Variability of Nutrients and Trace Metals Tissue Content in Two Pelagic *Sargassum* (Ochrophyta, Phaeophyceae) Species from South Florida Compared with Global Data

Variabilidad del Contenido de Nutrientes y Metales Traza en Tejido de Dos Especies de *Sargassum* (Ochrophyta, Phaeophyceae) Pelágico del Sur de la Florida Comparada con Datos Globales

Variabilité du Contenue de Nutriments et de Métaux Trace dans les Tissus de Deux Espèces de *Sargassum* Pélagic du Sud de la Floride Comparée avec les Données Mondiales

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ABSTRACT

The pelagic *Sargassum* bloom might be responding to nutrient enrichment of ocean waters; and the massive amount of biomass might be an opportunity to commercialize this resource. Safe use needs to be tested due to the metals' biosorption ability of *Sargassum*. Here we present nutrient and trace metal tissue content of pelagic *Sargassum* collected in South Florida. Samples of *S. fluitans*, and *S. natans* collected from three localities in the Biscayne area were cleaned, dried for 48 h at 68°C, and ground. Analysis were conducted at analytical facilitates at FIU. Mean N tissue content was 1.08 $\pm$ 0.23 and mean P was 0.0348 ± 0.0122. No deficit of nutrient content compared to global mean values for macrophytes were detected. The C:N ratio of 43.15 $\pm$ 7.43, and the C:P ratio of 3175 ± 1039 show a high content of C relative to N and P. The N:P ratio of 66$\pm$24.35 show a limitation of P content relative to N. The stoichiometric C:N:P ratio of 3175 ±1039: 66±24.35:1 of the South Florida samples compared to the global average of 1,106:38:1 demonstrate a large content of C and N. We suggest that an increase on C availability together with N should be explored as potential causes triggering this macroalgal mega bloom. A high variability in metal concentrations was found, it is noteworthy that arsenic was found in high concentrations in all samples ranging from 73 up to 120 ppm. The characteristic presence of alginates in brown algae, particularly in *Sargassum*, increases the affinity of species of this genus for trace metals. Variability might reflect individual physiological conditions as well as metals' availability along the trajectory of these pelagic species along the Atlantic. We suggest requesting estimations of tissue metal concentrations before approving *Sargassum* for human or animal consumption.

KEYWORDS: *Sargassum*, nutrients, trace metals, South Florida

INTRODUCTION

In recent years, macroalgal blooms are becoming a global concern, several events have occurred in different areas of the world's coasts and oceans with an increase in frequency and magnitude, causing alarm to fishery and tourism industries as well as resource managers (Collado-Vides et al. 2019, Lyons et al. 2014, Ye et al. 2011). Massive ephemeral increases of macroalgae are known for green (Ye et al. 2011), red (Martins et al. 2016) and brown (Collado-Vides et al. 2018) algal divisions; some are from introduced species (Ruesink and Collado-Vides 2006), others are native (Ye et al. 2011), or from large displacements of pelagic species (van Tussenbroek et al. 2017). Because macroalgal blooms are characterized by large amounts of biomass, the increases in nutrient availability from continental fertilizers, industrial and residential wastes, discharged at local scale and accumulated in the oceans, as well as climate change, are suggested as major causes that facilitate these massive growths (Wang et al. 2019, Ye et al. 2011). Particularly, pelagic blooming macroalgae may function as vectors transporting nutrients, fauna and flora, trace metals and other attached debris into coasts and beaches (van Tussenbroek et al. 2017).

The Caribbean region has been impacted, since 2011, by an unusual influx of brown macroalgae accumulating in several beaches causing environmental and socioeconomic problems (Rodríguez-Martínez et al. 2019). These brown macroalgae blooms are formed by species of the genus *Sargassum* (Fucales, Phaeophyceae) that has 358 recognized species (Guiry and Guiry 2019), two of which are free-floating pelagic species. Pelagic *Sargassum* offers an array of environmental benefits acting as habitat engineering species as well as providing food and shelter for aquatic migratory species across the Atlantic Ocean; they also transport nutrients and trace metals into terrestrial environments as they land on coastal areas (Huffard et al. 2014, Rodríguez-Martínez et al., 2020, van Tussenbroek et al. 2017). Similar to the rest of the Caribbean, South Florida has received variable amounts of *Sargassum* since 2011, following the patterns described for the region, our field observations in beaches of South Florida show that the two *Sargassum* pelagic species: *Sargassum natans* (Linnaeus) Gaillon 1828, and *Sargassum fluitans* (Børgesen) Børgesen 1914, are commonly forming the influxes (Olszak et al. 2019). South Florida has large extensions of seagrasses, and their coastal waters support a large tourism and fishery industry dependent on these healthy ecosystems (Santos et al. 2018). Furthermore, beaches of the region are nesting areas for several species of turtles (Bovery and Wyneken 2013, Maurer et al. 2018). We do not yet have comprehensive studies in South

Florida showing the impact *Sargassum* influxes are having in the ecosystems, however, for the Caribbean, losses of seagrasses in coastal areas where *Sargassum* is accumulating have been described (van Tussenbroek et al. 2017). This study reports pilot results that serve as a base line to estimate the potential enrichment by nutrients and potential impact of trace metals – arsenic – coming from *Sargassum* influxes in South Florida beaches. We provide tissue nutrient and trace metal content values for collection of samples from two species of *Sargassum* collected from a South Florida beaches, and compare our results with the published data for the same species, or species of the same genus from other parts of the world.

METHODOLOGY

Sargassum samples were collected in South Florida's Key Biscayne area in September 2018 for nutrient analysis, and in July 2019 for trace metals, samples for metals were collected at two different beaches, one in the Bill Baggs State Park area and the other in the Crandon Park area (Figure 1). Samples floating on the water along the shoreline were collected, by hand using gloves and plastic bags, before landing on the beach. All samples were properly labeled and transported to the laboratory at Florida International University. Samples for nutrient analyses were cleaned, dried for 48 h at 68°C; samples for metal analyses were not cleaned but directly dried avoiding any contact with metals. Samples were ground and stored in individual vials for processing. The samples were analyzed for carbon and nitrogen content using a CHN analyzer (Fisons NA1500; Fisons Instruments, Milan, Italy). A dry-oxidation-acid hydrolysis extraction followed by a colorimetric analysis of phosphate concentration was used to determine phosphorus content; elemental content was calculated based on dry weight and elemental ratios were calculated on a mole:mole basis (Fourqurean et al. 1992). Trace metals were analyzed using a PerkinElmer ELAN DRCe ICP-MS. Both nutrients and metals were done at Florida International University core lab facilities. Only data for arsenic are provided in this study. In order to compare our results with others from different areas of the world, a literature review using *Sargassum* trace metals and nutrients as key words was conducted using FIU library databases. Data included in those papers were extracted and used to compare with values from this study. The papers are included in the literature cited section labeled with an * and a number used in the results to recognize the source of information. Not enough samples were available to apply any statistical test. Results are reported using descriptive graphs.

RESULTS

A total of six samples for nutrients and six samples for metals were analyzed. Nutrient tissue content had a mean value of %N = 1.08, %P = 0.034 and a N:P = 72.73, and slight difference between species was found with higher values in *Sargassum natans* (%N = 1.22, %P = 0.041, and N:P 71.27) compared with *Sargassum fluitans* (%N = 0.94, %P = 0.02, and N:P = 74.18) (Figure 2). The literature search resulted in seven studies including different species of macroalgae (*1,2,6, and 8), and pelagic and benthic *Sargassum* species (*5, 7, 10,11). Species of macrophytes (*1, 2, 6 and 8), including other species of macroalgae had higher values of nitrogen tissue content than samples from this study; but not enough data was available to properly compare with phosphorus. Comparing with other species of *Sargassum*, in general benthic species (*10, 11) not a big difference was detected for nitrogen, however lower levels

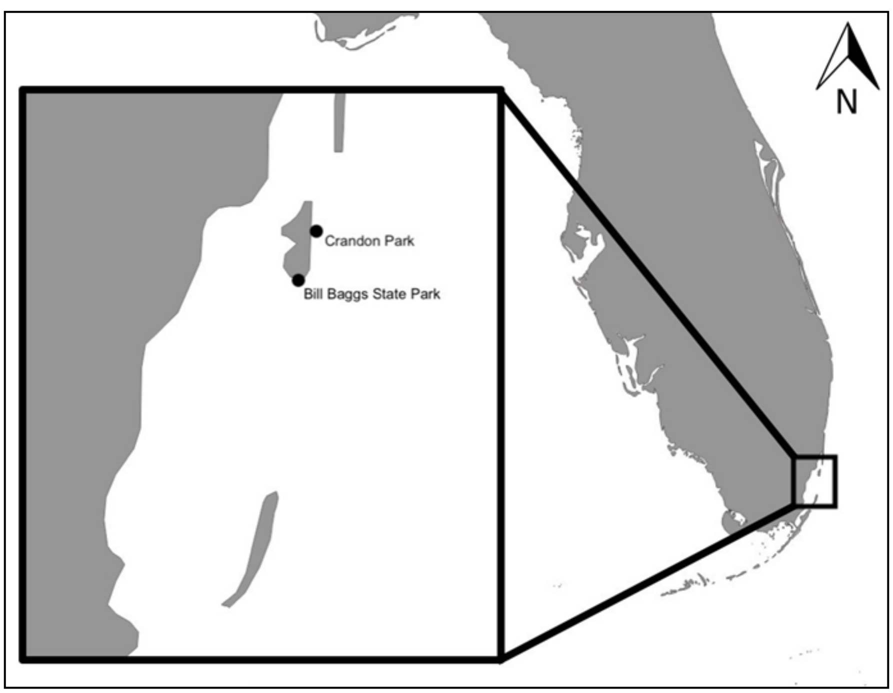

Figure 1. Study area

of phosphorus were found in samples from South Florida. In general, species collected close to shores (this study) showed lower values of %N compared with other species of macroalgae, but similar to pelagic *Sargassum* collected in open waters (*5). This pattern was different for %P, as species from this study showed lower values than pelagic *Sargassum* collected in open waters, resulting also with higher values on N:P in this study compared with pelagic *Sargassum* collected in open waters (Figure 2).

Samples collected from both sites for metal analyses were similarly and they will be analyzed as one locality: Key Biscayne. A total of 6 samples were obtained with a mean arsenic tissue content of 94.82 ppm, with a slightly high value for *S. fluitans* (116.16 – 119 ppm) when compared with *S. natans* (89.91 – 103 ppm). Four (*3, 4, 7 and 9) studies are used here to compare metals with other areas in the world, values reported in this study are within the range of those reported from pelagic *Sargassum* collected in the Mexican Caribbean (*9) (range 34 – 172 ppm) and those from South Africa's benthic *S. elegans* (*7) (range 63 – 105 ppm). However, our values are above of those reported from pelagic *Sargassum* collected in the Dominican Republic (*3) (range 13.68 – 42.30 ppm). Seagrass reports for South Florida (*4) were orders of magnitude lower (range 0.90 - 3.36 ppm).

DISCUSSION AND CONCLUSIONS

Macroalgal blooms are linked to an increase of nutrients in the waters where they develop, however several process need to be considered in the case of pelagic long term translocating blooms. While Redfield- adjusted ratios have been used to analyze primary producer status (Atkinson and Smith 1983, Duarte 1992, Fourqurean and Cai 2001), the interpretation of the values obtained need to take in consideration how far the algae are from their initial blooming area, and how old the thalli are. Results of this study show a slight limitation of nitrogen - data from this study had lower %DW N:1.08 compared with %DW N:1.9 for macrophytes considered not limiting - and strong limitation of phosphorus - data from this study had an order of magnitude lower %DW P:0.034 compared with %DW P:0.24 for macrophytes (Duarte 1992). Similar to many other brown algae, values of phosphorus were lower compared with green or red algae (Lapointe et al. 1992). Comparing the inshore samples to oceanic samples reported in 1995 (Lapointe 1995), tissue nitrogen content is very similar, however, inshore samples are strongly different for phosphorus content (Figure 2C). Two hypothesis can be followed to interpret the "limiting" nutrient results detected. First, the algae collected inshore are old and senescent, they have been floating for a large amount of time since their origin can be the *Sargassum* Great Belt (Wang et al. 2019). Alternatively, the algae are exposed all along their trajectory, to waters enriched with nitrogen, facilitating their massive growth until the limitation by phosphorus is too large. Both hypotheses will need experimental physiological approaches. Either way, the massive landings and stranding in the coasts will receive a large amount of nutrients that are still in the biomass that is translocated from open waters to beaches and shores.

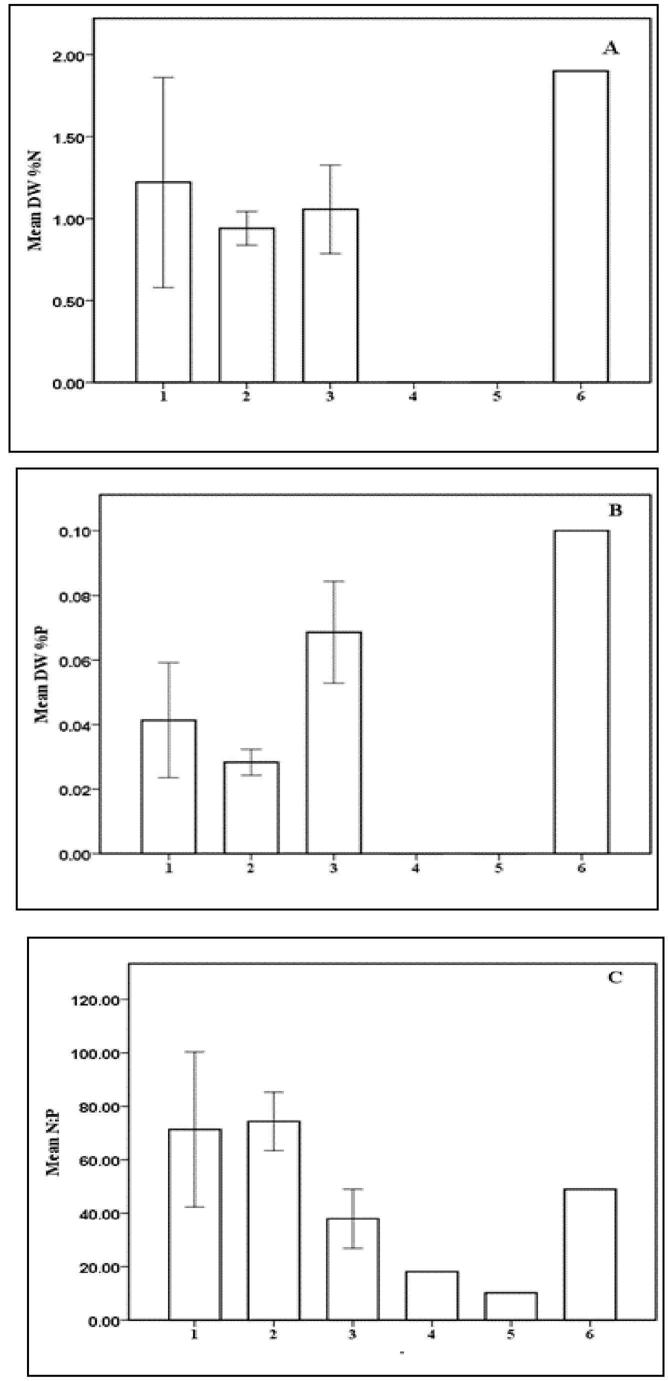

Figure 2. Tissue Nutrient content. 1= *S. natans* this study, 2 = *S. fluitans* this study, 3 = Other *Sargassum* spp, 4 = *S. natans* oceanic, 5 = *S. natans* neritic, 6 = Other macroalgae. A = Mean % Dry Weight Nitrogen, B = Mean % Dry Weight P, C = Mean N:P ratio all data.

Marine macroalgae are known to have the ability to intake and bioaccumulate metals (Francesconi and Edmonds, 1997), and like other brown algae, species of *Sargassum* (including the pelagic ones) have high capacity to absorb metals and other elements (Davis et al. 2000, Kuyucak and Volesky, 1988). This high absorption capacity is attributed to the unique mixture of polysaccharides, mainly alginates, in their cell walls (Fourest & Volesky, 1997). For the case or arsenic, Klumpp and Peterson (1979) show that macroalgal tissues can have up to levels 3–4 orders of magnitude higher arsenic concentrations than their environment. This ability can result in very high percentage of the dry weight of the algae corresponding to arsenic and other metals. In particular, the speciation of arsenic is a complex process that might be related with the process of phosphorylation due to the inorganic arsenate inhibiting the phosphate uptake. In fact, the inorganic arsenate is toxic, however the marine macroalge can reduce that arsenate into As (III) a less-toxic form of arsenic in a form of arsenosugar (Andreae and Klumpp 1979, Francesconi and Edmonds, 1997). Nevertheless that process is dynamic and might depend on the phosphrous availability, normally limited in tropical marine coastal waters (Fourqurean and Cai 2001), and a note of caution is important, Yokoi & Konomi (2012) demonstrated that providing rats with a 3% of their diet with *Sargassum* resulted in negative arsenic accumulation.

The influxes of *Sargassum* in the Caribbean and South Florida are massive. Even if the percentage of nutrients are low, due to the amount of biomass stranded in the beaches, we need to be prepared to evaluate the impact and mitigate the potential consequences to the ecosystems. Moreover, demonstrated by this study's results, *Sargassum* is a source of arsenic to the impacted areas. It is imperative to estimate the accumulation and evaluate the percentage of inorganic:organic species of arsenic that are in the batches landing, as those concentrations might vary depending on the availability of phosphorus in the environment as well as the stoichiometric relationships with nitrogen. We recommend not using temporal large influxes of *Sargassum* for human or animal consumption and support and encourage other uses of this potential resource.

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