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Article

Biochemical and Elemental Composition of Pelagic *Sargassum* Biomass Harvested across the Caribbean

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Abstract: Massive and recurrent strandings of pelagic *Sargassum* biomass have become the new norm in the Caribbean and the Western Africa since 2011, and there is no sign of this abating. These *Sargassum* events have negative environmental, socioeconomic and health impacts in the affected countries. In the meantime, various processing techniques and applications have been suggested for valorisation of this biomass. However, variability in quantity, quality and location creates substantial uncertainty for the development of reliable and robust industrial processes. As part of ongoing efforts to better characterise seasonal and geographical variations in the biochemical and elemental composition of the pelagic *Sargassum* biomass across the Caribbean, we analysed samples from Mexico, Jamaica and the Dominican Republic harvested during summer 2020 and winter 2021. Different degrees of variation were observed in the contents of ash, metals and metalloids, vitamins, fatty acids, amino acids and biogenic amines, and monosaccharides. Our results indicate that biomass is of highly variable quality depending on season and location. In this context, we suggest that biorefinery approaches geared towards controlled metal removal and focused on the extraction and purification of amino acids, fatty acids and vitamins should be prioritised to assess the potential valorisation of pelagic *Sargassum* biomass into standardised and high-value outputs.

Keywords: *Sargassum*; algal blooms; golden tides; metals and metalloids; amino acids; vitamins; fatty acids; monosaccharides; valorisation

1. Introduction

The impact of unwanted pelagic *Sargassum* on the environment, human health and tourist economies is legion [1–3]. The relentless inundation of Caribbean beaches with seaweed biomass creates a prolonged, multifaceted emergency situation that can oscillate between complete environmental disaster and local economic ruin. Removal of rotting

biomass is costly and has become a substantial burden to both the private tourist industry and local governments throughout the region [4–6]. Typically, recovered biomass is sent to landfill or left to rot in piles near to (or on) the beach. However, it is perhaps one of life's little ironies that the onset and continued prevalence of problematic *Sargassum* seaweed blooms over the past decade in the Caribbean region has been mirrored by a blooming global interest in exploiting seaweed as a sustainable and ecologically friendly biomass source for generating bulk commodity products, such as biofuels, fertilisers and chemical precursors. Clearly, part of the solution to the 'Sargassum problem' will involve a shift in attitude and the development of appropriate infrastructures so that it can instead be viewed as a 'Sargassum opportunity' through its conversion into useful or valuable products/services. When life gives you lemons, it is said the best response is to make lemonade. However, when life gives you *Sargassum*, the jury is still out on what it is best to make. Various processing techniques and applications have been suggested, from anaerobic digestion, plastic production and construction materials to liquefaction and pyrolysis, as well as higher value applications in food extracts, cosmeceuticals and nutraceuticals [4,6–8]. Variability in biomass quantity, quality and location creates substantial uncertainty during the development of reliable and robust industrial processes [9–12]. Comprising at least three similar-looking morphotypes of *Sargassum*, the free-floating populations that invade the Caribbean region include *Sargassum fluitans* III, *Sargassum natans* I and *Sargassum natans* VIII, in varying abundance [5,10,12]; any industrial process that relied upon sorting and distinguishing between types would be unpractical, difficult, and to all intents and purposes, pointless, unless the returns on investment (i.e., value of the product) were suitably large. Whilst oceanic currents reliably and consistently deliver biomass to the Caribbean over massive regions and long seasons on a geological scale, the precise timings and locales impacted are subject to considerable variation [13]. Local geographies and infrastructures influence the ability to retrieve and process biomass effectively, further exacerbating variation in the quality of potential input biomasses. This will undoubtedly impact on any truly scalable industrial process seeking to exploit this biomass.

Here, we undertake a biochemical and elemental analysis of pelagic *Sargassum* biomass harvested from across the Caribbean under conditions amenable to likely future recovery scenarios. Inconsistencies in processing, washing and age of biomass are embraced as factors for consideration, rather than elimination, with a view to identifying potential opportunities and limitations in turning this highly disruptive and problematic biomass into viable economic solutions to benefit the Caribbean community.

2. Materials and Methods

2.1. Collection and Preparation of Samples

Mexican samples were collected from the beach in Cancún (June 2020) and Puerto Morelos (January 2021) in the municipality of Benito Juárez, state of Quintana Roo (Figure 1). Samples were shipped to the Biorganix laboratory in Saltillo, Mexico, where they were cleaned from sand and non-*Sargassum* debris, and sundried for 48 h at temperatures between 25 and 35 °C during the day and 18 and 25 °C at night-time, with a constant flow of air from a ventilator.

Dominican Republic samples were collected from the beach in February 2021 in the municipality of Higuey, state of Punta Cana (Figure 1). The samples were shipped to Algaenova's drying plant and sun-dried for three days at temperatures between 23 and 32 °C during the day and 19 and 24 °C at night-time.

Jamaican samples were collected at Hellshire Bay, municipality of Hellshire, parish of St. Catherine, in August 2020 (Figure 1). Fresh samples were transported to the laboratory within two hours of collection, where they were cleaned of non-*Sargassum* debris and then spread to dry for ~36 h at temperatures of 30–35 °C (sun), 27.9 °C (shade) and 25 °C (night-time).

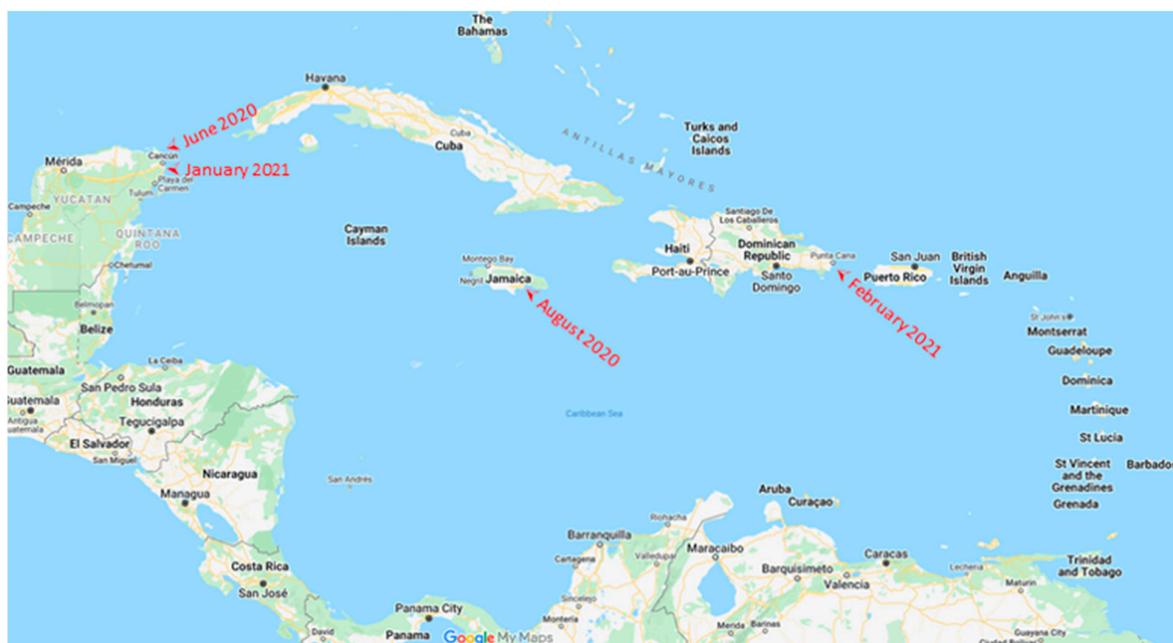


Figure 1. *Sargassum* sampling locations and dates across the Caribbean.

2.2. Ash and Moisture Analysis

Ash and moisture content were determined by Sciantec Analytical, a UKAS and GMP+ accredited laboratory located in Stockbridge Technology Centre, Cawood, Selby, North Yorkshire YO8 3SD, UK. Dried samples were considered as received, and analysis conducted according to protocols implemented by this laboratory: moisture content—protocol TST00205, and ash content—protocol TST00172. One sample from each location was considered, and three extractions were performed for each sample. The mean and standard deviation calculated based on the three extracts are reported for each sample.

2.3. Elemental Composition Analysis by Inductively Coupled Plasma Mass Spectrometry (ICP–MS)

One sample from each location was analysed in triplicates as previously described [10]. Briefly, eight mL of concentrated HNO₃ and two mL of 30% H₂O₂ were added in digestion vessels containing approximately 0.2 g of dried algae. After sealing, vessels were placed in a microwave set-up to heat the content of the vessels to 200 °C for over 30 min. Once at the desired temperature, contents were kept at 200 °C for 15 min. The digestion vessels were then cooled down at room temperature, diluted to 100 mL with distilled water, and 10 mL was considered for analysis. The ICP–MS calibration standard Agilent part number 5183-4688 was used to produce low (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn: 10,000 ppb) and high (Ca, Fe, K, Mg, Na: 1,000,000 ppb) concentration calibration solutions. These two solutions and the algal samples were analysed using an Agilent 7700× ICP–MS equipped with a helium collision cell. The mean and standard deviation calculated based on the three extracts are reported for each sample.

2.4. Amino Acid Analysis

Determination of amino acids contents was conducted by Sciantec Analytical, a UKAS and GMP+ accredited laboratory located in Stockbridge Technology Centre, Cawood, Selby, North Yorkshire YO8 3SD, UK. Dried samples were considered as received, and analysis conducted according to protocols implemented by this laboratory: amino acid profile (excluding tryptophan)—protocol TST00001; tryptophan—protocol TST00019. One sample from each location was considered, and three extractions were performed for each sample. The mean and standard deviation calculated based on the three extracts are reported for each sample.

2.5. Biogenic Amines Analysis

Biogenic amines were quantified by Sciantec Analytical, a UKAS and GMP+ accredited laboratory located in Stockbridge Technology Centre, Cawood, Selby, North Yorkshire YO8 3SD, UK. Dried samples were considered as received, and analysis conducted according to protocols implemented by this laboratory: protocol TST00363. One sample from each location was considered, and three extractions were performed for each sample. The mean and standard deviation calculated based on the three extracts are reported for each sample.

2.6. Vitamin Analysis

Quantities of vitamins were determined by Sciantec Analytical, a UKAS and GMP+ accredited laboratory located in Stockbridge Technology Centre, Cawood, Selby, North Yorkshire YO8 3SD, UK. Dried samples were considered as received, and analysis conducted according to protocols implemented by this laboratory: vitamins A and E—protocol TL00129; vitamin B1—protocol TST00351; vitamin B2—protocol TST00353; vitamin B3—protocol TST00354; vitamin B6—protocol TST00356; vitamin B9—protocol TST00359; vitamin B12—protocol TST00352; Vitamin C—protocol TST00360. One sample from each location was considered, and three extractions were performed for each sample. The mean and standard deviation calculated based on the three extracts are reported for each sample.

2.7. Fatty-Acid Analysis

Fatty-acid composition was analysed by Sciantec Analytical, a UKAS and GMP+ accredited laboratory located in Stockbridge Technology Centre, Cawood, Selby, North Yorkshire YO8 3SD, UK. Dried samples were considered as received, and analysis conducted according to protocols implemented by this laboratory: protocol TST00248. One sample from each location was considered, and three extractions were performed for each sample. The mean and standard deviation calculated based on the three extracts are reported for each sample.

2.8. Monosaccharide Analysis of the Non-Cellulosic Fraction

Three extracts were prepared for one sample from each location as previously described [10]. In each screw-capped tube, approximately 4 mg of biomass was mixed with 0.5 mL of 2 M trifluoroacetic acid for hydrolysis. After flushing with argon, tubes were heated at 100 °C for four hours with mixing at regular interval. Samples were then cooled and evaporated and solids rinsed twice with 2-propanol. After evaporation and resuspension in 200 µL of water, samples were centrifuged for 5 min at 1500 rpm, and the supernatant filtered with 0.45 µM PTFE filters. Samples were subsequently analysed by high-performance anion-exchange chromatography using a CarboPac PA-10 column (DIONEX, Camberley, UK). A standard solution containing arabinose, fucose, galactose, glucose, mannose, rhamnose, xylose, galacturonic acid, glucuronic acid, guluronic acid, mannuronic acid and mannitol was prepared, and different quantities dried before conducting hydrolysis as indicated above for the algal samples. The mean and standard deviation calculated based on the three extracts are reported for each sample.

3. Results and Discussion

3.1. Ash and Moisture

Variable ash and moisture contents were determined from samples investigated in our study (Table 1). Moisture content ranged between 8.50% and 18.80% of biomass DW, in line with previous data from samples harvested in Jamaica in February 2019 [10], but lower compared to values reported by [5], who analysed samples that were not dried.

Ash content represented more than 30% of the biomass dry weight, except in the sample harvested from the Dominican Republic, where it accounted for just 16.63%. Values of the Mexican and Jamaica samples determined in our study were in the same range as those previously reported for samples harvested in Turks and Caicos (June 2019) [5], and in Jamaica during February 2019 [10].

Table 1. Ash and moisture content in pelagic *Sargassum* biomass harvested at different locations in the Caribbean.

	Mexico (July 2020)	Mexico (January 2021)	Dom. Republic (February 2021)	Jamaica (August 2020)	Turks & Caicos (June 2019)	Jamaica (February 2019)
Ash	58.60 ± 0.43	30.07 ± 1.31	16.63 ± 0.09	36.97 ± 0.12	46.94 ± 1.31	34.12 ± 3.46
Moisture	11.83 ± 0.40	13.60 ± 0.14	18.80 ± 0.01	8.50 ± 0.08	81.98 ± 0.89 *	8.19 ± 0.71

Results are expressed as % biomass DW. Turks & Caicos data were taken for the samples Mixed “*Sargassum*” [5]. *, analysis was conducted on biomass that was not previously dried. Values for Jamaica (February 2019) have been reported in [10].

3.2. Elemental Composition

Amounts of metals and metalloids were lower in the sample from the Dominican Republic compared to the other samples, mainly because of the lowest level of Na measured in this sample (Table 2). When comparing the results for the most abundant elements, the content of Mg was found to be homogenous in the samples analysed. In contrast, large variations were observed for K and Ca, with values for the samples collected in Mexico, Jamaica and the Dominican Republic samples always lower than those determined for sample from Turks and Caicos [5].

Table 2. Element content determined by ICP–MS in pelagic *Sargassum* biomass harvested at different locations in the Caribbean.

	Mexico (July 2020)	Mexico (January 2021)	Dom. Republic (February 2021)	Jamaica (August 2020)	Turks & Caicos (June 2019)
Na	32,368.08 ± 2390.29	36,705.04 ± 745.92	7382.63 ± 60.28	30,803.70 ± 2714.54	NA
Mg	7424.02 ± 560.86	8574.62 ± 162.14	6553.47 ± 42.82	8306.53 ± 225.96	12,053.19
Al	10.75 ± 5.90	19.14 ± 5.56	28.45 ± 1.26	62.82 ± 9.45	37.50
K	34,177.79 ± 2687.81	48,213.60 ± 887.80	18,939.46 ± 138.93	56,013.25 ± 4395.27	69,359.39
Ca	24,198.68 ± 2062.31	36,894.929 ± 1672.95	41,717.14 ± 618.85	34,476.17 ± 3984.21	70,305.77
V	1.42 ± 0.18	5.38 ± 1.03	2.18 ± 0.09	1.57 ± 0.20	NA
Cr	0.69 ± 0.35	0.73 ± 0.15	1.99 ± 0.36	1.47 ± 0.93	<0.3
Mn	11.03 ± 0.84	13.60 ± 0.30	14.49 ± 0.17	22.30 ± 0.72	30.15
Fe	45.30 ± 11.39	47.90 ± 8.67	58.79 ± 3.80	53.35 ± 11.63	3811.37
Co	0.54 ± 0.02	0.70 ± 0.02	0.47 ± 0.02	0.46 ± 0.07	NA
Ni	4.59 ± 0.84	4.72 ± 0.15	4.40 ± 0.62	3.75 ± 0.34	NA
Cu	2.38 ± 0.16	2.25 ± 0.15	3.53 ± 0.02	2.11 ± 0.11	2.51
Zn	4.84 ± 2.05	11.49 ± 2.39	13.73 ± 2.99	3.87 ± 1.52	5.81
As	55.91 ± 4.53	53.89 ± 1.30	21.42 ± 0.93	86.84 ± 5.11	123.69
Cd	0.40 ± 0.086	0.77 ± 0.20	0.35 ± 0.01	0.39 ± 0.02	0.13
Ba	22.56 ± 2.24	19.63 ± 0.06	26.93 ± 0.82	15.17 ± 1.77	NA
Pb	0.50 ± 0.50	3.12 ± 1.76	0.45 ± 0.19	0.85 ± 0.05	0.26
U	0.35 ± 0.03	0.54 ± 0.01	0.59 ± 0.02	0.47 ± 0.01	NA
TOTAL	98,329.83 ± 7686.39	130,572.04 ± 3448.87	74,770.46 ± 550.06	129,855.076 ± 4623.48	NA

Results are expressed as µg/g of biomass DW. Turks and Caicos data were taken for the samples Mixed “*Sargassum*” [5]; NA, not available.

Of interest for future valorisation of the pelagic *Sargassum* biomass is the arsenic content, this chemical element being highly toxic in its inorganic form. Amounts of As were found to be very variable in the samples investigated, but within the range of previously published values for pelagic *Sargassum* biomass [5,9,14]. While no elemental analysis was conducted in [10] on the mixed *Sargassum* samples, levels measured in samples from Mexico, Jamaica and the Dominican Republic were in the same range as those measured for individual *Sargassum* morphotypes. The lowest level of arsenic (21.42 µg/g biomass DW) was monitored in the sample from the Dominican Republic. This value was below the maximum level permitted for seaweed-derived feed in Europe (40 µg/g DW; Official

Journal of the European Union, 2019), and was also in the range of natural levels of arsenic found in soil (1 to 40 mg/kg) [15].

3.3. Vitamins

To our knowledge, this is the first report on the determination of the content of vitamins in pelagic *Sargassum* biomass. DL tocopherol acetate, being a synthetic form of vitamin E with a conversion rate of 1 IU = 0.45 mg (<https://ods.od.nih.gov/factsheets/VitaminE-HealthProfessional/> (accessed on 25 January 2022) was used to determine that vitamin E content ranged between 1.67 and 3.25 mg/kg of biomass DW in the samples examined. This indicated that vitamin E, together with vitamin B3, is the most abundant of the vitamins investigated (Table 3). The presence of the other vitamins was expected, as these have been previously quantified in brown algae [16]. However, values were low compared to data recently described for other species of Phaeophyceae, in particular for vitamin A, C and E [17].

Table 3. Vitamin content in pelagic *Sargassum* biomass harvested at different locations in the Caribbean.

	Mexico (July 2020)	Mexico (January 2021)	Dom. Republic (February 2021)	Jamaica (August 2020)
Vitamin A (trans-retinol, IU/g)	<1.00	<1.00	<1.00	<1.00
Vitamin B1 (thiamine HCl, mg/kg)	0.30 ± 0.15	0.19 ± 0.07	0.11 ± 0.04	0.07 ± 0.01
Vitamin B2 (riboflavin, mg/kg)	0.29 ± 0.15	1.77 ± 0.04	0.41 ± 0.03	0.29 ± 0.03
Vitamin B3 (mg/kg)	1.39 ± 0.05	4.21 ± 0.43	2.24 ± 0.28	2.16 ± 0.66
Vitamin B6 (pyridoxine, mg/kg)	<0.50	<0.50	<0.50	<0.50
Vitamin B9 (free folic acid, mg/kg)	0.31 ± 0.03	0.25 ± 0.02	<0.12	<0.12
Vitamin B12 (cyanocobalamin, µg/100 g)	4.97 ± 0.17	4.86 ± 0.38	5.74 ± 0.33	2.28 ± 0.15
Vitamin C (ascorbic acid, mg/kg)	<1.00	<1.00	<1.00	<1.00
Vitamin E (as DL tocopherol acetate, IU/kg)	3.70 ± 0.91	7.23 ± 0.26	5.97 ± 0.37	6.70 ± 0.16

As indicated between brackets, different units were considered to report quantities of vitamins in the samples investigated.

3.4. Fatty Acids

The most abundant fatty acids were the palmitic and oleic acids from our analysis, and this was similar to previous reports [5,12] (Table 4). Saturated and monounsaturated fatty acids accounted for at least 50% of the fatty acids identified. In the sample from Turks and Caicos, a high level of polyunsaturated fatty acid was determined compared to the other samples, notably higher percentages of the long-chain polyunsaturated arachidonic, eicosapentaenoic and docosahexaenoic acids. This latter is rather surprising, because brown algae are not known to produce high levels of this health-beneficial compound.

Table 4. Fatty-acid composition of pelagic *Sargassum* biomass harvested at different locations in the Caribbean.

	Mexico (July 2020)	Mexico (January 2021)	Dom. Republic (February 2021)	Jamaica (August 2020)	Turks & Caicos (June 2019)
Caprylic Acid—C08:0	<0.05	0.07 ± 0	<0.05	<0.05	<0.05
Capric Acid—C10:0	<0.05	0.10 ± 0.01	0.05 ± 0.01	<0.05	<0.05
Undecylic Acid—C11:0	<0.05	0.19 ± 0.01	<0.05	0.25 ± 0.01	<0.05
Lauric Acid—C12:0	0.24 ± 0.01	1.32 ± 0.02	0.20 ± 0.01	0.08 ± 0.01	0.14
Tridecylc Acid—C13:0	0.05 ± 0.01	0.06 ± 0.01	0.34 ± 0.02	0.05 ± 0.01	<0.05
Myristic Acid—C14:0	2.58 ± 0.01	2.58 ± 0.03	1.60 ± 0.04	3.83 ± 0.01	2.01
Myristoleic Acid—C14:1	0.22 ± 0.01	0.27 ± 0.01	0.56 ± 0.03	0.33 ± 0.01	0.43
Pentadecanoic Acid—C15:0	0.54 ± 0.01	0.51 ± 0.01	0.48 ± 0.02	0.65 ± 0.01	0.46
Pentadecenoic Acid—C15:1	<0.05	0.28 ± 0.05	0.05 ± 0.01	<0.05	0.39

Table 4. Cont.

	Mexico (July 2020)	Mexico (January 2021)	Dom. Republic (February 2021)	Jamaica (August 2020)	Turks & Caicos (June 2019)
Palmitic Acid—C16:0	31.90 ± 0.44	22.13 ± 0.33	25.57 ± 0.84	34.19 ± 0.094	26.68
Palmitoleic Acid—C16:1	6.41 ± 0.06	7.87 ± 0.10	6.26 ± 0.01	7.52 ± 0.01	4.03
Heptadecanoic Acid—C17:0	0.70 ± 0.02	0.92 ± 0.04	0.28 ± 0.03	0.77 ± 0.04	1.17
Heptadecenoic Acid—C17:1	0.49 ± 0.01	0.14 ± 0.01	0.27 ± 0.02	0.37 ± 0.01	<0.05
Stearic Acid—C18:0	3.12 ± 0.04	3.45 ± 0.06	2.50 ± 0.01	2.75 ± 0.01	4.73
Oleic Acid—C18:1	13.06 ± 0.09	14.80 ± 0.13	20.84 ± 0.39	13.09 ± 0.02	12.71
Linoleic Acid—C18:2	5.00 ± 0.05	7.52 ± 0.12	12.72 ± 0.30	5.89 ± 0.01	5.32
Linolenic Acid—C18:3	1.89 ± 0.04	3.12 ± 0.05	3.75 ± 0.07	4.15 ± 0.01	4.4
Stearidonic Acid—C18:4	0.20 ± 0.01	0.39 ± 0.16	0.21 ± 0.12	0.47 ± 0.01	0.07
Arachidic Acid—C20:0	0.52 ± 0.02	0.75 ± 0.06	0.64 ± 0.01	0.59 ± 0.02	0.47
Gadoleic Acid—C20:1	0.64 ± 0.67	0.27 ± 0.15	0.54 ± 0.23	0.19 ± 0.01	0.18
Arachidonic Acid—C20:4	4.71 ± 0.08	0.57 ± 0.01	0.43 ± 0.01	0.45 ± 0.01	7.79
Eicosapentaenoic Acid—C20:5	0.38 ± 0.01	0.98 ± 0.01	0.43 ± 0.02	0.79 ± 0.01	3.75
Behenic Acid—C22:0	1.09 ± 0.04	0.94 ± 0.01	0.85 ± 0.02	0.68 ± 0.01	0.63
Erucic Acid—C22:1	0.18 ± 0.02	0.49 ± 0.06	0.25 ± 0.01	0.31 ± 0.03	1.59
Adrenic Acid—C22:4	0.10 ± 0.01	0.66 ± 0.01	0.19 ± 0.01	0.15 ± 0.01	1.17
Docosapentaenoic Acid—C22:5	<0.05	<0.05	0.16 ± 0.02	0.113 ± 0.03	0.36
Docosahexaenoic Acid—C22:6	0.29 ± 0.01	0.89 ± 0.01	0.19 ± 0.01	0.24 ± 0.01	6.44
Lignoceric Acid—C24:0	0.56 ± 0.01	0.52 ± 0.01	0.58 ± 0.02	0.41 ± 0.01	0.42
Saturated Fatty Acids	41.41 ± 0.40	33.54 ± 0.51	33.09 ± 0.93	44.14 ± 0.14	36.71
Monounsaturated Fatty Acids	20.84 ± 0.86	24.13 ± 0.36	28.78 ± 0.49	21.84 ± 0.03	19.33
Polyunsaturated Fatty Acids	12.57 ± 0.06	14.12 ± 0.24	18.07 ± 0.43	12.25 ± 0.02	29.3
Unidentified Fatty Acids	25.17 ± 0.86	28.20 ± 0.63	20.07 ± 0.17	21.77 ± 0.15	14.66

Results are expressed as % of total fatty acids. Turks and Caicos data were taken for the samples Mixed "Sargassum" [5].

3.5. Amino Acids and Biogenic Amines

The content of 18 amino acids was determined (Table 5), and they accounted for 3.87 to 5.84% of the biomass DW. This is close to values reported in [5]. The highest contents were measured for glutamic acid, aspartic acid, leucine and glycine. Among the aromatic amino acids, phenylalanine was the most abundant, as previously reported for other samples from the Caribbean. Levels were quite homogenous in all the samples examined so far, suggesting limited variations between pelagic *Sargassum* biomass harvested at different seasons and different locations. Based on results of the Turks and Caicos sample [5], it was acknowledged that the amino acid profile of pelagic *Sargassum* compared favourably with the profile of essential amino acids recommended by the World Health Organisation, and our results support this observation.

Biogenic amines (BAs) are important nitrogenous compounds formed mainly by decarboxylation of amino acids, or by amination and transamination of aldehydes and ketones. They can occur in different types of food products, where they can have potential toxicity to human health and can also be considered as indicators of food quality [18]. Information on BAs content in seaweeds is scarce, which justifies their investigation in pelagic *Sargassum* samples. Among the biogenic amines investigated in this study, putrescine is produced by decarboxylation of ornithine and arginine, and then can be further transformed into spermidine and spermine. Cadaverine, histamine, and tyramine are produced by decarboxylation of lysine, histidine and tyrosine respectively. Amounts for the six BAs investigated were below 10 mg/kg biomass DW (data not shown), suggesting that BAs may not be a main driving factor when assessing pelagic *Sargassum* suitability for food- and feed-related applications.

Table 5. Amino acid composition of pelagic *Sargassum* biomass harvested at different locations in the Caribbean.

	Mexico (July 2020)	Mexico (January 2021)	Dom. Republic (February 2021)	Jamaica (August 2020)	Turks & Caicos (June 2019)
Alanine	0.32 ± 0.02	0.32 ± 0.01	0.37 ± 0.01	0.30 ± 0.01	0.34
Arginine	0.26 ± 0.01	0.28 ± 0.01	0.37 ± 0.01	0.20 ± 0.01	0.18
Aspartic acid	0.56 ± 0.03	0.6 ± 0.01	0.70 ± 0.01	0.52 ± 0.01	0.47
Cystine	<0.10	0.11 ± 0.01	0.13 ± 0.01	<0.10	0.09
Glutamic acid	0.64 ± 0.01	0.71 ± 0.01	0.76 ± 0.01	0.81 ± 0.01	0.85
Glycine	0.35 ± 0.01	0.38 ± 0.01	0.45 ± 0.01	0.35 ± 0.01	0.32
Histidine	<0.10	<0.10	<0.10	<0.10	0.06
Isoleucine	0.23 ± 0.02	0.22 ± 0.01	0.27 ± 0.01	0.17 ± 0.01	0.16
Leucine	0.33 ± 0.01	0.33 ± 0.01	0.43 ± 0.01	0.25 ± 0.01	0.27
Lysine	0.22 ± 0.01	0.25 ± 0	0.30 ± 0.01	0.20 ± 0.01	0.24
Methionine	<0.10	0.11 ± 0.01	0.14 ± 0.01	<0.10	0.10
Phenylalanine	0.23 ± 0.01	0.22 ± 0.01	0.30 ± 0.01	0.19 ± 0.01	0.18
Proline	0.16 ± 0.03	0.27 ± 0.04	0.34 ± 0.01	0.20 ± 0.01	0.18
Serine	0.22 ± 0.01	0.27 ± 0.01	0.32 ± 0.01	0.22 ± 0.01	0.22
Threonine	0.23 ± 0.01	0.26 ± 0.01	0.32 ± 0.01	0.21 ± 0.01	0.19
Tryptophan	0.07 ± 0.01	0.06 ± 0.01	0.07 ± 0.01	<0.05	0.04
Tyrosine	<0.10	<0.10	0.19 ± 0.01	<0.10	0.01
Valine	0.31 ± 0.01	0.31 ± 0.01	0.38 ± 0.01	0.25 ± 0.01	0.24

Results are expressed as % of biomass DW. Turks and Caicos data were taken for the samples Mixed “*Sargassum*” [5].

3.6. Monosaccharide Composition of the Non-Cellulosic Fraction

Analysis of monosaccharide content is presented in Figure 2 (and Supplementary Table S1) as mg/g biomass DW, and in Figure 3 (and Supplementary Table S2) as % of total monosaccharides. In contrast to the results observed for the amino acid content, clear variations were observed among the samples investigated in this study, and also in comparison with previous data from Jamaica [10]. The total monosaccharide content ranged between 50.54 and 193.98 mg/g biomass DW, with the Jamaican samples containing the highest amounts and the sample from Mexico harvested in summer 2020 the lowest quantity. No trend related to season and or location could be identified based on the data presented.

When comparing the profile of individual monosaccharides, mannuronic was the main compound observed in all the samples, except for the one harvested in July 2020 in Mexico. Interestingly, very different quantities of guluronic acid, the other component of the brown seaweed cell wall alginate, were determined, and this impacted the M/G ratio (Table 6) that ranged from 1.83 (Jamaica, February 2019) to 6.47 (Dominican Republic, February 2021). Other polysaccharides found in the cells of brown algae are fucose-containing sulphated polysaccharides, and fucose represented between 9.37% (Jamaica February 2019) and 28.45% (Mexico, July 2020) of the total monosaccharides. Among the other monosaccharides investigated, xylose, galactose and galacturonic acid were high in the Mexico July 2020 and in the Dominican Republic February 2021 samples, both showing a very similar monosaccharide profile. In addition, high glucuronic acid contents in Mexico January 2021 and Jamaica 2020 samples were noticed. To finish, the content of mannitol, a compound used as local osmolyte and as carbon storage by brown algae, was quite low in all the samples except in Jamaica August 2020, where it represented 13.84% of the total monosaccharides.

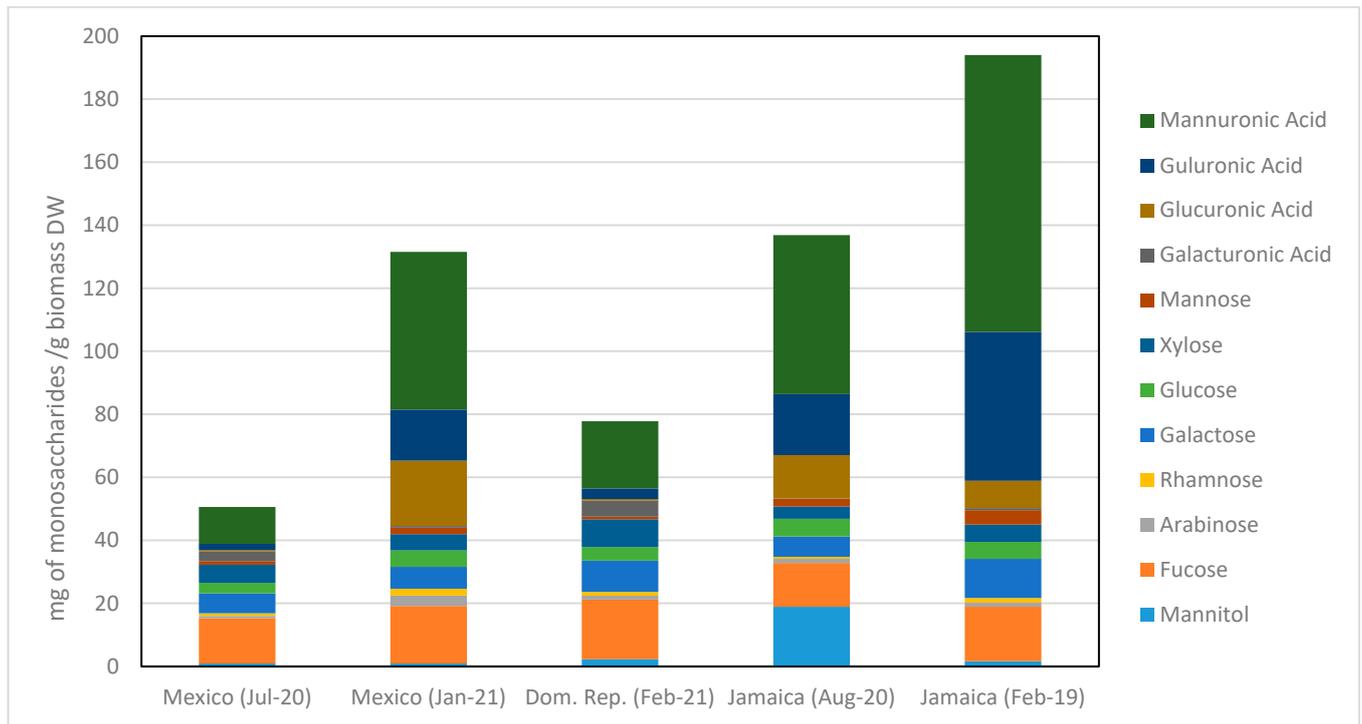


Figure 2. Monosaccharide composition in the non-cellulosic fraction of pelagic biomass harvested at different locations in the Caribbean. Results are expressed as mg/g of biomass DW. Values for Jamaica (February 2019) have been reported in [10].

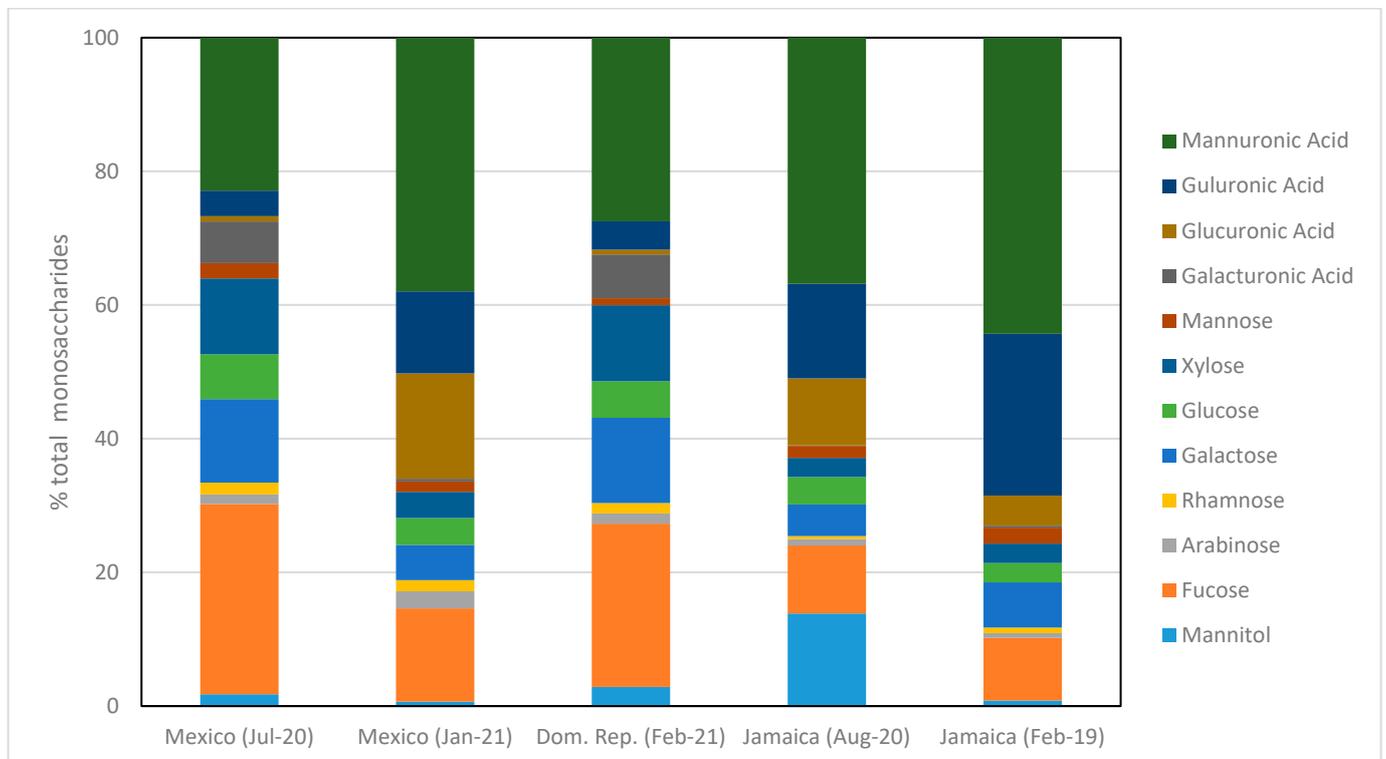


Figure 3. Monosaccharide composition in the non-cellulosic fraction of pelagic biomass harvested at different locations in the Caribbean. Results are expressed as % of total monosaccharides. Values for Jamaica (February 2019) have been reported in [10].

Table 6. Alginate content determined by quantification of mannuronic (M) and guluronic (G) acid monomers in pelagic *Sargassum* samples harvested at different locations in the Caribbean.

	Mexico (July 2020)	Mexico (January 2021)	Dom. Republic (February 2021)	Jamaica (August 2020)	Jamaica (February 2019)
Alginate (% biomass DW)	1.36 ± 0.30	6.62 ± 0.87	2.46 ± 0.13	6.98 ± 0.65	13.50 ± 4.61
Alginate (% total monosaccharides)	26.72 ± 3.73	50.23 ± 2.36	31.72 ± 2.56	50.97 ± 2.36	68.51 ± 4.29
M/G ratio	5.98 ± 0.51	3.10 ± 0.11	6.47 ± 0.22	2.61 ± 0.05	1.83 ± 0.11

Values for Jamaica (February 2019) have been reported in [10].

4. Conclusions and Recommendations

Beyond composting or burying, there are clearly opportunities for the use of *Sargassum* biomass. However, with a high degree of variation in biochemical composition, the development of higher-value applications is challenging. With little to no control over where and when biomass arrives, this could prove an insurmountable obstacle to commercialisation pipelines reliant on bulk processing. Degradation status, processing mechanisms as well as seasonal and location specific differences all add further complications to an already complex scenario. However, the potential clearly exists to develop useful and viable products for which established markets (and rapidly growing markets, e.g., vegan food) already exist: amino acid extracts were found to be very stable, while vitamin extraction has hitherto not been considered, to our knowledge. In addition, potential phytohormone analysis may present beneficial plant growth properties for agricultural/horticultural purposes [19]. Applications relating to specific sugars could remain challenging, presumably because they are prone to rapid and variable degradation under natural environmental conditions. Moreover, little is currently known about the polysaccharide composition of these specific species of *Sargassum*, especially in regard to laminarin (storage) content, and their cell walls. We observed an important abundance of fucose in our monosaccharide analysis. This is consistent with the existing cell-wall model of brown algae, in which cellulose fibrils are imbedded in a matrix of fucose containing sulfated polysaccharide and alginates [20]. The highly variable amount of guluronic acid observed in our sample may relate to variation in this latter cell-wall polysaccharide. However, these can only be suppositions at this stage, since much variability exists among brown algae, especially within *Sargassum* species. Further investigation of the composition and structure of *S. fluitans* III, *S. natans* I and *S. natans* VIII cell walls would certainly help in defining the bioprocess-based degradation of the material, and in assessing the potential opportunities and limitations for polysaccharide extraction and valorisation. Whilst feeds are often suggested as potential uses for *Sargassum* biomass, the metal composition is worryingly variable for applications involving direct consumption of lightly- or unprocessed biomass. Variable metal compositions also highlight the risks involved in burning and/or burying biomass, which would potentially allow metals to leach into fragile local ecosystems. To this end, biorefinery approaches geared towards controlled metal removal, and focused on the extraction and purification of amino acids, fatty acids and vitamins, may well prove to be successful in the future, where biomass of highly variable quality can be processed into standardised, high-value outputs.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/phycology2010011/s1>. Table S1: Monosaccharide composition in the non-cellulosic fraction of pelagic *Sargassum* biomass harvested at different locations in the Caribbean; Table S2: Monosaccharide composition in the non-cellulosic fraction of pelagic *Sargassum* biomass harvested at different locations in the Caribbean.

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