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Trace metal content from holopelagic *Sargassum* spp. sampled in the tropical North Atlantic Ocean: Emphasis on spatial variation of arsenic and phosphorus

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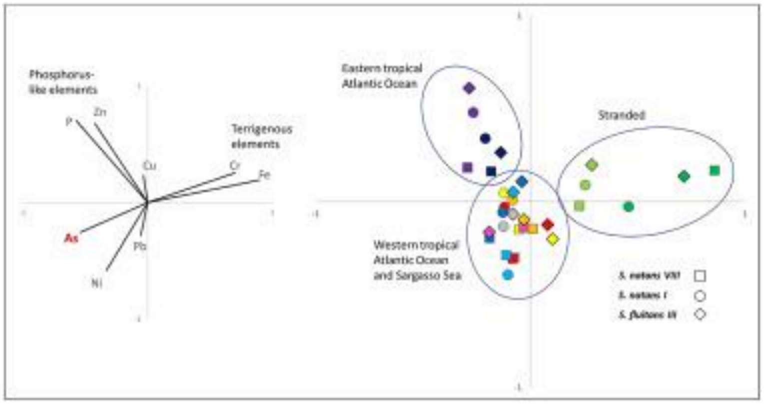
Abstract :

We document for the first time, the spatial distribution at basin scale (North tropical Atlantic Ocean) of As, P and trace metal (TM) concentrations in the three morphotypes belonging to the two holopelagic species Sargassum natans and S. fluitans and three morphotypes: S. natans VIII, S. natans I and S. fluitans III. These samples collected in the North equatorial current (NEC) and in the subtropical Sargasso Sea (sSS) (~25°N, 60°W) were also compared to coastal samples collected downwind Guadeloupe Island and on the strand of Martinique (mangrove and beach). Along the studied zonal oceanic transect, the highest values of As (range 120–240 µg g−1, dry wet) were found in the sSS area where primary production is highly limited by phosphorus. At these stations, the P content of Sargassum spp. was minimal (range 500–1000 µg g−1, dry wet) as well as the content in Cd and Zn known for their nutrient-like oceanic behaviors and distributions very similar to P. This illustrates for the first time in the natural environment, the higher bioaccumulation of arsenic in Sargassum spp. in P-limiting conditions which is due to the competition in the phosphate transporter between arsenate and phosphate. As compared to samples collected at sea, the Sargassum spp. collected in the strand of Martinique had (1) lower As concentrations (typical range 30–45 µg g−1, dry wet) and (2) much higher Al, Fe, Mn, Cr and Co concentrations, showing a certain ability of Sargassum spp. to be depurated of its As content in the coastal zone following competitive exchange with terrigenous metals.

Graphical abstract



Highlights

► Arsenic and cadmium levels are a constraint for *Sargassum* spp valorization. ► We analyzed metal concentrations in holopelagic *S. natans* and *S. fluitans*. ► Three morphotypes and Offshore *vs* stranded biomass were compared. ► The bioaccumulation of arsenic is high under phosphorus limitation. ► Terrigenous metals (Al, Fe, Mn …) compete with arsenic in the coastal zone.

Keywords : Holopelagic Sargassum, Arsenic, Phosphorus, Trace Metal, Tropical Atlantic, Caribbean

1. Introduction

Massive strandings of holopelagic *Sargassum* spp., i.e. *S. natans* and *S. fluitans* originally living in the Sargasso Sea, have been recurring since 2011 over the whole Caribbean zone, on the coasts of West Africa and northern Brazil (Oviatt et al., 2019; Wang et al., 2019). Their expansion into the entire North Atlantic Ocean resulted presumably from an extreme negative phase of the North Atlantic Oscillation in 2009 to 2010 (Johns et al., 2020), followed notably by nutrient input partially from rivers and upwelling systems that allowed their growth, and oceanic currents and winds promoting their spreading (Jouanno et al., 2020; Lapointe et al., 2021). In the Caribbean and tropical Atlantic areas, three morphotypes of holopelagic *Sargassum* have been reported (Schell et al., 2015; Amaral-Zettler et al., 2017; Ody et al., 2019): *S. natans* VIII, *S. natans* I and *S. fluitans* III. These strandings cause economic, sanitary, environmental and ecological problems and require extensive removal efforts (Sissini et al., 2017; Milledge & Harvey, 2018; Oviatt et al., 2019). In order to respond to this problem of massive stranding, new tracks of valorization are considered such as biochemical products, biosourced molecules, human food, animal feed or fertilizer (Milledge & Harvey, 2016 ; Rushdi et al., 2020; Stiger-Pouvreau & Zubia, 2020; Amador-Castro et al., 2021). However, a major constraint for valorization of brown macroalgae usually relies on their metal content which can occur at high levels. Among the different toxic elements, arsenic and cadmium are of particular concern. Indeed, concentrations of total arsenic and total cadmium in the genus *Sargassum* are usually found in the range 10-200 $\mu g\ g^{-1}$ dw and 0.1-5 $\mu g\ g^{-1}$ dw, respectively (Devault et al., 2021) and can thus be potentially higher than the maximum levels authorized for example in algae for animal feed in the European Union (i.e. 40 $\mu g\ g^{-1}$ dw and 1 $\mu g\ g^{-1}$ dw for As and Cd, respectively; 2002/32/EC; 2019/1869/EC). In the case of arsenic, it is worth noting that there is still a discrepancy between studies that still generally report only total As concentrations and current regulations that are now based on inorganic As levels (As_i). For example, regulations in China give a maximum level of 1 $\mu g\ g^{-1}$ dw for As_i in products for human consumption (Cherry et al., 2019), and regulations in the European Union give a maximum value of 2 µg g^{-1} dw for As_i in algae for animal feed (2002/32/EC; 2019/1869/EC). Metal content in *S. natans* and *S. fluitans* have been recorded by several studies over the last five years. These studies have been devoted to biomass stranded on different coasts of the Caribbean area, including Dominican Republic (Fernandez et al., 2017; Milledge et al., 2020), Mexico (Rodríguez-Martínez et al., 2020; Vázquez-Delfín et al., 2021) and Jamaica (Davis et al., 2021). As other species of the genus *Sargassum*, *S. natans* and *S. fluitans* also display relatively high As concentrations (i.e. in the range 14-120 µg g^{-1} dw) but also significant amounts of other metals such as Cd (range 0.1-0.8 µg g^{-1} dw) or Cu (range 2-11 µg g^{-1} dw). The inorganic arsenic content in *S. natans* and *S. fluitans* is however virtually unknown and very little comprehensive information about elemental content is available for biomass collected at sea (e.g. inter-species differences, spatial and seasonal variabilities,...). Such information is however needed to understand the reasons driving differential assimilation, in particular between arsenic and phosphorus whose principal species in seawater, i.e. $HAsO_4^{2-}$ and HPO_4^{2-}, have strong similarities in size and geometry and follow the same pathways into the cells (Reis & Duarte, 2018; Garbinski et al., 2019). The knowledge of elemental concentration for at-sea *Sargassum* biomass is also important to determine whether it is better to consider harvesting at sea rather than on the coast for valorization purposes.

The objective of the present study was to describe and understand the spatial variability of arsenic (As), inorganic arsenic (As_i) phosphorus (P) and metal trace element (TE) levels in the three holopelagic *Sargassum* morphotypes, i.e. *S. natans* VIII, *S. natans* I and *S. fluitans* III. These levels were then compared with those of *Sargassum* spp. that have reached the coastal area and were found in different conditions like downwind of a large Caribbean island (Guadeloupe) or stranded on a beach or in a mangrove swamp (Martinique). Finally, the elemental content differences between the three morphotypes were also compared and discussed.

2. Material and methods

2.1. Sampling

The Caribbean (http://dx.doi.org/10.17600/17004300) and Transatlantic (http://dx.doi.org/10.17600/17016900) expeditions, carried out in June-July 2017 and October 2017 respectively, allowed the collection of holopelagic *Sargassum* spp. samples (see Ody et al. 2019 for details). For the present study, 31 individual samples were collected at seven oceanic stations in the tropical Atlantic east and west areas as well as from four coastal stations (Figure 1). It is worth noting that two stations on the western tropical Atlantic ocean (S19 and S20) were located in the subtropical Sargasso Sea (sSS) whereas all the other oceanic stations were located in the North equatorial current (NEC) also described as the "great trans-Atlantic *Sargassum* belt" (Wang et al., 2019). The coastal samples were obtained (1) downwind of Guadeloupe Island (S12 and S23) and (2) on different strands of Martinique Island: the mangrove of Baie du Trésor (station M) and the beach of Le Vauclin (station B). At each station, the three morphotypes were systematically collected, i.e. *S. natans* VIII, *S. natans* I and *S. fluitans* III. It should be noted that *S. natans* I was not present at station S20. According to Ody et al. (2019), rafts at stations S4, S15, S19 and S20, consisted of isolated *Sargassum* or windrows with possible small patches (type 1, 2 or 3) whereas rafts at stations S12 and S23 corresponded to large patches (tens of meter, type 4) and at station S9 it corresponded to a very large patch and deep patch (hundreds of meters, about 7 meter seep, type 5). The stranded samples (Mangrove and Beach) were collected after a few days of stranding and the biomass was relatively degraded (orange color indicating a degradation of photosynthetic pigments and a cessation of photosynthesis).

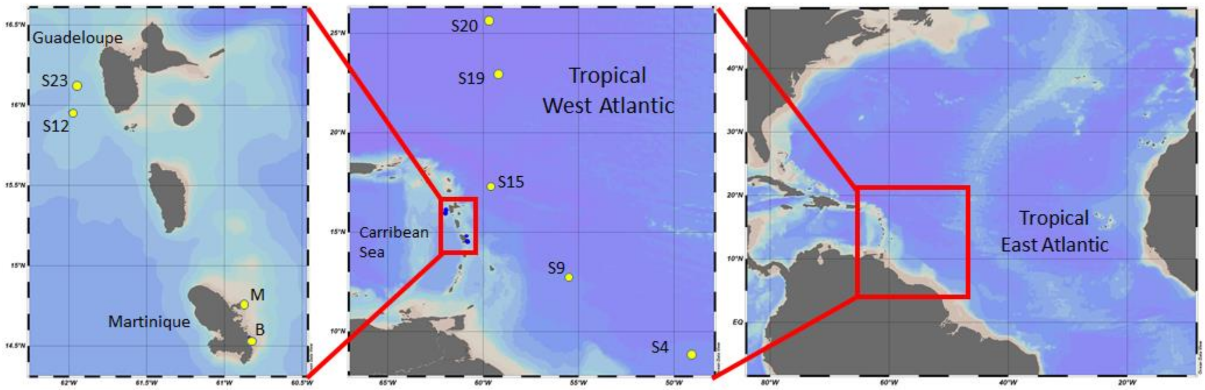


Figure 1: Study area and sampling stations where the three morphotypes of holopelagic *Sargassum* spp. were collected to determine their elemental composition. Note that exact coordinates of stations Ya and Yb are not known but corresponded to sampling in the tropical East Atlantic area.

2.2. Samples preparation and composition analysis

Just after collection, *Sargassum* samples were frozen. Back to the laboratory, the samples were dried using a freeze-dryer (Christ, Germany) and then ground into a fine powder (MM400, Retsch, Germany). From this powder, three subsamples were then processed as follows. After weighing 50 mg of dried and powdered material, digestions were performed at 105 °C for 4 h in closed 15-mL Teflon screw-cap vials (Savillex, Minnetonka, MN, USA) with 1 mL suprapur 65% nitric acid (Merck, Darmstadt, Germany) and 0.25 mL suprapur 30% hydrogen peroxide (Merck,Darmstadt, Germany). Measurements of concentrations of 13 elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, V and Zn) were conducted on diluted mixtures (2.3% HNO_3) using an ICP-quadrupole mass spectrometer (X-series II, Thermo Scientific) operated at the Pole Spectrometry Ocean Brest (PSO, Brest, France). All concentrations shown in the present study were well above detection limits while digestion blanks were below detection limits. *Ulva lactuca* BCR-279, Fish Protein DORM-4 (National Research Council of Canada, Ottawa, ON, Canada) and *Sargassum fusiforme* CRM 7405-b (National Metrology Institute of Japan) were used to assess the method accuracy. Table 1 summarizes the values obtained for this certified reference material.

Determination of inorganic arsenic (As_i) was conducted after its extraction from the dried and powdered material (typically 50 mg) in ultrapure water (typically 5 mL) under sonication for 30 min. The mixture was then centrifuged at 3000 *g* for 5 min and 100 µL of supernatant was used for the analysis. As recommended by Rubio et al. (2010), measurements were made immediately after the extraction step. As_i was then determined using an electrochemical method at a gold microwire electrode (scTRACE gold, Metrohm) using a procedure adapted from Salaün et al. (2007). Electrochemical determination of As_i was systematically repeated three times for each extract.

2.3. Statistical analysis

All data were statistically analyzed with the R program (R Development Core team, 2008). All extractions were performed in triplicate, and results expressed as average ± standard deviation (SD). All data are reported in µg per gram of dry weight (µg g^{-1}, dw). In a first step, the normality and homogeneity of variances were checked by a Shapiro test and a Bartlett test, respectively. Due to the large differences between morphotypes and stations, normality or homogeneity of the data were not met. Therefore, non-parametric tests were applied (Kruskal-Wallis followed by a Dunn test). A significance level of 95% ($p<0.05$) was accepted for all the statistical analyses. A Spearman test was also applied to evidence significant correlations between the different parameters (element concentrations). A PCA analysis was also used to determine groups of stations with *Sargassum* spp. of similar composition. Parameters demonstrating high significant correlation ($p<0.001$) were excluded for the PCA analyses.

Table 1. Determination of elemental concentrations (in µg g^{-1} dw; mean ± SD) in the certified reference materials *Ulva lactuca* BCR-279, *Sargassum fusiforme* CRM 7405-b and Fish protein DORM-4 (from four different preparations of each CRM) compared to certified values.

	Ulva lactuca BCR-279		*S. fusiforme* CRM 7405-b		Fish Protein DORM-4	
	measured	certified	measured	certified	measured	certified
As	3.2 ± 0.2	3.1 ± 0.2	50.5 ± 1.9	49.5 ± 1.0	7.6 ± 0.7	6.9 ± 0.5
Cd	0.26 ± 0.02	0.27 ± 0.02	1.06 ± 0.03	1.25 ± 0.04	0.31 ± 0.04	0.30 ± 0.02
Co					0.28 ± 0.03	0.25*
Cr					1.5 ± 0.1	1.9 ± 0.2
Cu	11.2 ± 0.5	13.1 ± 0.4	3.7 ± 0.2	4.5 ± 0.2	16.1 ± 0.9	15.7 ± 0.5
Mn	1800 ± 100	2100 ± 100	19.0 ± 0.7	22.6 ± 0.5	3.0 ± 0.2	3.2 ± 0.3
Ni	13.2 ± 0.9	15.9 ± 0.4			1.20 ± 0.08	1.3 ± 0.2
Pb	11.7 ± 1.6	13.0 ± 0.4			0.3 ± 0.1	0.42 ± 0.06
Zn	46 ± 3	51 ± 2	11.8 ± 0.4	13.6 ± 0.5	49 ± 7	52 ± 3
P			760 ± 50	780*		
V					1.5 ± 0.1	1.6 ± 0.2

*indicative value

3. Results

Before examining the spatial variability, we first tested the differences between the three morphotypes, i.e. *S. natans* VIII, *S. natans* I and *S. fluitans* III (Table 2). No significant differences between morphotypes were found in the case of Cd, V, Zn, P and Ni. On the other hand, *S. natans* VIII was found to be significantly enriched in As (96±33 µg g^{-1} dw) as compared to the group composed of *S. natans* I and *S. fluitans* III (72±25 and, 81±59 µg g^{-1} dw, respectively). *S. natans* VIII also differs from the two other morphotypes as it contains lower levels of several elements including Al, Fe, Co and Cu. Thus, *S. natans* I appears to be significantly more enriched in P and Mn as compared to the other morphotypes.

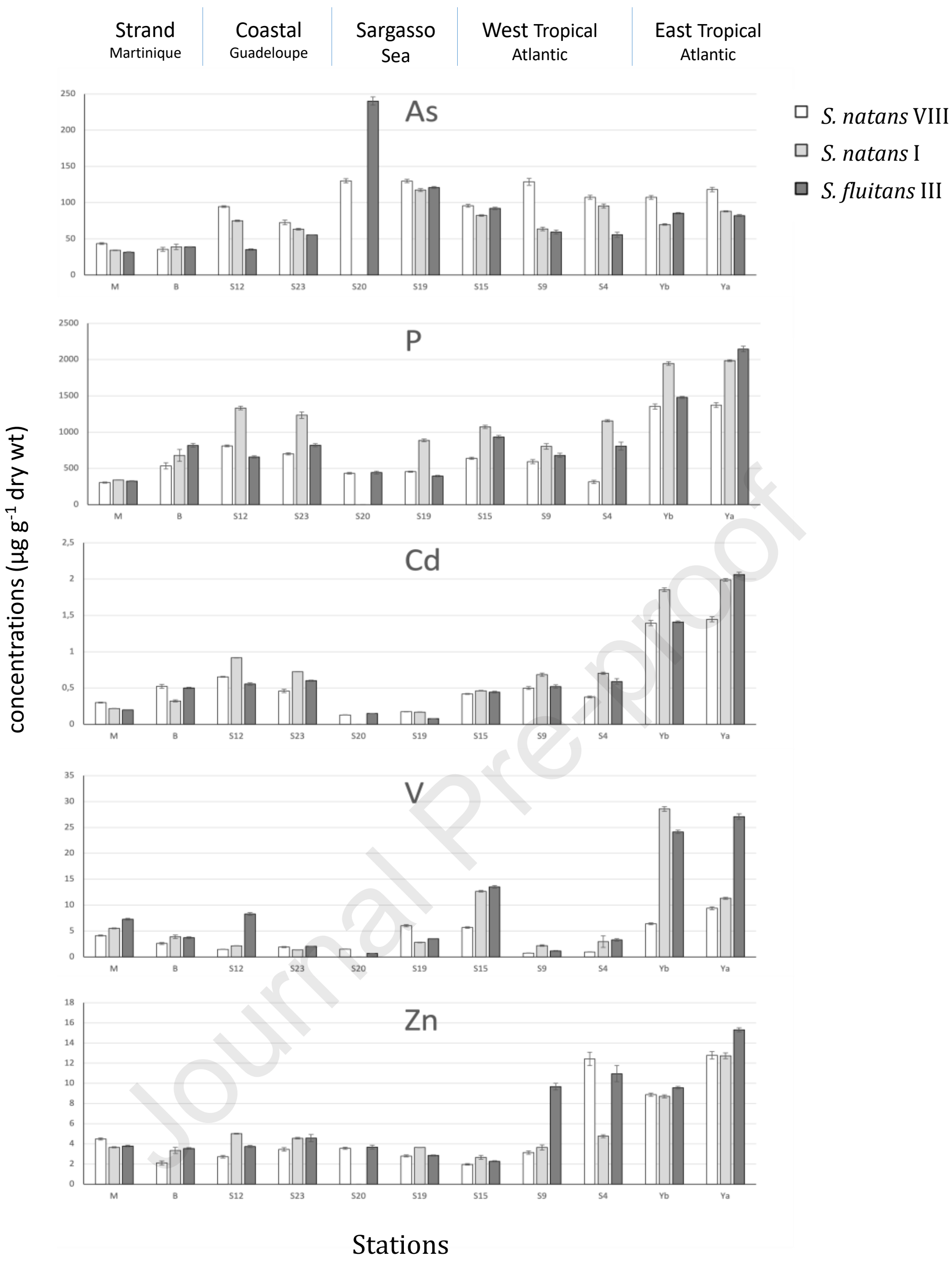
The spatial distributions of the elemental concentrations in the different morphotypes are shown in Figure 2 and Figure 3. It should be noted that these distributions are described hereafter by taking into account any significant differences found between morphotypes or groups of morphotypes which are summarized in Table S1. In the case of As, a similar spatial distribution was observed for *S. natans* VIII and the group composed of *S. natans* I and *S. fluitans* III. In the tropical Atlantic Ocean, As concentrations were generally found in the range 60-130 µg g^{-1} dw. However, higher values (range 120-240 µg g^{-1} dw) were found North of the western area (25°N, 60°W) corresponding to the samples collected in the subtropical Sargasso Sea (sSS; stations S19 and S20). Compared to the oceanic samples, the *Sargassum* spp. collected in the Caribbean Sea downwind Guadeloupe (stations S12 and S23), or stranded in Martinique (stations M and B) displayed lower concentrations with ranges of 55-94 µg g^{-1} dw and 31-43 µg g^{-1} dw, respectively.

A first group of elements, i.e. P, Cd, V and Zn, exhibited a spatial distribution that differed strongly from that observed for As. For these four elements a zonal gradient was observed in the tropical Atlantic Ocean with values generally decreasing towards the West (From Ya-Yb to S4-S9-S15) and then towards the North (S19 and S20 in subtropical Sargasso Sea, sSS). The samples collected downwind Guadeloupe (S12 and S23), generally displayed concentrations in these elements close to those observed in the western oceanic area. The samples collected in the mangrove of Martinique (station M) were characterized by relatively low Cd and P content. A second group of elements, composed of Al, Mn, Fe, Co and Cr is characterized by a distribution that differs significantly from that of the first group but also from that of As. The *Sargassum* spp. stranded in Martinique (stations M and B) had generally higher levels of these elements compared to the *Sargassum* spp. collected at sea. It should be noted that the *Sargassum* spp. at station M (mangrove) had particularly high levels of Fe, Co, Cr and especially Mn as compared to station B (beach). For example, Mn concentrations of ~120 µg g^{-1} dw were observed at station M as compared to values in the range 14-22 µg g^{-1} dw at station B and in the range 4-25 µg g^{-1} dw at sea stations.

The other studied elements, i.e. Pb, Cu and Ni have unique distributions. While Cu and Ni do not show particularly marked spatial variations, Pb stands out by its particularly high levels at stations located downwind of Guadeloupe (S12 and S23) with concentrations up to ~2 µg g^{-1} dw and very low levels (< 0.2 µg g^{-1} dw) in the *Sargassum* spp. biomass stranded in Martinique. Spearman correlation (Figure S1) showed significant correlation ($p<0.05$) between all the elements of the first group (P, Cd, V and Zn) as well as between the elements of the second group (Al, Mn, Fe, Co and Cr). On the other hand, As, Pb, Cu and Ni did not show any significant correlations with the other elements. In the PCA analysis (Figure 4), the two above-mentioned groups appear also well separated with P-like nutrients on the one hand and land-based (Fe-like) trace metals on the other hand. As and Ni stand out from these two main groups and a low representativity is observed for Cu and Pb.

Table 2: Elemental concentrations (mean ± SD) in the three different morphotypes of holopelagic *Sargassum* spp. Significant differences between morphotypes are displayed with different letters. Concentrations are expressed as µg g^{-1} dw

	As	P	Cd	V	Zn	Al	Mn	Fe	Co	Cr	Pb	Cu	Ni
S. natans VIII	96 ± 33[b]	680 ± 370[a]	0.58 ± 0.44	3.7 ± 2.8	5.3 ± 4.1	70 ± 150[a]	21 ± 30[a]	190 ± 450[a]	0.27 ± 0.30[a]	2.1 ± 4.7[a]	0.25 ± 0.26	1.12 ± 0.24[a]	3.3 ± 0.9
S. natans I	72 ± 25[a]	1140 ± 520[b]	0.80 ± 0.64	7.3 ± 8.4	5.3 ± 3.1	80 ± 120[b]	28 ± 28[b]	270 ± 540[b]	0.42 ± 0.27[b]	0.9 ± 0.6[a]	0.45 ± 0.53	1.68 ± 0.47[b]	3.3 ± 1.0
S. fluitans III	81 ± 59[a]	860 ± 530[a]	0.65 ± 0.59	8.6 ± 9.2	6.4 ± 4.3	110 ± 190[b]	22 ± 35[a]	360 ± 730[b]	0.39 ± 0.30[b]	1.9 ± 1.3[b]	0.52 ± 0.59	1.93 ± 0.48[b]	2.8 ± 0.7



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174 Figure 2: Elemental concentrations of As, P, Cd, V and Zn (µg g^{-1} dw) in the three morphotypes of holopelagic

175 *Sargassum* spp. collected at different locations of the tropical Atlantic Ocean. Error bars correspond to the

176 standard deviation on the three subsample preparations. See Figure 1 and sampling section for the characteristics

177 of stations and *Sargassum* spp. raft structures.

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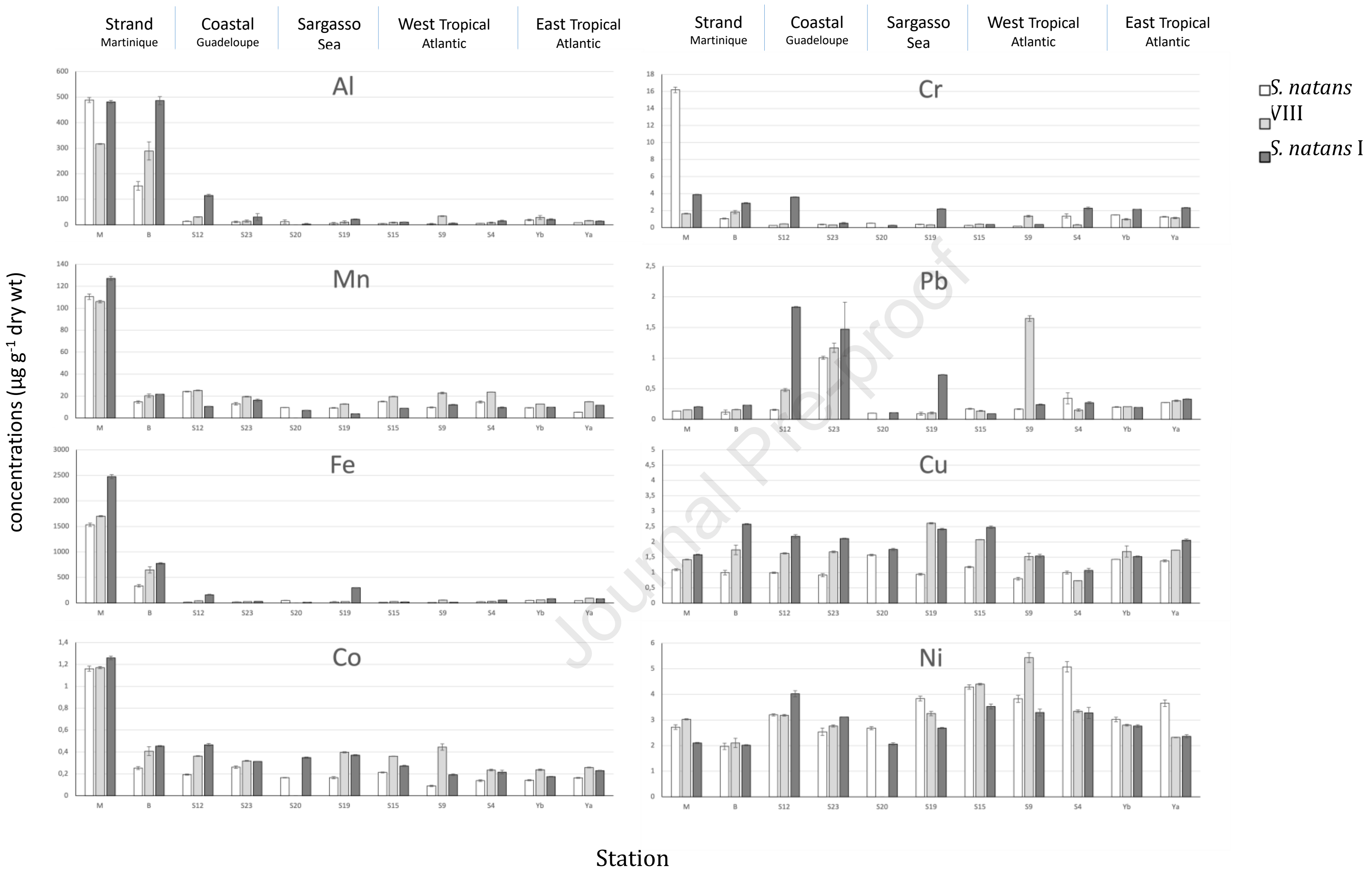

Figure 3: Elemental concentrations of Al, Mn, Fe, Co, Cr, Pb, Cu and Ni (µg g^{-1} dw) in the three morphotypes of holopelagic *Sargassum* spp. collected at different locations of the tropical Atlantic Ocean. Error bars correspond to the standard deviation on the three subsample preparations.

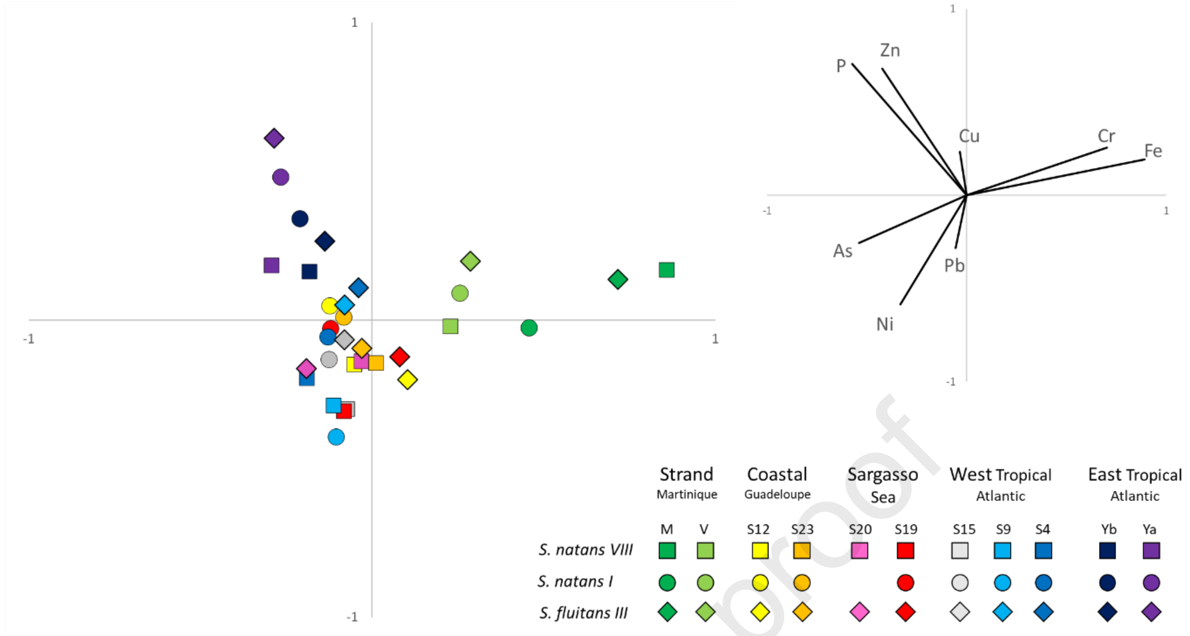

Figure 4: Principal component analysis based on the elemental composition of the three pelagic *Sargassum* morphotypes according to their sampling sites. The two main components displayed explain 48% of the variability. Note that Cd and V (which are highly correlated with P and/or Zn, P<0.001) as well as Al, Mn and Co (highly correlated with Fe and/or Cr, P<0.001) are not displayed.

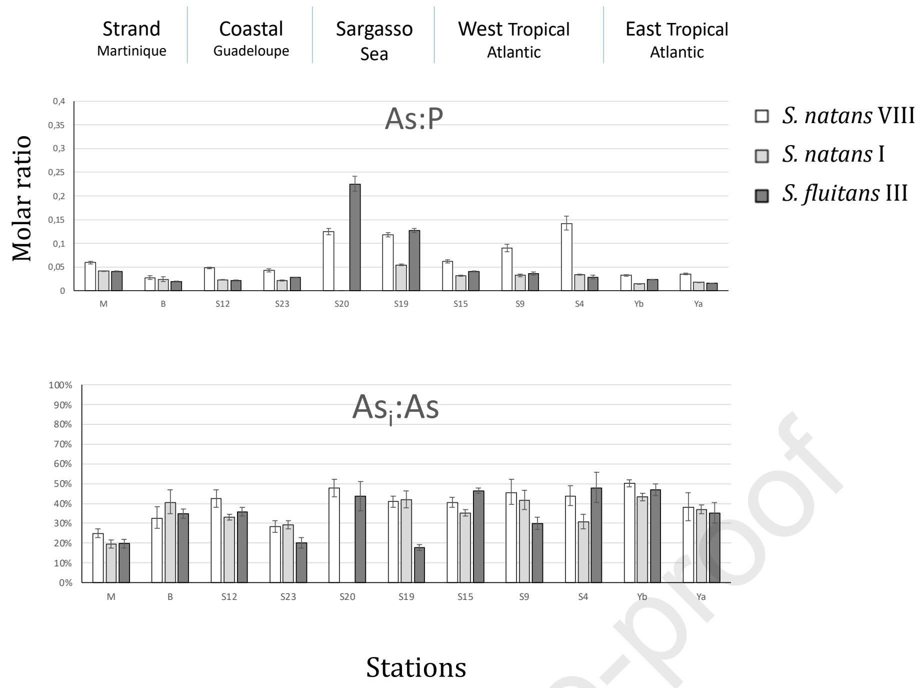

Figure 5: As:P and As$_i$:As mass ratio in the three morphotypes of holopelagic *Sargassum* spp. collected at different locations of the tropical Atlantic Ocean. Error bars for each ratio correspond to the combination of standard deviations on three different determinations.

4. Discussion

The first question we address is why are *Sargassum* spp. particularly rich in arsenic (As) in the subtropical Sargasso Sea (sSS; stations 19 and 20)? The tropical North Atlantic is identified as a zone where primary production is limited in phosphate. This is illustrated by the low phosphate concentrations of surface waters which are generally below 20 nM (Ratten et al., 2015). The limitation in phosphate is particularly strong in the sSS where phosphate concentrations are in the range 0.2-1 nM and are thus associated with high N:P molar ratios above 30 (Wu et al., 2000). In this area, the *Sargassum* spp. also face this P-limitation (Lapointe, 1986) and we indeed found that the P content of the different *Sargassum* spp. morphotypes was minimal at stations 19 and 20 with values in the range 390-460 µg g^{-1} dw for *S. natans* VIII and *S. fluitans* III and ~900 µg g^{-1} dw for *S. natans* I.

In contrast to P, As does not show very marked depletion in oceanic surface waters in relation to its profile described as "hybrid" between nutrient-type and conservative. In the tropical Atlantic Ocean, it has been shown that As levels in surface waters are always in the 10-15 nM range (Cutter et al., 2001; Wurl et al., 2015). As a result, the North tropical Atlantic surface waters are characterized by high molar As:P ratios, i.e. close or above unity, which highlights an As stress for the primary production (Wurl et al., 2015). In the particular case of the sSS area, where values in phosphate and As are in the range 0.2-1 nM and 10-15 nM, respectively, the molar As:P ratio reaches values above 10 and the As stress is thus maximal. Such stress should not only explain why the As content in *Sargassum* spp. is high in the sSS area (above 120 µg g^{-1} dw for *S. natans VIII* and *S. fluitans III*) but also why the high As:P molar ratio in *Sargassum* spp. is so pronounced (in the range 0.10-0.25 for *S. natans* VIII and *S. fluitans* III, Figure 5). According to Garbinski et al. (2019) most organisms take up As incidentally through several types of transporters, particularly through transporters of nutrients such as phosphate for autotrophic organisms as macroalgae, but also glucose and glycerol for mixotrophic or heterotrophic organisms. In the case of *Sargassum* spp. growing in oxygenated marine waters, the main form to deal with and absorbed by organisms is most likely inorganic pentavalent arsenate AsO_4^{3-}. It should be noted that the works of Cutter et al. (2001) and Wurl et al. (2015) confirmed that this ion is the principal chemical form of As in the surface waters of the tropical Atlantic Ocean. Due to its similarity in size and geometry to the phosphate ion (PO_4^{3-}), AsO_4^{3-} most likely uses phosphate absorption pathways (Reis & Duarte, 2018) and the most common strategy used by organisms to tolerate such cellular uptake is to limit the entrance of As in the cytosol (Garbinski et al., 2019). This is in line with the recent NanoSIMS elemental imaging observations made on another brown seaweed, *Laminaria digitata*, by Ender et al. (2019) showing that inside the cells is almost As free and that the majority of As is accumulated as hydrophilic compounds in the cell walls and cell membranes. According to these authors, such accumulation of As, essentially in the form of inorganic arsenic (As_i) but also in the form of arsenosugars, could correspond to an effective detoxification strategy of brown seaweeds. Our measurements of As_i within the hydrophilic fraction of *Sargassum* spp., showing that As_i represents a substantial fraction of total As (range 15%-50%, Fig. 5), are also in line with the finding of Ender et al. (2019).

It should be noted that the minimum values in P in the *Sargassum* spp. in the sSS are also accompanied by particularly low values in Cd and Zn. These observations can be related to the fact that Zn and especially Cd have nutrient-like biogeochemical cycles, very close to that of phosphate. In particular, it has been shown that surface waters of the western tropical Atlantic Ocean (including the Sargasso Sea) are particularly depleted in these two trace elements (Wu and Roshan, 2015; Middag et al., 2019).

Arsenic concentrations in holopelagic *Sargassum* spp. appear to be controlled by the availability of phosphate. Thus, the *Sargassum* spp. growing in the sSS (~25°N) display the highest As content (above 120 µg g^{-1} dw for *S. natans* VIII and *S. fluitans* III). *Sargassum* spp. collected further south, i.e. along the zonal radial around 10-15°N, are associated with the NEC where phosphate is slightly more abundant. In this large area, where large *Sargassum* spp. populations have been established since 2011 and which corresponds to the "great trans-Atlantic *Sargassum* belt" described by Wang et al. (2019), the As content of *Sargassum* spp. is generally in the range of 50-100 µg g^{-1} dw. *Sargassum* spp. collected in the coastal waters of Guadeloupe (15°N), fed by the same NEC, logically show As contents in the same concentration range. However, the *Sargassum* spp. stranded on the coast of Martinique display lower As concentrations. These lower As levels in stranded *Sargassum* samples compared to sea samples have been recently reported by López-Contreras et al. (2021) in samples from the Dutch Caribbean and Florida.

The second issue we address is the high abundance of Al, Fe, Mn, Co and Cr in stranded biomass. The *Sargassum* spp. stranded on the coast of Martinique are also brought by the westward NEC. By comparison to the *Sargassum* spp. collected at sea, they display lower As content (range 31-43 µg g^{-1} dw) but also a very significant enrichment in a certain number of elements, i.e. Al, Fe and Mn. It is worth noting that the composition we observed for stranded *Sargassum* spp. in Martinique, with relatively low As values as well as high Al, Fe or Mn concentrations, is consistent with the composition observed for other Caribbean shores including Jamaica (Davis et al., 2021), Dominican Republic (Fernández et al., 2017) and Yucatan (Rodríguez Martínez et al., 2020). This can be illustrated by the As content (range 58-65 and 14-42 µg g^{-1} dw for Jamaica and Dominican Republic shores, respectively) by the Al content (range 200-220 and 190-430 µg g^{-1} dw for Yucatan and Jamaica shores, respectively) or by the Fe content (range 240-830 and 20-660 µg g^{-1} dw for Jamaica and Dominican Republic shores, respectively). The elements that are significantly enriched in stranded *Sargassum* spp., ie Al, Fe, Mn and Co are usually described as terrigenous (Taylor and McLennan, 1985) and are characterized by much higher concentrations in coastal waters receiving terrigenous inputs than in oceanic waters. Mangroves, for example, are characterized by the presence of fine particles known for their high aluminum content, i.e. Al > 5%, as described by Holloway et al. (2016). Mangroves waters are also subject to hypoxic conditions linked to significant degradation of organic material. This results in high contents in some metals, in particular in dissolved Mn and dissolved Fe (Holloway et al., 2016) whose reduced forms (Mn^{2+} and Fe^{2+}) are stable in solution. It has also been shown that Co, which is associated with Mn and Fe hydroxides, also follows a dissolution pattern sensitive to redox conditions (Gendron et al., 1986). Thus, Thanh-Nho et al. (2021) carried out in a tropical mangrove showed concentrations of dissolved Mn, Fe and Co of the order of 10 µM, 1 µM and 10 nM, respectively. These levels are much higher than those observed in the surface waters of the West Atlantic Ocean, i.e. 3 nM, 1 nM and 20 pM, respectively (Rijkenberg et al., 2014; Dulaquais et al., 2014). While sandy beaches are generally environments in which the water column is well oxygenated, the presence of stranded *Sargassum* spp. can quickly lead to the prevalence of hypoxic or even anoxic conditions (van Tussenbroek et al., 2017). In such hypoxic conditions, it has been shown that sandy beach sediments can also bring significant fluxes of metals such as Fe or Mn as divalent cations to the water column (Kristiansen et al., 2002).

The presence of large quantities of terrigenous elements in stranded *Sargassum* spp. can only be conceived in terms of biosorption which corresponds to passive binding by the senescing biomass. This must be distinguished from bioaccumulation, which corresponds to an active process of metal removal linked to metabolic activity. Brown algae have very good biosorption capacities (Davis et al., 2003) due to the chelating properties of some constituent of their cell-wall, i.e. alginates which are mannuronic (M) and guluronic (G) acids polymers, and fucose-containing sulfated polysaccharides named fucoidan (Deniaud-Bouët et al., 2017). Carboxylate groups of alginates have been identified as the main metal binding site in brown macroalgae

(Davis et al., 2003). According to Haug & Smisrød (1970), their affinity is particularly high in the case of the divalent metals Cu, Pb and Cd and this affinity increases with the guluronic acid content (ie, low M:G ratio). The ions identified as being exchangeable at these chelating sites are essentially light divalent cations (mainly Ca^{2+} and Mg^{2+}) and heavier divalent metal cations (such as Pb^{2+}, Cu^{2+}, Co^{2+} Cd^{2+}, Zn^{2+}, Fe^{2+} or Mn^{2+}) (Davis et al., 2003; He & Chen, 2014). Such an ion-exchange mechanism can thus be envisaged in the case of Pb for the samples collected downwind Guadeloupe. The Pb found in excess in this area could correspond to anthropogenic inputs of this metal from the island of Guadeloupe (~20 km away from stations S12 and S23), via recent rainfall. Indeed, wet deposition has been identified and is still a major pathway for oceanic Pb (Church et al., 1984).

However, an important question remains unanswered here: can arsenic also participate in such an ion-exchange mechanism through competition with other metal cations (e.g. Fe^{2+} or Mn^{2+}) which could explain the lower As content of the stranded biomass? If this is conceivable for two reasons: firstly, because As seems to be mainly present in the cell walls of brown macroalgae (Ender et al., 2019) and secondly, because some studies, although scarce, indicate a certain capacity for biosorption of As by brown seaweeds (Hansen et al., 2006), chelating sites of As and As speciation at the level of algal cell walls need to be better identified. It is worth noting here that preliminary measurements on *Sargassum* spp. extracts indicate that ~30% of total As can be released into water as inorganic As (V) which supports the hypothesis that As can be easily exchanged with other cations.

Moreover, some differences in metal content were observed among morphotypes with, for example, *Sargassum natans* I showing minimal values for several metals (Al, Fe, Co and Cu) except As. These differences could result from discrepancies in their metabolomic composition. As previously explained, alginates are one of the main chelating agents of brown macroalgae. Rhein-Knudsen et al. (2017) and Mohammed et al. (2018) analysed the alginates from *Sargassum natans*: they were rich in guluronic acids (ratio M:G=0.6 and 0.51, respectively) and guluronic blocks enabling these alginates to combine with many divalent ions in structure called “egg-box”. However, the short length of *S. natans* alginates compared to other brown seaweeds and probably the position of guluronic blocks within the alginate probably limit the retention of cation such as some metals (Rhein-Knudsen et al., 2017). Both studies were performed on *S. natans* but no information was available on the *S. natans* morphotypes (either I or VIII), both presenting very different morphologies (fleshy and tiny for *S. natans* I and tough and large for *S. natans* VIII) and thus probably different alginate content and/or composition which could explain the difference in metal content.

Sulphonate groups of fucoidan could also potentially contribute to metal complexation but their absolute role has not yet been evaluated (Davis et al., 2000). Moreover, as for alginates, there is actually not enough data on pelagic *Sargassum* spp. composition to consider that differences in their affinity for metal cations may be related to specific differences in their fucoidan content and/or composition. Arsenic, whose inorganic forms are either neutral ($As(OH)_3$) or anionic ($HAsO_4^{2-}$), does not belong to the cationic group. Ender et al. (2019) in their study on the brown macroalga *Laminaria digitata*, recently hypothesized that fucoidan could bind arsenate to the carbohydrate structure as arsenic acid ester. This is highly conceivable for holopelagic *Sargassum* because we found here a high proportion of hydrolysable inorganic As (15-50%). The fact that *S. natans* VIII contains significantly more As than the other morphotypes, could be related to its composition in fucoidans. Although little information is available in the literature, it is worth noting that Davis et al. (2021) recently found a higher proportion of fucose, which is the main monomer of fucoidan (sulfated polysaccharides), in *S. natans* VIII as compared to *S. fluitans* III.

A recent study from Vázquez-Delfín et al. (2021) presents the composition of stranded *Sargassum* spp. from six different Mexican localities. Although the *Sargassum* occurrence (from 41% *S. fluitans* III – 37% *S. natans* I – 1.5% *S. natans* VIII to 91% *S. fluitans* III – 5.5 % *S. natans* I) was different among localities, they found in the mix stranded *Sargassum* biomass an almost uniform alginate (~31%), uronic acid (19.8 to 24.4%) and fucoidan (8.2 to 9.3%) contents, with however a different metal (Cd, Cu, Fe, Pb, Zn, As) content among localities. For example, the total As content varied from 23 to 118 µg g^{-1} dw and no link was observed with the *Sargassum* occurrence. Again in this study, the three morphotypes were not analyzed separately and these stranded seaweeds probably started to degrade, not allowing a comprehensive composition of the holopelagic *Sargassum*. Future studies should then focus on better describing and discriminating the (bio) chemical composition in holopelagic *Sargassum* responsible for massive influx in Caribbean and African areas as there is currently not enough metabolomic data to understand the different metal content of the three morphotypes of holopelagic *Sargassum* spp.

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Highlights

Arsenic and cadmium levels are a constraint for *Sargassum* spp valorization

We analyzed metal concentrations in holopelagic *S. natans* and *S. fluitans*

Three morphotypes and Offshore *vs* stranded biomass were compared

The bioaccumulation of arsenic is high under phosphorus limitation

Terrigenous metals (Al, Fe, Mn…) compete with arsenic in the coastal zone

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: