixed with 20 mL aqua regia for 48 h, refluxed on a hot plate, and diluted to 50 mL with DI for heavy metal analysis by FAAS and GFAAS [65]. The precision and recovery of the procedures were checked using NIES No. 9 Sargasso seaweed certified standard reference materials. The concentration sequence of the most abundant elements was found to be Fe > Mn > Zn > Cu, with Cd and Ag being the least abundant elements. The heavy metal load of seaweed at the sites investigated was similar to that of other polluted areas of the British coastline. Ag accumulation in seaweed was more prominent at sites affected by past mining activities.

The presence of Cu, Pb, and Zn in the seaweed species *E. compressa* collected from 10 different stations in the lower Gangetic delta complex over three seasons was evaluated with AAS fitted with a graphite furnace atomizer [66]. A quantity of 1 g of the dried sample was digested using a mixture of H_2O_2 and HNO_3, followed by HCl. The order of accumulated heavy metals was Zn > Cu > Pb, and the seasonal variation pattern was monsoon > postmonsoon > premonsoon, which was similar to the trend of dissolved heavy metals. The authors concluded that traditional rope culture of *E. compressa* in the vicinity of the industrial discharge points might be an eco-friendly approach to cost-effectively purify contaminated water.

2.2.3. Solid Sampling Zeeman Atomic Absorption Spectrometry (SS-ZAAS)

As mentioned in the sections above, wet digestion with strong acids as the pretreatment and sample decomposition stage is one of the most crucial steps in conventional AAS analytical procedures. As an alternative to methods using wet digestion, direct solid sampling Zeeman atomic absorption spectrophotometry (SS-ZAAS) serves as a very fast and precise method where chemical sample pre-treatment is not needed [67]. Minimum chances of contamination and very low sample consumption are among the advantages of this technique. Since a chemical pretreatment step is not included and the sample is used directly, in general, solid sampling techniques achieve lower limits of detection than wet digestion methods.

Detcheva et al. developed an SS-ZAAS method to determine Hg, Cd, Pb, and Mn levels in seaweed [68]. The proposed method was validated by analyzing certified reference materials (CRMs) with similar matrices. No chemical modifiers were used, and no matrix effects were observed under the optimized conditions. For Hg determination, mussel tissue BCR CRM-278, cod mussel BCR CRM-422, and human hair BCR CRM-397 were used for calibration, and a 0.008 mg/g limit of detection was achieved. The 228.8 nm and 326.1 nm resonance lines were used in two-field and three-field modes, respectively, with rice flour NIST SRM-1568 and mussel tissue BCR CRM-278 references and achieved 0.0013 mg/g detection limits for Cd content determination. Similarly, Pb concentration was measured at two different wavelengths: 283.3 nm (two-field mode, bovine muscle BCR CRM-184 and bovine liver BCR CRM-185 as references) and 261.4 nm (two-field mode, pepperbush NIES-1 and Olea europaea BCR CRM-62 as references). The limit of detection was estimated to be 0.008 mg/g Pb. Due to the high Mn contents in all of the investigated samples, a less sensitive resonance line of 403.1 nm and the dynamic measurement mode were applied. A calibration with mussel tissue BCR CRM-278R, plankton BCR CRM-414, and tea leaves NIES-7 were used to create the calibration curves. Overall, the study showed a good agreement between the experimental and certified values. From the collected data, it was concluded that by avoiding sample dilution and chemical modifiers, direct SS-ZAAS is a reliable, rapid, and low-cost technique for the determination of trace elements in aquatic plants.

2.3. Atomic Emission Spectroscopy

Single element measurement, poor sensitivity, and slow analysis rates are some of the limitations of atomic absorption spectroscopy that have been overcome with atomic emission spectroscopy techniques. Although it is possible to attain the emission spectrum of an element using atomic spectrometers, such as FAAS, the flame may not be the best excitation source of the elements. Inductively coupled argon plasma (ICP) has proven to provide higher temperatures than flames to give broader elemental coverage and higher sensitivity than AAS techniques. ICP can reach temperatures close to 10,000 K, which results in complete atomization and significant ionization of the analyte. Therefore, molecular interferences are reduced, and the detection of atom and ion emissions is better achieved [69].

2.3.1. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Sample analysis with ICP-OES is usually safer than FAAS due to the use of inert argon gas as an atomizer instead of a flammable gas, such as acetylene. Not requiring a lamp for each element, simultaneous multi-elemental analysis, and low ppb detection limits are among the advantages that make ICP-OES the favored technique for elemental determination in many industries, including the food industry. Additionally, heavy workloads of analysis created the need for a fast analysis technique and the ability to measure multiple elements in many samples. ICP-OES takes less than one minute to measure the concentration of up to 74 elements in a sample. In addition, samples that contain very high percent levels of total dissolved solids (TDSs) or suspended solids are easier to analyze using ICP-OES due to the high temperature of the plasma. However, unlike GFAAS, ICP-OES cannot reach sub-ppb and ppt detection ranges; therefore, it is not a suitable technique for measuring trace elements; however, the use of axially viewed ICP/OES systems has narrowed the gap [70,71]. ICP/OES provides a linear dynamic range of five orders of magnitude or greater (compared with two orders of magnitude for AAS) that makes both macro- and microanalysis of samples possible. The introduction of charge transfer device (CTD) detectors provides more flexibility in analytical line selection, and the use of several lines of the same element extends the dynamic range and reduces possible matrix effects or spectral interferences [72]. The combination of sample injection into an air carrier stream with a low sample consumption system has been evaluated for the analysis of microsamples through ICP/OES [73]. Reports of heavy metal analysis in seaweeds using ICP-OES are presented in the following sections, and the measured concentrations are depicted in Table 3.

Table 3. Concentrations of the heavy metals in seaweed species at different geographical locations measured by ICP-OES. All values are in µg/g dry weight. The following data show the range of minimum and maximum values where applicable.

	Seaweed Farms in Malaysia [24]	**Coastal Regions of Sri Lanka [26]**	**Canary Islands, Spain [5]**	**Wandoor Area of Southern Andaman Island [47]**	**Abandoned Intertidal Cu and Zinc Mine, Brooksville, ME, USA [20]**	**Zhejiang, China [29]**	**Southeast Coast of India [48]**
V			0.36–3.12				
Cr	23.8–47.37	33.5–77.5		0.002–0.334		0.853–6.846	0.029–0.89
Mn	2.5–25.6			0.118–7.736		11.30–46.56	0.53–7.36
Fe	133–324.2		49.1—629				1.11–58.5
Co							0.02–5.12
Ni	6.9–14.3	3.5–10.7	0.88–2.30			1.023–2.138	0.03–13.26
Cu	0.85–2.9	1.5–8.4		0.003–0.291	<1.0–234	1.099–21.94	0.19–1.38
Zn	12–31.2			0.019–5.537	22.9–2570		0.36–2.11
As	1.35-7.9	ND *–8.1				12.44–30.5	
Ag	0.1–0.25						
Cd	1.23–2	3.1–6.8	0.13–0.22	0–0.311	<1.0–20.1	0.117–4.323	0.01–0.60
Hg		ND *				0.008–0.087	
Pb	2.75–11.94	ND *	0.34–2.70	0–0.165	<1.0–55.2	0.532–1.186	0.13–11.31

* ND stands for "not detected".

In a study by Kreissig et al., fresh seaweed samples of *Eucheuma cottoni* were collected from three major seaweed farms in East and West Malaysia [24]. A quantity of 0.5 g of dried sample was digested in a Teflon vessel with 10 mL of HNO_3 and 3 mL of HCl at 100 °C for 2 h. The elements Ag, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were analyzed with ICP-OES. Instrument calibration was carried out with a multi-element calibration standard solution diluted to the concentration range of 10 mg/L to 100 mg/L. The NIST standard reference material SRM 1400 and the NMIJ certified reference material CRM 7405-a were used to validate the results, which showed over 96% recovery values for all of the analyzed metals. Measurement data for the essential mineral elements, such as Fe, Mn, and Zn, were consistent with the literature data, suggesting that the seaweed is a good source of nutrients. The daily estimated intakes of most metals (calculated with measured values, consumption rates, and average body weight) were within the recommended daily dietary allowance levels. However, upon considering the health hazards of the potentially toxic elements, the authors concluded that the cumulative carcinogenic risk (calculated based on lifetime period of exposure to the ingested metals) was non-negligible. In addition, the total hazard index (HI), which represents non-carcinogenic chemical risk, was found to be 4.38, indicating a level of major concern [24].

In another study, samples from each of the three seaweed types (*Sargassum* sp.-Phaeophyta, *Ulva fasciata*-Chlorophyta, and *Gracilaria* sp.-Rhodophyta) were obtained from four sites in the coastal regions of Sri Lanka [26]. A quantity of 0.25 g of dried sample was microwave-digested with 4 mL concentrated HNO_3 and 1 mL H_2O_2. A quantity of 0.1 mL of 50 ppm of Au and Lu mix was also added. Digestion was carried out at 190 °C for 15 min. Analysis of the metal elements As, Cd, Cr, Cu, Hg, Ni, and Pb was performed with ICP-OES. NIST-SRM 3232 for kelp powder was used for method validation, with recovery values ranging from 85.9 to 97.4. The concentrations of the seven metal elements measured in this study were in the order: Cr > Ni > Cd > Cu > As > Pb = Hg, where both Pb and Hg were not detected in any of the samples. The high concentration of Cr was hypothesized to be due to the increased levels of industrialization in these areas. The authors also assessed the health risk of seaweed consumption, based on consumption data in Mainland China, since most of the harvest from Sri Lanka is exported.

Rubio et al. collected 64 seaweed samples of various species from the *Phaeophyta* group from three areas in the Canary Islands, Spain [5]. After the homogenization step, 3 g of each sample was dried in an oven at 70 to 75 °C for 24 h, then digested with 65% HNO_3 and incinerated in a muffle furnace at 420 °C for 24 h. The resulting ashes were dissolved in up to 25 mL of 1.5% HNO_3 and subject to ICP-OES analysis for the metal elements Cd, Fe, Ni, Pb, and V. Three reference materials (SRM 1515, SRM 1570a, and BCR 279) were used for method validation, and the recovery percentages were found to be over 94%. The authors concluded that the growing area is an important factor affecting seaweed metal concentrations, possibly due to the differences in marine currents and human activity. Among the various species, *P. pavonica* contained the highest concentrations of toxic metals and trace metals. While none of the metals analyzed (in all the seaweed samples) pose a health risk for human adults, assuming the daily consumption to be 5 g of dehydrated seaweed, estimated daily intake (EDI) of Pb in *P. pavonica* does reach as high as 57.2% of tolerable daily intake (TDI).

Four species of seaweed were collected from the Wandoor area of Southern Andaman Island during three different seasons to assess the potential of seaweed to monitor heavy metal pollution in aquatic ecosystems [74]. Quantities of 0.5 g of each sample were digested with 5 mL aqua regia HCl and HNO_3 (3:1). The digested samples were filtered, diluted to 50 mL, and analyzed with ICP-OES for concentrations of Cd, Cr, Cu, Mn, Pb, and Zn. The average metal accumulation was ordered as Mn > Zn > Cu > Cr > Cd > Pb for three collection seasons. The highest accumulation was found in the seaweed species *P. pavonica*, with 7.736 µg/g of Mn. After comparing accumulation levels in brown and green algae from this study, the authors suggested that brown algae can be better used as a biomonitor for trace metal studies since they retained higher levels of all the metals reported in this paper. On the other hand, the authors also pointed out that, in a previous study [75], a green algae species was observed to have potential for metal uptake, especially Zn. Furthermore, based on the measured concentrations of all six metal elements and the calculated metal pollution index (MPI), the authors concluded that the Wandoor area of Southern Andaman Island remains mostly unaffected by industrial pollution.

Seaweeds (eight species) were collected at various sites from the area of an abandoned intertidal copper and zinc mine in Brooksville, ME, USA [20]. The collection sites included two estuary locations where the mine was situated and locations with slower water movement, one waterfall site near the estuary outlet, and some clean sites. The seaweed samples were carefully cleaned to remove metal particulate contaminants, then rinsed, scraped, and bathed in a solution of 10% ethanol and 3.5% NaCl, followed by two baths in DI water while being gently scrubbed. The cleaned seaweed samples were dried, ground, and ashed at 350 °C. The resulting ash was dissolved in 50% HCl on a hotplate and subjected to ICP-OES analysis for the determination of concentrations of Cd, Cu, Pb, and Zn. The metal concentrations followed the pattern: Zn > Cu > Pb > Cd. Although the metal concentrations of some species at the first two sites were much higher than background levels, the third site showed metal levels close to the clean sites, suggesting that the metal pollution caused by the Cu/Zn mine did not extend to outside the estuary area. Besides proposing future monitoring of seaweed diversity and tissue chemistry in this area, the authors also brought up the possibility of utilizing seaweeds to remediate metal pollution.

In a comprehensive study by Chen et al., 295 dried seaweed samples (142 red seaweeds and 153 brown seaweeds) were collected at four sites in Zhejiang, China, and analyzed for concentrations of As, Cd, Cr, Cu, Hg, Ni, Mn, Pb, and Se to address food safety concerns [38]. Quantities of 0.5–2 g of each sample were digested in 6 mL HNO_3 at 180 °C for 30 min in a microwave digestion system. The digested solutions were evaporated to 0.5 mL, further diluted to 5 or 10 mL with DI water, and then analyzed for metal concentrations with ICP-OES. Two CRMs (GBW 10023 and GBW 08517) were used as quality controls, and the authors deemed the analysis results acceptable, since the mean recoveries for CRMs were between 82.6 and 99.4%. Considering all seaweed samples, the metal concentrations were ordered in this way: Mn > As > Cu > Cr > Ni > Cd > Se > Pb > Hg, though red seaweeds and brown seaweeds showed significant concentration differences for some of the metal elements. When comparing the four geographical origins, Hg and Pb showed significant differences. Pairwise association was examined, and only a weak correlation was found between the following pairs: Ni-Cr, Mn-Cu, and Mn-Pb. Food safety was assessed with targeted hazard quotients (THQs) and hazard indices (HIs), which both indicated low risk to human health, assuming 5.2 g/capita/day consumption in China. The authors also pointed out the uncertainty of health risk assessments due to potential interactive effects among multiple metals as well as possible loss of elements caused by the food preparation process.

Five species of green seaweeds were collected along the Southeast Coast of India and analyzed to assess their nutritional values [76]. A quantity of 0.5 g of dried sample was digested in two microwave cycles: in 2 mL H_2O_2, 8 mL purified concentrated HNO_3, and 2.0 mL HF for the first cycle; then 2.0 mL purified concentrated HNO_3 and 2.0 mL $HClO_4$ were added before the second cycle. The selection of microwave power and time was optimized to ensure complete dissolution of the different types of tissues [77]. The resulting digests were evaporated and dissolved in 2.5 mL of concentrated HNO_3 and diluted to volume with double-distilled water (DDW). The samples were then measured via ICP-OES for metal concentrations (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn). The results showed that the metal concentrations varied in different species.

The possibility of utilizing concentration profiles of some major and trace elements to characterize edible seaweed harvested from Northwestern Spain was studied by Hortas et al. [6]. Thirty-five edible seaweed samples were supplied by a local manufacturer. For the dry seaweed samples, 100 g were oven-dried, cut by hand, pulverized, and sieved, while canned seaweed in brine was lyophilized then pulverized. Dried powder samples were further subjected to a microwave-assisted acid digestion method: 8 mL of concentrated HNO_3 and 2 mL concentrated H_2O_2 were added to 0.2 g of powdered seaweed samples, followed by a timed program of microwave irradiation. After cooling, the samples were diluted to 25 mL with Millli-Q water, and the concentrations of Cu, Mn, and Zn were measured with ICP-OES. The microwave digestion method as well as ICP-OES analysis were validated by analyzing NIES-09 CRM: measured values were found to agree well with certified values. Statistical analysis was performed on the measured values of Cu, Mn, and Zn and various other elements measured by HG-AFS and ICP-MS in order to classify the seaweed samples, though with mixed outcomes. For example, LDA (linear discriminant analysis) correctly classified brown, red, and green seaweeds, while SIMCA (soft independent modeling of class analogy) was only able to classify red seaweeds with satisfactory results. The authors also concluded that different metal elements offer varying discrimination powers for distinguishing among brown, red, and green seaweeds: based on the classification approach used in this paper, Ca, Cu, and Mg concentrations have the highest discriminating capabilities, while Zn concentration has poor discriminating power.

The fates, transportation, and impacts of three recognized *Sargassum* (brown seaweed) genotypes from seven sampling stations along a 3600 km transect extending from the middle of the Atlantic Ocean (open sea) to Guadeloupe were studied by Cipolloni et al. [78].

The concentrations of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, V, and Zn were assessed using ICP-OES. Quantities of 70–80 mg of each dried powdered sample were mineralized for 3 h at 100 °C in plastic tubes closed with 1 mL of HNO_3 and diluted with 5 mL DI water upon completion of the process. DOLT-5, TORT-3, and IAEA-413 were used as certified reference materials. The elements Co, Pb, Se, and Sr were below the limits of detection (LODs). As and Hg were the most and the least abundant elements, respectively. The study confirmed the high As content of *Sargassum* at a large spatial scale. The authors emphasized the potential use of *Sargassum* as a construction material and as a source of bioenergy [79,80] rather than as a fertilizer component in order to avoid environmental and health issues. The studied brown seaweeds could also cause environmental and health problems by discharging contaminants into the coastal marine environment.

2.3.2. Laser-Induced Breakdown Spectrometry (LIBS)

LIBS, as a type of atomic emission spectroscopy technique, has been used to determine metal contents in gas, solid, and liquid samples [81]. In this technique, a high-power pulsed laser beam is irradiated on the sample surface, which creates high-temperature plasma containing atoms, ions, and free electrons. Upon cooling of the plasma, the atoms, ions, and electrons lose energy and the released emission lines provide spectral signatures detectable by a spectrometer for the elements present in the target material. In recent years, LIBS has been used by researchers as an attractive and promising optical technique in food and agriculture [82,83]. LIBS has the advantages of analyzing multiple elements simultaneously, being nondestructive, offering real-time, fast, online detection, with no need for chemical reagents [84]. It is an entirely optical technique for qualitative and quantitative chemical analysis, which makes it suitable as a PAT (process analytical technology) or portable tool. Researchers have reported using LIBS in analyses of milk, bakery products, tea, vegetable oils, water, cereals, flour, potatoes, palm dates, and meat [82]. Quantitative elemental analysis of fresh foods with complex organic compositions using LIBS faces some challenges due to low signal-to-noise ratios and matrix effects [85,86]. Furthermore, LIBS is very sensitive to any inhomogeneity in the sample material, since a small amount of target is ablated. To obtain reliable results, careful sample preparation is important, although it is a minimal process when compared to methods applied in AAS or ICP-MS analysis. In general, food products are washed, dried to a constant mass, ground, homogenized, and in some cases additional milling is required to improve particle size distribution and microhomogeneity. Often powders are pressed into pellets to prevent defocusing of the focal spot and pulse-to-pulse fluctuation during the laser irradiation [87].

In a study by Su et al., seaweed samples were manually contaminated with 20 mg/L of As, Cd, Cr, Cu, Hg, Pb, and Zn solutions in seawater and cultivated for 15 days for metal uptake. Seaweed pellets with a diameter of 14 mm and a thickness of approximately 0.2 mm were prepared from dried samples for the subsequent acquisition of LIBS data [88]. Laser light with a short pulse and high energy was emitted from the Nd:YAG laser source for the analysis. A framework consisting of the threshold variables (TVs) method and partial least squares regression (PLSR) model was developed and combined with the LIBS technique to simultaneously analyze the seven studied heavy metal contents. These results demonstrated the effectiveness of the developed framework for quantitatively analyzing the heavy metals in seaweed.

2.4. Atomic Mass Spectrometry

Mass spectrometry, where separation and quantification of metals are achieved on the basis of different trajectories of moving ions with different mass/charge (m/z) ratios in electrical and/or magnetic fields, is an important tool for heavy metal analysis in the food industry. The removal of spectral interference provided by the newly emerged triple quadrupole mass spectrometers has enabled researchers to develop methods to measure some of the elements/metals that used to be challenging [89,90].

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Although ICP-OES is an excellent and powerful tool for the analysis of metals in food samples, ICP-MS can offer even lower detection limits and a higher dynamic range (6–7 orders of magnitude) in trace metal analysis in one run. The ICP-MS technique, which involves the use of an atomic mass spectrometer, benefits from the high temperature of plasma as a highly efficient ionization source to separate and measure atoms or elements. The instrument is equipped with a quadrupole mass spectrometer that provides high sensitivity, simple spectra, and fast scanning capability. ICP-MS combines the rapid, simultaneous, multi-element capability of ICP-OES and the sensitivity of GFAAS. Since in ICP-MS, only the generated ions are measured, the plasma is optimized and focused for more efficient ionization which results in higher sensitivity. Analysis at levels below the 10 ppb to ppt range can be performed using ICP-MS. However, when comparing ICP-OES and ICP-MS, if all the target elements are consistently at concentrations above 10 ppb, then ICP-OES is the better option, since ICP-MS is affected by different types of interferences. While selection of the most appropriate combination of reactive gas and scan settings can help with removing the interferences, this demands a more sophisticated level of operational skills from most users of ICP-MS instrumentation [71].

The most common disadvantages of ICP-MS include relatively low tolerance to total dissolved solids and susceptibility to matrix effects. Despite the simplicity of mass spectra in comparison with emission spectra, spectral interferences, such as isobaric overlap, overlap from polyatomics, and doubly charged species, need to be addressed. Furthermore, the possible nonspectral interferences are transport effects, ionization interferences, and ion sampling effects [91]. The effects of nonspectral interferences can be alleviated by the addition of suitable internal standards that are similar in terms of mass, ionization potential, and concentration to the target analytes. Recently, sector field high resolution instruments provide better sensitivity and partial solutions for spectral interferences. Moreover, newer ICP/MS techniques using collision cell and dynamic reaction cells help in reducing polyatomic interferences. These advancements in ICP-MS instrumentation have made the quantification of P and S at low levels or isotope measurements of essential elements, such as Fe and Se, possible. Examples of heavy metal analysis in seaweeds at different geographical locations using ICP-MS are given in the following sections, and the detected concentrations are presented in Table 4.

Table 4. Concentrations of the heavy metals in seaweed species at different geographical locations measured by ICP-MS. All values are in µg/g dry weight. The following data show the range of minimum and maximum values where applicable.

	Northwestern Spain [17]	Gulf of Thessaloniki, Aegean Sea [19]	South Korea [60]	Southeast Asia [7]	Coast of the Northwestern Mediterranean Sea [4]	Greenland [24]
V		9.802–26.21		0.303–5.85	4.9–43	
Cr	0.56	2.767–53.39		0.063–15.8	1.4–35	0.657–7.04
Mn	19.3	38.88–757.4		5.68–58.5	14–379	3.35–36.5
Fe				95.1–2295	125–14,148	82.2–702
Co		0.474–9.199		0.082–0.911	0.75–5.6	
Ni	2.42	3.187–48.34		0.275–6.73	2.1–32	0.783–7.80
Cu		2.021–26.65		1.01–48.1	4.1–73	1.40–19.10
Zn	70.6	70.39–218.6		11.9–137.2	8.2–52	12.3–75.5
As	19.7	0.593–45.65	1.84–6.48	12.5–92.5	2.0–37	6.93–63.1
Sr		51.88–2223.0		23.9–1560		
Mo		0.006–0.934		0.072–1.090	0.30–4.7	
Ag						

Table 4. *Cont.*

	Northwestern Spain [17]	Gulf of Thessaloniki, Aegean Sea [19]	South Korea [60]	Southeast Asia [7]	Coast of the Northwestern Mediterranean Sea [4]	Greenland [24]
Cd	0.86	0.016–1.121	0.038–0.119	0.234–7.33	0.62–0.54	0.134–2.96
Sn				0.004–0.947	0.043–4.6	
Sb				0.002–0.313	0.045–1.1	
Hg			<DL *–0.006	0.005–0.068	0.010–0.12	<0.078
Tl				0.0004–0.02	0.010–0.13	
Pb	0.02	2.697–27.94	0.032–0.988	0.141–28.40	2.2–40	0.101–1.59
U		0.037–1.542		0.015–1.260		

* DL stands for “detection limit”.

Malea et al. collected 26 seaweed samples from the Gulf of Thessaloniki, Aegean Sea. They were wet-digested with $HNO_3/HCLO_4$ (4/1) after the initial freeze-drying and grinding [19]. Multiple trace elements (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, U, V, and Zn) were analyzed using an ICP-MS instrument. Reference materials (one for seaweed and sediment, one for seawater) were also analyzed for validation. Concentration factors (seaweed/seawater) were calculated and the potential to use the seaweeds as biomonitors for various elements was assessed.

The authors found that the accumulation levels of some elements (e.g., As and Cr) largely depends on the species, with *Cystoseira* spp. (brown seaweeds) having the highest As concentrations and *Cladophora prolifera* (green seaweed) having the highest Cr concentration, while the accumulation levels of other elements (particularly Cd, Co, Cr, Cu, Mn, and V) depend more on thallus morphology and growth strategy (filamentous versus sheet-like, coarsely-branched and/or thick-leathery), instead of the phylogeny of the seaweed species.

In a study by Rocha et al., 0.5 g samples of edible red and brown seaweeds (*Porphyra* and *Laminaria*, respectively) from several countries in Europe and Asia were digested in 5 mL optimized acid mixture of HNO_3 (4.5 mL) and H_2O_2 (0.5 mL) and analyzed for trace element (As, Cd, Co, Cr, Mo, Ni, Pb, Sb, Se, and V) concentrations [39]. The analyses were run on a Quadrupole ICP-MS instrument in standard mode. Four different concentrations of a multi-elemental standard solution containing all the elements of interest were used for calibration. Internal standards were also included in the standard solutions to correct for instrument drift and potential matrix effects. A series of solutions with increasing NaCl concentrations were used to correct for the polyatomic interferences of the elements As and V with chlorine ions, while the selected isotopes of the other elements of interest were free from any isobaric or polyatomic interferences. Assay validation was performed with biological certified reference materials (CRMs). The within-run and between-run accuracy and precision of CRMs were both within acceptable criteria. Good linearity was achieved for all the elements throughout the concentration range studied, and detection limits were comparable to those of previous studies. The authors found significant differences in metal concentrations, except for Co, Ni, and Sb, between *Porphyra* and *Laminaria.* The amounts and compositions of polysaccharides in the cell walls of the seaweeds; environmental factors, such as water temperature, pH, and salinity; the relative abundances of the elements in seawater; as well as the presence of other metals were hypothesized to have caused these differences.

The pressurized hot water extraction (PHWE) method was used to extract multiple trace metal elements (As, Cd, Cr, Mn, Ni, Pb, and Zn) from seven edible seaweed samples harvested from Northwestern Spain, and this was followed by ICP-MS analysis [17]. Several PHWE parameters (modifier concentration, extraction temperature, pressure, extraction steps, etc.) were evaluated and optimized. The optimal condition was found to be with 150 mM acetic acid, at an extraction temperature of 130 °C and a pressure of 3000 psi, for a static time of 5 min and three cycles. The resulting extract was measured on an

ICP-MS instrument in standard mode. Based on the optimized modifier concentration, ICP-MS calibration was performed with 150 mM acetic acid aqueous standard solutions. The seaweed samples were also subjected to the standard extraction method of microwave-assisted acid digestion to assess the total metal contents as well as for comparison with the PHWE method. Validation was performed with a CRM which has certified values for As, Cd, Pb, and Zn. Analysis data for some of the other elements (Cr, Mn, and Ni) were compared with data reported in the literature, and similar values were found. The authors concluded that PHWE serves as a fast, simple, "green", and effective method to extract metal elements from seaweed.

Edible seaweed from South Korea (five species) were analyzed for levels of toxic heavy metals (As, Cd, Hg, and Pb), among which As, Cd, and Pb, as well as various As species, were measured with ICP-MS in standard mode [92]. Quantities of 0.25–0.5 g of the seaweed samples were subjected to the microwave-assisted acid digestion procedure using HNO_3:H_2O_2 (7:2 v/v) in PTFE digestion vessels. The As species were extracted with 50% methanol in 1% HNO_3 and separated with liquid chromatography prior to quantification on an ICP-MS instrument, allowing for the determination of individual As species, including the more toxic inorganic species, such as As(III) and As(V). Calibration was performed at eight different concentration points to ensure linearity over the data range. Blanks and calibration standards were analyzed at regular intervals to check for instrumental drift and cross-contamination. Method validation was performed with a CRM. Spike recovery for all of the elements analyzed and the As species was between 94.5 and 107%, thus verifying the described method as efficient and accurate for monitoring toxic heavy metals in edible seaweed. Since the concentrations of all four toxic heavy metals were found to be lower than the recommended PTWIs (provisional tolerable weekly intakes), the authors concluded that these five species of edible seaweed are safe to consume.

Ninety-two samples belonging to three species of edible seaweed from Southeast Asia were analyzed for 19 trace elements (As, Cd, Co, Cr, Cu, Fe, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Sr, Tl, U, V, and Zn) with ICP-MS [7]. Quantities of 0.5 g of homogenized and powdered samples were mineralized with the standard microwave-assisted acid digestion method with 6 mL HNO_3 and 2 mL H_2O_2. Single isotopes were selected for all the elements, except for Pb, where, in order to improve sensitivity, the signals from three isotopes were summed. Among these trace elements, As, Co, Cr, Cu, Fe, Mn, Ni, Se, V, and Zn were analyzed in DRC (dynamic reaction cell) mode. Methane gas was used as a reaction gas for Se, and ammonia gas was used as a reaction gas for the other elements analyzed in DRC mode. Calibration was carried out with the standard addition approach, and five addition levels were selected per element to ensure linearity. Method validation was performed with a CRM, while for elements without certified values, spike recovery was determined with the addition of standard monoelement solutions. The authors found that the trace element profiles of the samples mainly depended on taxonomic species and, to a lesser extent, on geological origin as well. Comparisons of the measured values and tolerable levels of some toxic elements were made, and, alarmingly, 26% of the samples were found to be non-compliant with respect to Cd. In addition, pairwise correlation of the trace elements was also looked into with statistical analysis; a strong correlation was observed between Sn-Fe and Cr-Ni. However, comparisons with existing data could not be made due to the lack of such studies.

In a study by Squadrone et al., seaweed samples were collected at three sites along the coast of the Northwestern Mediterranean Sea [4]. The three sites varied in their shipping traffic, industrial activity, and population densities. Quantities of 1.0–1.5 g of samples were digested in a mixture of 7 mL HNO_3 and 1.5 mL H_2O_2. After microwave-assisted acid digestion of the samples, the ICP-MS method was used to measure multiple trace metal contents (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn), while Hg contents were measured using a direct mercury analyzer. Calibration was performed with an external multi-element standard solution, with rhodium and germanium as internal standards. The samples were run in CCD mode (H_2 as reaction gas) and KED mode (He as collision gas). The results showed significant intersite differences between most of the trace metals, suggesting that growth site conditions play an important role in the degree of trace metal accumulation in seaweed. The authors also compared the trace metal levels with the maximum levels allowed for animal feed and human nutrition. While the toxic elements As and Cd were below the set limit, Hg concentrations were close to the maximum limit in some samples of brown and red alga, and Pb exceeded the maximum limit in most species from site 1. However, the authors concluded that seaweeds could be safe as animal feed since they are usually diluted with other feed sources. On the other hand, some seaweed species from these sampling sites could pose potential risks for human consumption since they contain considerable amount of some trace elements, such as Fe and Pb. In addition, comparisons were made with other Mediterranean areas. While most data were comparable to those from other studies, not surprisingly, seaweed samples from site 1, which had the highest shipping traffic and industrial activity, contained higher contents of the trace metals Pb, Cr, Fe, and Zn.

To assess risk and provide regulatory guidelines for seaweed consumption in Europe, where seaweed is growing in popularity as a healthy and sustainable food source, seven species of seaweed were cultivated and harvested in Denmark [3]. ICP-MS was used to analyze the levels of As, Cd, Hg, and Pb. In particular, inorganic As was separated from total As using HPLC prior to ICP-MS analysis, though these data were not available at the time of publication. Based on the assumption of 5 g dry weight of seaweed consumption per week, by comparison with current regulations or recommendations on the upper limits or tolerable intakes for these elements, the authors concluded that seaweed consumption poses low health risks with respect to Cd, Hg, and Pb, though more studies on this topic are needed, especially in regard to species-specific consumption data in Europe.

Researchers in Greenland collected 77 samples belonging to 10 species of seaweed and analyzed them for 17 elements (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn) to study their nutritional profiles and potential food safety risks [24]. A quantity of 0.2 g of each sample was extracted with microwave-assisted acid digestion with a HNO_3 (4 mL): H_2O (1 mL) mixture. Concentrations of these elements were measured with ICP-MS: Pb was analyzed in standard mode, As and Se were analyzed in reaction cell mode using O_2 as the reaction gas, and the other elements were analyzed in KED mode with He as the collision gas. Measurement of these elements was also performed with different parts of the seaweed. The authors observed that element concentrations vary with thallus parts, species, as well as geological locations, though samples from the same family of seaweed tend to have similar profiles. A portion-size survey was conducted to estimate consumption amounts and compare these with recommended intake values. The authors concluded that all species included in this study serve as good sources of essential minerals and trace elements. Concentrations of toxic elements, such as Hg, Cd, and Pb, were below current EU maximum levels. As reported by Miedico et al., pairwise correlation was investigated and strong correlation was found between Cr-Fe, Fe-Pb, and Ni-Mn [7].

Thirty-three purchased samples belonging to nine species of edible seaweed were analyzed for As (total and inorganic) and heavy metals (Cd, Hg, Ni, and Pb) to address food safety concerns [23]. Quantities of 0.5 g of dry seaweeds were microwave-digested in a HNO_3 (3 mL), H_2O (5 mL), HCl (0.5 mL), and H_2O_2 (2 mL) mixture. HPLC was used to purify the inorganic As species prior to measurement. In addition, 0.4 mg/L of gold was added to stabilize the Pb signal. Element concentrations were measured with ICP-MS in KED mode, with He as the collision gas. The results showed that the levels of Hg and Ni do not pose a threat to human health. On the other hand, Cd and Pb may contribute to health risk in some seaweed species, such as kelp, nori, wakame, and dulse. Inorganic As was especially high in hijiki seaweed and greatly exceeded the tolerable daily intake (TDI) level, while the levels in the other species were much lower.

3. Conclusions and Future Directions

From the studies included in this review, it is evident that the determination of heavy metals in seaweed is critical for assessing nutritional composition and identifying contamination sources. In general, the analysis of any food for metals that might be harmful to health is an important part of ensuring food safety. Metals can contaminate raw products through exposure to contaminated environments during growth. During an expert meeting organized by the Food and Agriculture Organization (FAO) of the United Nations, the World Health Organization (WHO) reported on food safety hazards linked to the consumption of seaweed and future work in developing relevant Codex guidance on this subject was recommended [13]. There is a general lack of attention to the evaluation of the role of seaweeds in foodborne illnesses; therefore, close monitoring of the same is advocated [93]. In a scoring matrix developed by Banach et al. to rank 22 food safety hazards in seaweed, the presence of As, Cd, Hg, and Pb was identified as a major heavy metal hazard. The study emphasizes that the occurrence of heavy metal hazards, mainly due to bioaccumulation, require attention in seaweed [94]. Since food safety legislation and related best-practice instruments are based on information on the occurrence of (potential) hazards, documenting and/or screening for the presence of heavy metals and therefore establishing various analysis methods to facilitate heavy metal assessment in seaweed is vital. In order to monitor for food safety hazards, many data are needed for the assessment of heavy metal concentrations per species and per product of raw and processed seaweeds within various national and regional contexts.

The sites of wild harvesting as well as seaweed farming have substantial impacts on the final quality and safety of products. Presence of heavy metals is directly corelated with uptake from the environment and accumulation over time. Seaweeds growing in sites close to untreated industrial effluent and run-off and touristic harbors show higher metal bioaccumulation [4]. The longer seaweed stays in a contaminated cultivation environment, especially in the case of wild-harvested seaweed, the greater the exposure and the uptake of metals.

Studies suggest that interspecific variations due to differences in morphology, growth rates, and affinity for metals play an important role in the bioaccumulation of heavy metals in seaweed [95,96]. Sánchez-Quiles et al. compiled over 20,000 estimates of trace metal levels in natural seaweeds across the globe. They concluded that brown seaweeds had the highest and that red seaweeds had the lowest accumulation capacities, regardless of sampling location [97]. Similar observations have been reported by other researchers [98].

This review compiles the most widely used techniques for metal measurement in different seaweed species using atomic absorption, emission, and mass spectrometry. The analyte concentration range is an important factor in selecting the atomic spectroscopy technique for analysis. Among the techniques used by most of the studies in this article, GFAAS and ICP-MS can achieve measurements at trace levels (less than 10 ppb) or even ultra-trace levels (ppt). Although GFAAS has lower running costs than ICP-MS, it has the disadvantage of measuring each element separately. In contrast, ICP-MS has the capability to simultaneously measure multiple metal elements, which allows for faster sample processing; in addition, it has a much wider linear dynamic range and fewer interferences. In comparison to GFAAS and ICP-MS, the FAAS and ICP-OES methods are less sensitive and can be used to measure higher levels (more than 10 ppb) of the target elements in samples. Food and environmental industries often use FAAS due to the availability of regulated and standard analysis methods. Since FAAS instrumentation has been used for a longer time compared to other atomic spectroscopies, many well-documented analysis methods have been established, which makes FAAS user-friendly.

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References

1. Khandaker, M.U.; Chijioke, N.O.; Heffny, N.A.B.; Bradley, D.A.; Alsubaie, A.; Sulieman, A.; Faruque, M.R.I.; Sayyed, M.I.; Al-mugren, K.S. Elevated Concentrations of Metal(loids) in Seaweed and the Concomitant Exposure to Humans. *Foods* **2021**, *10*, 381. [CrossRef] [PubMed]
2. Morais, T.; Inácio, A.; Coutinho, T.; Ministro, M.; Cotas, J.; Pereira, L.; Bahcevandziev, K. Seaweed Potential in the Animal Feed: A Review. *J. Mar. Sci. Eng.* **2020**, *8*, 559. [CrossRef]
3. National Food Institute, Technical University of Denmark, Denmark; Sá Monteiro, M.; Sloth, J.; Holdt, S.; Hansen, M. Analysis and Risk Assessment of Seaweed. *EFSA J.* **2019**, *17*, e170915. [CrossRef]
4. Squadrone, S.; Brizio, P.; Battuello, M.; Nurra, N.; Sartor, R.M.; Riva, A.; Staiti, M.; Benedetto, A.; Pessani, D.; Abete, M.C. Trace Metal Occurrence in Mediterranean Seaweeds. *Environ. Sci. Pollut. Res.* **2018**, *25*, 9708–9721. [CrossRef] [PubMed]
5. Paz, S.; Rubio, C.; Frías, I.; Gutiérrez, A.J.; González-Weller, D.; Revert, C.; Hardisson, A. Metal Concentrations in Wild-Harvested Phaeophyta Seaweed from the Atlantic Ocean (Canary Islands, Spain). *J. Food Prot.* **2018**, *81*, 1165–1170. [CrossRef]
6. Romarís-Hortas, V.; García-Sartal, C.; Barciela-Alonso, M.C.; Moreda-Piñeiro, A.; Bermejo-Barrera, P. Characterization of Edible Seaweed Harvested on the Galician Coast (Northwestern Spain) Using Pattern Recognition Techniques and Major and Trace Element Data. *J. Agric. Food Chem.* **2010**, *58*, 1986–1992. [CrossRef]
7. Miedico, O.; Pompa, C.; Tancredi, C.; Cera, A.; Pellegrino, E.; Tarallo, M.; Chiaravalle, A.E. Characterisation and Chemometric Evaluation of 21 Trace Elements in Three Edible Seaweed Species Imported from South-East Asia. *J. Food Compos. Anal.* **2017**, *64*, 188–197. [CrossRef]
8. Nguyen, P.T.; Ruangchuay, R.; Lueangthuwapranit, C. Patterns of Element Concentrations and Heavy Metal Accumulations in Edible Seaweed, Gracilaria Fisheri (Xia and Abbott) Abbott, Zhang and Xia (Gracilariales, Rhodophyta) Cultivation in Southern Thailand. *J. Fish. Environ.* **2018**, *42*, 13–25.
9. Silva, A.; Silva, S.A.; Carpena, M.; Garcia-Oliveira, P.; Gullón, P.; Barroso, M.F.; Prieto, M.A.; Simal-Gandara, J. Macroalgae as a Source of Valuable Antimicrobial Compounds: Extraction and Applications. *Antibiotics* **2020**, *9*, 642. [CrossRef]
10. Veluchamy, C.; Palaniswamy, R. A review on marine algae and its applications. *Asian J. Pharm. Clin. Res.* **2020**, *13*, 21–27. [CrossRef]
11. Kinley, R.D.; Martinez-Fernandez, G.; Matthews, M.K.; de Nys, R.; Magnusson, M.; Tomkins, N.W. Mitigating the Carbon Footprint and Improving Productivity of Ruminant Livestock Agriculture Using a Red Seaweed. *J. Clean. Prod.* **2020**, *259*, 120836. [CrossRef]
12. Food and Agriculture Organization of the United Nations (FAO). *The State of World Fisheries and Aquaculture 2016*; Contributing to Food Security and Nutrition for All; FAO: Rome, Italy, 2016; 200p.
13. FAO; WHO. *Report of the Expert Meeting on Food Safety for Seaweed—Current Status and Future Perspectives*; FAO: Rome, Italy; WHO: Geneva, Switzerland, 2022. [CrossRef]
14. Boucetta, S.; Benchalel, W.; Ferroudj, S.; Bouslama, Z.; Elmsellem, H. Trace Metal Biomonitoring of Algae (*Ulva lactuca*), and Mollusks (*Patella caerulea*; *Stramonita haemastoma*; *Phorcus turbinatus*) along the Eastern-Algerian Coast. *Moroc. J. Chem.* **2019**, *7*, 444–459. [CrossRef]
15. Tresnati, J.; Yasir, I.; Zainuddin; Syafiuddin; Aprianto, R.; Tuwo, A. Metal Bioaccumulation Potential of the Seaweed Kappaphycus Alvarezii. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *763*, 012059. [CrossRef]
16. Vázquez-Arias, A.; Pacín, C.; Ares, Á.; Fernández, J.Á.; Aboal, J.R. Do We Know the Cellular Location of Heavy Metals in Seaweed? An up-to-Date Review of the Techniques. *Sci. Total Environ.* **2023**, *856*, 159215. [CrossRef] [PubMed]
17. Rey-Rubio, R.; Moreda-Piñeiro, J. Trace Metal Determination of Edible Seaweeds by Pressurized Hot Water Extraction and Determination by Inductively Coupled Plasma Mass Spectrometry. *At. Spectrosc.* **2012**, *33*, 179–185. [CrossRef]
18. Dadolahi-Sohrab, A.; Nikvarz, A.; Nabavi, S.M.B.; Safahyeh, A.; Ketal-Mohseni, M. Environmental Monitoring of Heavy Metals in Seaweed and Associated Sediment from the Strait of Hormuz, I.R. Iran. *World J. Fish Mar. Sci.* **2011**, *3*, 576–589.

19. Malea, P.; Kevrekidis, T. Trace Element Patterns in Marine Macroalgae. *Sci. Total Environ.* **2014**, *494–495*, 144–157. [CrossRef]
20. Medeiros, I.D.; Mathieson, A.C.; Rajakaruna, N. Heavy Metals in Seaweeds from a Polluted Estuary in Coastal Maine. *Rhodora* **2017**, *119*, 201–211. [CrossRef]
21. El-Naggar, N.E.-A.; Hamouda, R.A.; Abuelmagd, M.A.; Alharbi, M.M.; Darwish, D.B.E.; Rabei, N.H.; Farfour, S.A. A Cost-Effective and Eco-Friendly Biosorption Technology for Complete Removal of Nickel Ions from an Aqueous Solution: Optimization of Process Variables. *Green Process. Synth.* **2022**, *11*, 631–647. [CrossRef]
22. Kumari, B.; Sharma, V. Assessment of Seaweeds in Biomonitoring and Biosorption of Heavy Metals. *Int. J. Biol. Technol.* **2012**, *3*, 59–61.
23. Asensio, J.P.; Arnaiz Uceda, D.; Navarro, P.J. Studying Inorganic Arsenic, Heavy Metals, and Iodine in Dried Seaweed. *Spectrosc. Suppl.* **2021**, *36*, 24–34.
24. Kreissig, K.J.; Hansen, L.T.; Jensen, P.E.; Wegeberg, S.; Geertz-Hansen, O.; Sloth, J.J. Characterisation and Chemometric Evaluation of 17 Elements in Ten Seaweed Species from Greenland. *PLoS ONE* **2021**, *16*, e0243672. [CrossRef] [PubMed]
25. Devault, D.A.; Pierre, R.; Marfaing, H.; Dolique, F.; Lopez, P.-J. Sargassum Contamination and Consequences for Downstream Uses: A Review. *J. Appl. Phycol.* **2021**, *33*, 567–602. [CrossRef]
26. Makawita, G.I.P.S.; Wickramasinghe, I.; Wijesekara, I. Analysis of Metals and Metalloids Present in Sri Lankan Dried Seaweeds and Assessing the Possibility of Health Impact to General Consumption Patterns. *Aquat. Living Resour.* **2020**, *33*, 16. [CrossRef]
27. Monchanin, C.; Devaud, J.-M.; Barron, A.B.; Lihoreau, M. Current Permissible Levels of Metal Pollutants Harm Terrestrial Invertebrates. *Sci. Total Environ.* **2021**, *779*, 146398. [CrossRef]
28. Wu, Y. *CODEX STAN 193-1995*; General Standard for Contaminants and Toxins in Food and Feed Adopted in 1995. Revised in 1997, 2006, 2008, 2009. Amendment 2010, 2012, 2013, 2014. China National Center for Food Safety Risk Assessment: Beijing, China, 2014. [CrossRef]
29. *Codex Stan 193-1995*; FAO/WHO General Standard for Contaminants and Toxins in Food and Feed. FAO: Rome, Italy; WHO: Geneva, Switzerland, 2015; pp. 1–59. Available online: www.fao.org/input/download/standards/17/CXS_193e_2015.pdf (accessed on 1 November 2022).
30. Commission Regulation (EU) 2015/1006. *Commission Regulation (EU) 2015/1006 of 25 June 2015 Amending Regulation (EC) No 1881/2006 as Regards Maximum Levels of Inorganic Arsenic in Foodstuffs (OJ L161)*; Report No.: OJ L161.; EU: Brussels, Belgium, 2015. Available online: http://data.europa.eu/eli/reg/2015/1006/oj/eng (accessed on 1 November 2022).
31. Commission Regulation (EC) No 1881/2006. *Commission Regulation (EC) No 1881/2006 of 19 December 2006 Setting Maximum Levels for Certain Contaminants in Foodstuffs (OJ L364)*; EU: Brussels, Belgium, 2006. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02006R1881-20100701 (accessed on 1 November 2022).
32. Li, J.; Xie, Z.M.; Xu, J.M.; Sun, Y.F. Risk Assessment for Safety of Soils and Vegetables around a Lead/Zinc Mine. *Environ. Geochem. Health* **2006**, *28*, 37–44. [CrossRef]
33. European Commission. *Proposal for a Directive of the European Parliament and of the Council on the Quality of Water Intended for Human Consumption (COM/2017/0753)*; EU: Brussels, Belgium, 2019.
34. US EPA. Drinking Water Regulations (Safe Drinking Water Act). 2017. Available online: https://www.epa.gov/dwreginfo/drinking-water-regulations (accessed on 1 November 2022).
35. *GB 5749-2006*; Standards for Drinking Water Quality. Ministry of Health: Beijing, China, 2006.
36. Cherry, P.; O'Hara, C.; Magee, P.J.; McSorley, E.M.; Allsopp, P.J. Risks and Benefits of Consuming Edible Seaweeds. *Nutr. Rev.* **2019**, *77*, 307–329. [CrossRef]
37. Biancacci, C.; Sanderson, J.C.; Evans, B.; Callahan, D.L.; Francis, D.S.; Skrzypczyk, V.M.; Cumming, E.E.; Bellgrove, A. Nutritional Composition and Heavy Metal Profiling of Australian Kelps Cultured in Proximity to Salmon and Mussel Farms. *Algal Res.* **2022**, *64*, 102672. [CrossRef]
38. Chen, Q.; Pan, X.-D.; Huang, B.-F.; Han, J.-L. Distribution of Metals and Metalloids in Dried Seaweeds and Health Risk to Population in Southeastern China. *Sci. Rep.* **2018**, *8*, 3578. [CrossRef]
39. Ródenas de la Rocha, S.; Sánchez-Muniz, F.J.; Gómez-Juaristi, M.; Marín, M.T.L. Trace Elements Determination in Edible Seaweeds by an Optimized and Validated ICP-MS Method. *J. Food Compos. Anal.* **2009**, *22*, 330–336. [CrossRef]
40. Lavergne, C.; Celis-Plá, P.S.M.; Chenu, A.; Rodríguez-Rojas, F.; Moenne, F.; Díaz, M.J.; Abello-Flores, M.J.; Díaz, P.; Garrido, I.; Bruning, P.; et al. Macroalgae Metal-Biomonitoring in Antarctica: Addressing the Consequences of Human Presence in the White Continent. *Environ. Pollut.* **2022**, *292*, 118365. [CrossRef] [PubMed]
41. Rakib, M.R.J.; Jolly, Y.N.; Dioses-Salinas, D.C.; Pizarro-Ortega, C.I.; De-la-Torre, G.E.; Khandaker, M.U.; Alsubaie, A.; Almalki, A.S.A.; Bradley, D.A. Macroalgae in Biomonitoring of Metal Pollution in the Bay of Bengal Coastal Waters of Cox's Bazar and Surrounding Areas. *Sci. Rep.* **2021**, *11*, 20999. [CrossRef] [PubMed]
42. Billah, M.M.; Mustafa Kamal, A.H.; Idris, M.H.; Ismail, J. Mangrove Macroalgae as Biomonitors of Heavy Metal Contamination in a Tropical Estuary, Malaysia. *Water Air Soil Pollut.* **2017**, *228*, 347. [CrossRef]
43. Karthick, P.; Siva Sankar, R.; Kaviarasan, T.; Mohanraju, R. Ecological Implications of Trace Metals in Seaweeds: Bio-Indication Potential for Metal Contamination in Wandoor, South Andaman Island. *Egypt. J. Aquat. Res.* **2012**, *38*, 227–231. [CrossRef]
44. Laursen, K.H.; Schjoerring, J.K.; Kelly, S.D.; Husted, S. Authentication of Organically Grown Plants—Advantages and Limitations of Atomic Spectroscopy for Multi-Element and Stable Isotope Analysis. *TrAC Trends Anal. Chem.* **2014**, *59*, 73–82. [CrossRef]

45. Baker, S.A.; Miller-Ihli, N.J.; Fodor, P.; Woller, Á. Atomic Spectroscopy in Food Analysis Update Based on the Original Article by Scott A. Baker and Nancy J. Miller-Ihli, Encyclopedia of Analytical Chemistry, © 2000, John Wiley & Sons, Ltd. In *Encyclopedia of Analytical Chemistry*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2012. [CrossRef]
46. Cubadda, F. Applications of Inductively Coupled Plasma Mass Spectrometry to Trace Element Research and Control. In *The Determination of Chemical Elements in Food*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2007; pp. 223–295. [CrossRef]
47. Andrade Korn, M.D.G.; da Boa Morte, E.S.; Batista dos Santos, D.C.M.; Castro, J.T.; Barbosa, J.T.P.; Teixeira, A.P.; Fernandes, A.P.; Welz, B.; dos Santos, W.P.C.; Nunes dos Santos, E.B.G.; et al. Sample Preparation for the Determination of Metals in Food Samples Using Spectroanalytical Methods—A Review. *Appl. Spectrosc. Rev.* **2008**, *43*, 67–92. [CrossRef]
48. Levine, K.E.; Batchelor, J.D.; Rhoades, C.B.R., Jr.; Jones, B.T. Evaluation of a High-Pressure, High-Temperature Microwave Digestion System. *J. Anal. At. Spectrom.* **1999**, *14*, 49–59. [CrossRef]
49. Krishna, M.V.B.; Arunachalam, J. Ultrasound-Assisted Extraction Procedure for the Fast Estimation of Major, Minor and Trace Elements in Lichen and Mussel Samples by ICP-MS and ICP-AES. *Anal. Chim. Acta* **2004**, *522*, 179–187. [CrossRef]
50. Costas, M.; Lavilla, I.; Gil, S.; Pena, F.; de la Calle, I.; Cabaleiro, N.; Bendicho, C. Evaluation of Ultrasound-Assisted Extraction as Sample Pre-Treatment for Quantitative Determination of Rare Earth Elements in Marine Biological Tissues by Inductively Coupled Plasma-Mass Spectrometry. *Anal. Chim. Acta* **2010**, *679*, 49–55. [CrossRef]
51. Ashoka, S.; Peake, B.M.; Bremner, G.; Hageman, K.J.; Reid, M.R. Comparison of Digestion Methods for ICP-MS Determination of Trace Elements in Fish Tissues. *Anal. Chim. Acta* **2009**, *653*, 191–199. [CrossRef]
52. Hill, S.J.; Fisher, A.S. Atomic Absorption, Methods and Instrumentation. In *Encyclopedia of Spectroscopy and Spectrometry*, 3rd ed.; Lindon, J.C., Tranter, G.E., Koppenaal, D.W., Eds.; Academic Press: Oxford, UK, 2017; pp. 37–43. [CrossRef]
53. Jorhem, L. Determination of Metals in Foods by Atomic Absorption Spectrometry after Dry Ashing: NMKL Collaborative Study. *J. AOAC Int.* **2000**, *83*, 1204–1211. [CrossRef] [PubMed]
54. Van Loon, J.C. *Selected Methods of Trace Metal Analysis*; Wiley: New York, NY, USA, 1985.
55. Nascentes, C.C.; Kamogawa, M.Y.; Fernandes, K.G.; Arruda, M.A.Z.; Nogueira, A.R.A.; Nóbrega, J.A. Direct Determination of Cu, Mn, Pb, and Zn in Beer by Thermospray Flame Furnace Atomic Absorption Spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2005**, *60*, 749–753. [CrossRef]
56. Díaz, J.P.; Navarro, M.; López, H.; López, M.C. Determination of Selenium Levels in Dairy Products and Drinks by Hydride Generation Atomic Absorption Spectrometry: Correlation with Daily Dietary Intake. *Food Addit. Contam.* **1997**, *14*, 109–114. [CrossRef]
57. Daryaii, L.B.; Samsampour, D.; Bagheri, A.; Sohrabi, J. High Content of Heavy Metals in Seaweed Species: A Case Study in the Persian Gulf and the Gulf of Oman in the Southern Coast of Iran. *Phycol. Res.* **2020**, *4*, 544–560.
58. Trifan, A.; Breabăn, I.G.; Sava, D.; Bucur, L.; Toma, C.-C.; Miron, A. Heavy Metal Content in Macroalgae from Roumanian Black Sea. *Rev. Roum. Chim.* **2015**, *60*, 915–920.
59. AOAC. *Official Methods of Analysis, Association of Official Analytical Chemists (AOAC)*, 17th ed.; AOAC: Arlington, VA, USA, 2000; pp. 1–62.
60. Qari, R.; Siddiqui, S.A.; Qureshi, N.A. A Comparative Study of Heavy Metal Concentrations in Surficial Sediments from Coastal Areas of Karachi, Pakistan. *Mar. Pollut. Bull.* **2005**, *50*, 595–599. [CrossRef]
61. Miller-Ihli, N.J. Influence of Slurry Preparation on the Accuracy of Ultrasonic Slurry Electrothermal Atomic Absorption Spectrometry. *J. Anal. At. Spectrom.* **1994**, *9*, 1129–1134. [CrossRef]
62. Cabrera, C.; Lorenzo, M.L.; Lopez, M.C. Electrothermal Atomic Absorption Spectrometric Determination of Cadmium, Copper, Iron, Lead, and Selenium in Fruit Slurry: Analytical Application to Nutritional and Toxicological Quality Control. *J. AOAC Int.* **1995**, *78*, 1061–1067. [CrossRef]
63. Carlosena, A.; Gallego, M.; Valcárcel, M. Evaluation of Various Sample Preparation Procedures for TheDetermination of Chromium, Cobalt and Nickel in Vegetables. *J. Anal. At. Spectrom.* **1997**, *12*, 479–486. [CrossRef]
64. Viñas, P.; Campillo, N.; López-García, I.; Hernández-Córdoba, M. Electrothermal Atomic Absorption Spectrometric Determination of Molybdenum, Aluminium, Chromium and Manganese in Milk. *Anal. Chim. Acta* **1997**, *356*, 267–276. [CrossRef]
65. Giusti, L. Heavy Metal Contamination of Brown Seaweed and Sediments from the UK Coastline between the Wear River and the Tees River. *Environ. Int.* **2001**, *26*, 275–286. [CrossRef] [PubMed]
66. Agarwal, S.; Albeshr, M.F.; Mahboobb, S.; Atique, U.; Pramanick, P.; Mitra, A. Bioaccumulation Factor (BAF) of Heavy Metals in Green Seaweed to Assess the Phytoremediation Potential. *J. King Saud Univ.—Sci.* **2022**, *34*, 102078. [CrossRef]
67. Grobecker, K.H.; Kurfürst, U. Solid sampling by Zeeman graphite-furnace-AAS, a suitable tool for environmental analysis. In *Element Concentration Cadasters*; Lieth, H., Markert, B., Eds.; VCH: New York, NY, USA, 1990; pp. 121–137.
68. Detcheva-Tchakarova, A.; Grobecker, K.-H. Determination of Trace Elements in Sea Food by Solid Sampling Zeeman Atomic Absorption Spectrometry (SSZAAS). JRC Publications Repository. Available online: https://publications.jrc.ec.europa.eu/repository/handle/JRC33216 (accessed on 27 January 2023).
69. Thirumdas, R.; Janve, M.; Siliveru, K.; Kothakota, A. 10—Determination of Food Quality Using Atomic Emission Spectroscopy. In *Evaluation Technologies for Food Quality*; Zhong, J., Wang, X., Eds.; Woodhead Publishing Series in Food Science, Technology and Nutrition; Woodhead Publishing: Sawston, UK, 2019; pp. 175–192. [CrossRef]
70. Monaster, A.; Golightly, D.W. *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*; VCH: New York, NY, USA, 1987.

71. Grosser, Z.; Thompson, L.; Davidowski, L.; Neubauer, K. A Comparison of ICP-OES and ICP-MS for the Determination of Metals in Food. *LCGC Suppl.* **2008**, 36–41.
72. Mermet, J.M. Is It Still Possible, Necessary and Beneficial to Perform Research in ICP-Atomic Emission Spectrometry? *J. Anal. At. Spectrom.* **2005**, *20*, 11–16. [CrossRef]
73. Todolí, J.L.; Maestre, S.E.; Mermet, J.M. Compensation for Matrix Effects in ICP-AES by Using Air Segmented Liquid Microsample Introduction. The Role of the Spray Chamber. *J. Anal. At. Spectrom.* **2004**, *19*, 728–737. [CrossRef]
74. Kaviarasan, T.; Gokul, M.S.; Henciya, S.; Muthukumar, K.; Dahms, H.-U.; James, R.A. Trace Metal Inference on Seaweeds in Wandoor Area, Southern Andaman Island. *Bull. Environ. Contam. Toxicol.* **2018**, *100*, 614–619. [CrossRef]
75. Farias, D.R.; Hurd, C.L.; Eriksen, R.S.; Simioni, C.; Schmidt, E.; Bouzon, Z.L.; Macleod, C.K. In Situ Assessment of Ulva Australis as a Monitoring and Management Tool for Metal Pollution. *J. Appl. Phycol.* **2017**, *29*, 2489–2502. [CrossRef]
76. Lalitha, N.; Dhandapani, R. Trace Metals and Mineral Contents of Some Green Algal Seaweeds from Vadakadu (Rameswaram) Coastal Regions, Tamil Nadu, India. *J. Pharm. Phytochem.* **2018**, *7*, 2558–2561.
77. Farías, S.; Arisnabarreta, S.P.; Vodopivez, C.; Smichowski, P. Levels of Essential and Potentially Toxic Trace Metals in Antarctic Macro Algae. *Spectrochim. Acta Part B At. Spectrosc.* **2002**, *57*, 2133. [CrossRef]
78. Cipolloni, O.-A.; Gigault, J.; Dassié, É.P.; Baudrimont, M.; Gourves, P.-Y.; Amaral-Zettler, L.; Pascal, P.-Y. Metals and Metalloids Concentrations in Three Genotypes of Pelagic Sargassum from the Atlantic Ocean Basin-Scale. *Mar. Pollut. Bull.* **2022**, *178*, 113564. [CrossRef]
79. Chávez, V.; Lithgow, D.; Losada, M.; Silva-Casarin, R. Coastal Green Infrastructure to Mitigate Coastal Squeeze. *J. Infrastruct. Preserv. Resil.* **2021**, *2*, 7. [CrossRef]
80. López Miranda, J.L.; Celis, L.B.; Estévez, M.; Chávez, V.; van Tussenbroek, B.I.; Uribe-Martínez, A.; Cuevas, E.; Rosillo Pantoja, I.; Masia, L.; Cauich-Kantun, C.; et al. Commercial Potential of Pelagic *Sargassum* spp. in Mexico. *Front. Mar. Sci.* **2021**, *8*, 1692. [CrossRef]
81. Bilge, G.; Sezer, B.; Boyaci, I.H.; Eseller, K.E.; Berberoglu, H. Performance Evaluation of Laser Induced Breakdown Spectroscopy in the Measurement of Liquid and Solid Samples. *Spectrochim. Acta* **2018**, *145*, 115–121. [CrossRef]
82. Markiewicz-Keszycka, M.; Cama-Moncunill, X.; Casado-Gavalda, M.P.; Dixit, Y.; Cama-Moncunill, R.; Cullen, P.J.; Sullivan, C. Laser-Induced Breakdown Spectroscopy (LIBS) for Food Analysis: A Review. *Trends Food Sci. Technol.* **2017**, *65*, 80–93. [CrossRef]
83. Senesi, G.S.; Senesi, N. Laser-Induced Breakdown Spectroscopy (LIBS) to Measure Quantitatively Soil Carbon with Emphasis on Soil Organic Carbon. A Review. *Anal. Chim. Acta* **2016**, *938*, 7–17. [CrossRef] [PubMed]
84. Peña-Icart, M.; Pomares-Alfonso, M.S.; Batista De Aquino, F.W.; Alonso-Hernandez, C.; Bolaños-Alvarez, Y.; Pereira-Filho, E.R. Fast and Direct Detection of Metal Accumulation in Marine Sediments Using Laser-Induced Breakdown Spectroscopy (LIBS): A Case Study from the Bay of Cienfuegos, Cuba. *Anal. Methods* **2017**, *9*, 3713–3719. [CrossRef]
85. Da Silva Gomes, M.; Santos, D.; Nunes, L.C.; de Carvalho, G.G.A.; de Oliveira Leme, F.; Krug, F.J. Evaluation of Grinding Methods for Pellets Preparation Aiming at the Analysis of Plant Materials by Laser Induced Breakdown Spectrometry. *Talanta* **2011**, *85*, 1744–1750. [CrossRef]
86. Andersen, M.-B.S.; Frydenvang, J.; Henckel, P.; Rinnan, Å. The Potential of Laser-Induced Breakdown Spectroscopy for Industrial at-Line Monitoring of Calcium Content in Comminuted Poultry Meat. *Food Control* **2016**, *64*, 226–233. [CrossRef]
87. Jantzi, S.C.; Motto-Ros, V.; Trichard, F.; Markushin, Y.; Melikechi, N.; De Giacomo, A. Sample Treatment and Preparation for Laser-Induced Breakdown Spectroscopy. *Spectrochim. Acta Part B At. Spectrosc.* **2016**, *115*, 52–63. [CrossRef]
88. Su, L.; Shi, W.; Chen, X.; Meng, L.; Yuan, L.; Chen, X.; Huang, G. Simultaneously and Quantitatively Analyze the Heavy Metals in Sargassum Fusiforme by Laser-Induced Breakdown Spectroscopy. *Food Chem.* **2021**, *338*, 127797. [CrossRef]
89. Watson, J.T.; Sparkman, O.D. *Introduction to Mass Spectrometry—Instrumentation, Applications and Strategies for Data Interpretation*, 4th ed.; John Wiley and Sons: Chichester, UK, 2007.
90. Removal of Spectral Interferences on Noble Metal Elements Using MS/MS Reaction Cell Mode of a Triple Quadrupole ICP-MS—Journal of Analytical Atomic Spectrometry (RSC Publishing). Available online: https://pubs.rsc.org/en/content/articlelanding/2015/ja/c5ja00308c/unauth (accessed on 1 October 2022).
91. Crews, H.M. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for the Analysis of Trace Element Contaminants in Foods. In *Progress in Food Contaminant Analysis*; Gilbert, J., Ed.; Springer: Boston, MA, USA, 1996; pp. 147–186. [CrossRef]
92. Khan, N.; Ryu, K.Y.; Choi, J.Y.; Nho, E.Y.; Habte, G.; Choi, H.; Kim, M.H.; Park, K.S.; Kim, K.S. Determination of Toxic Heavy Metals and Speciation of Arsenic in Seaweeds from South Korea. *Food Chem.* **2015**, *169*, 464–470. [CrossRef]
93. Kumar, M.S.; Sharma, S.A. Toxicological effects of marine seaweeds: A cautious insight for human consumption. *Crit. Rev. Food Sci. Nutr.* **2021**, *61*, 500–521. [CrossRef] [PubMed]
94. Banach, J.L.; Hoek-van den Hil, E.F.; van der Fels-Klerx, H.J. Food Safety Hazards in the European Seaweed Chain. *Compr. Rev. Food Sci. Food Saf.* **2020**, *19*, 332–364. [CrossRef] [PubMed]
95. Conti, M.E.; Cecchetti, G. A Biomonitoring Study: Trace Metals in Algae and Molluscs from Tyrrhenian Coastal Areas. *Environ. Res.* **2003**, *93*, 99–112. [CrossRef] [PubMed]
96. Akcali, I.; Kucuksezgin, F. A Biomonitoring Study: Heavy Metals in Macroalgae from Eastern Aegean Coastal Areas. *Mar. Pollut. Bull.* **2011**, *62*, 637–645. [CrossRef] [PubMed]

97. Sánchez-Quiles, D.; Marbà, N.; Tovar-Sánchez, A. Trace Metal Accumulation in Marine Macrophytes: Hotspots of Coastal Contamination Worldwide. *Sci. Total. Environ.* **2017**, *576*, 520–527. [CrossRef] [PubMed]
98. Duinker, A.; Kleppe, M.; Fjære, E.; Biancarosa, I.; Heldal, H.E.; Dahl, L.; Lunestad, B.T. *Knowledge Update on Macroalgae Food and Feed Safety-Based on Data Generated in the Period 2014–2019 by the Institute of Marine Research, Norway*; Havforskningsinstituttet: Bergen, Norway, 2020. Available online: https://www.hi.no/hi/nettrapporter/rapport-fra-havforskningen-en-2020-44 (accessed on 23 March 2023).