

Macro and microelement analysis of *Sargassum fluitans* and *Sargassum natans* arriving in the coastal zone of Cancun, Quintana Roo, Mexico

Análisis de macro y microelementos de *Sargassum fluitans* y *Sargassum natans* que arriban a la zona costera de Cancún, Quintana Roo, México

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Resumen. - En los últimos años el aumento masivo de los arribazones de *Sargassum* en las costas del Caribe Mexicano ha generado repercusiones negativas ambientales, sociales y económicas. Este estudio tiene dos objetivos principales (1) analizar los macro y micronutrientes de *Sargassum fluitans* y *S. natans* con el fin de (2) utilizarlas en la industria local y regional como biofertilizante en la producción de plantas de ornato. Se recolectaron las muestras de sargazo de arribazones flotantes en el mar y el recalado en la zona de tres playas de Cancún, Quintana Roo, México en el año 2018. La cuantificación de los elementos en las muestras se realizó utilizando el método de parámetros fundamentales. La concentración de los macronutrientes Ca, Na, K y Cl fue mayor que los elementos Mg, S, Si y Sr, así como dos órdenes de magnitud superior al Al y P. Adicionalmente, se encontraron los elementos traza Fe, Mn, Zn, Cu, y Ni en ambas especies. Cabe mencionar que la mayoría de estos elementos son esenciales para completar el ciclo de vida de las plantas; por lo tanto, *S. fluitans* y *S. natans* pueden ser considerados como un excelente recurso natural y alternativa de aprovechamiento como mejorador de suelos para el cultivo de plantas de ornato.

Palabras clave: *Sargassum* pelágico, composición química, Caribe mexicano

Abstract. - In recent years, the massive increase in *Sargassum* landings on the Mexican Caribbean coast has generated negative environmental repercussions. This study has two main objectives (1) to analyze the macro and micronutrients of *Sargassum fluitans* and *S. natans* in order to (2) use them in the local and regional industry as a biofertilizer in the production of ornamental plants. Sargasso samples were collected from floating arrivals in the sea and landfall in the area of three beaches in Cancun, Quintana Roo, Mexico in 2018. The quantification of the elements in the samples was carried out using the method of fundamental parameters. The concentration of the macronutrients Ca, Na, K and Cl was higher than the elements Mg, S, Si and Sr, as well as two orders of magnitude higher than Al and P. Additionally, the trace elements Fe, Mn, Zn, Cu, and Ni were found in both species. It is worth mentioning that most of these elements are essential to complete the life cycle of plants; therefore, *S. fluitans* and *S. natans* can be considered as an excellent natural resource and alternative as a soil improver for the cultivation of ornamental plants.

Key words: *Sargassum* pelagic, chemical composition, Mexican Caribbean

INTRODUCTION

Pelagic *Sargassum* is a brown seaweed, and an important constituent of the marine flora in tropical and subtropical zones (Huffard *et al.* 2014), having a key role in the development of a wide range of marine species, such as turtles, fish, invertebrates, and birds (Casazza & Ross 2008, Trott *et al.* 2010). This genus provides a place for reproduction and breeding for many organisms, some of them of commercial importance (Pendleton *et al.* 2014). However, arrivals of

Sargassum masses to the African and Caribbean coasts are currently having negative impacts, due to their local and regional effects on economic aspects such as tourism, fishing, water sports, and the environment. The masses of these macroalgae have negative effects on coastal species, reduce oxygenation, generate leachates, disrupt sea turtle nesting and promote beach erosion. In addition, sanitary problems are created as the algae decompose (Louime *et al.* 2017, Rodríguez-Martínez *et al.* 2019, 2020).



To date, the exact reason for massive overgrowths of this macroalgae is not known with certainty, they may be triggered by global climate change or an excess of nutrients that end up in the sea due to urbanization and poor practices in the agricultural sector (Fernandez *et al.* 2007). According to Dreckmann & Sentías (2013), the largest accumulations have occurred on the coast of Quintana Roo (Cancun and Puerto Morelos), Mexico.

Because macroalgae arrival is currently an ongoing problem, it is necessary to discover the composition of macro and microelements of the most frequent and abundant species that arrive on the coasts of Quintana Roo, *Sargassum fluitans* (Børgesen) Børgesen and *Sargassum natans* (Linnaeus) Gaillon, in order to propose alternative uses and promote exploitation of these large amounts of macroalgae. For example, Dreckmann & Sentías (2013) showed that the most abundant taxon that has been found in the Mexican Caribbean is *Sargassum*.

Sargassum is a genus of multicellular pelagic macroalgae of the class Phaeophyceae (brown algae) in the order Fucales. These algae can grow up to several meters in size. They are brown or blackish green and differentiated into holdfasts, stipes and blades. Some species have gas-filled bladders to help them stay afloat to promote photosynthesis (Critchley *et al.* 1983). *Sargassum fluitans* and *S. natans* are two free-living algae (Davis *et al.* 2003) that float by means of these bladders or vesicles and reproduce by fragmentation of the thallus (Széchy *et al.* 2012).

The main macroelements that have been identified in other species of marine algae are C, H, O, K, N, S, P, Ca, and Mg. The microelements identified in marine algae are Fe, Cu, Zn, Mn, Si, I, Br and Na (Booth 2009). Algae also contain fatty acids, proteins, amino acids, various vitamins; pantothenic, folic, and folinic acids, β -carotene, and other potential precursors.

Seventeen essential elements are needed for plant growth, including O, H and C from H₂O, CO₂ and air. The rest are mineral nutrients, which are classified into macronutrients and micronutrients according to the amount absorbed by the plant (Marschner 1998). The essential macronutrients include phosphorus, potassium, sulfur, calcium and magnesium. Phosphorus plays an important role in the energy metabolism of plants, because it is part of adenosine monophosphate, adenosine diphosphate and adenosine triphosphate molecules (Salisbury & Ross 1992, Barceló *et al.* 1995). These are the quintessential catalytic elements since they are essential in biological redox reactions. The elements accepted as essential are B, Cl, Cu, Fe, Mn, Mo, Ni and Zn (Welch 1995). *Sargassum* species have great potential for use in the

ornamental plant industry; these algae have shown the ability to efficiently absorb metals and other elements in a matter of hours (Fernandez *et al.* 2007), including metals that can be toxic in large quantities (Davis *et al.* 2000).

Therefore, it is expected that *Sargassum* species that arrive on the northern coasts of Quintana Roo contain a high concentration of nutrients, but also may contain other elements such as heavy metals that can be absorbed during their journey through the Atlantic Ocean.

Therefore, it is imperative to analyze *S. fluitans* and *S. natans*, to find the concentration of elements and to determine main macro and micronutrients. This will aid their use in local and regional industry to produce biofertilizers for ornamental plants.

This study carried out a macro and micronutrient analysis of the two species of *Sargassum* that arrive on the northern coasts of Quintana Roo, particularly the littoral zone of Cancun, considered the most important tourist city in Mexico. The main purpose of the study was to determine the elemental chemical content of these macroalgae to facilitate their use as biofertilizers for ornamental plants.

MATERIALS AND METHODS

STUDY AREA

The study area is located in the southeast of Mexico, on the Mexican Caribbean coast of Quintana Roo. This zone receives a current from the Sargasso Sea, which transports great masses of pelagic algae parallel to the Mexican Caribbean coast. Sargasso was collected from three beaches in Cancun, Quintana Roo, Mexico: Las Perlas Beach (21.156°N, 86.799°W), Tortugas Beach (21.139°N, 86.769°W) and Coral Beach (21.025°N, 86.811°W) (Fig. 1).

COLLECTION DATA

Sargassum was collected between October and November 2018 from three different beaches in Cancun. Samples were collected manually from floating masses near the shore (2-20 m) and floating on the ocean (>5 km from shore). The total biomass of *S. fluitans* and *S. natans* that arrived at the three beaches of Cancun was classified as high, medium, or low load (Table 1).

Subsequently, about 5 kg of macroalga were selected *in situ*, thoroughly washed with seawater to remove impurities and excess sand, and then placed in a refrigerator with ice and seawater to keep samples fresh.

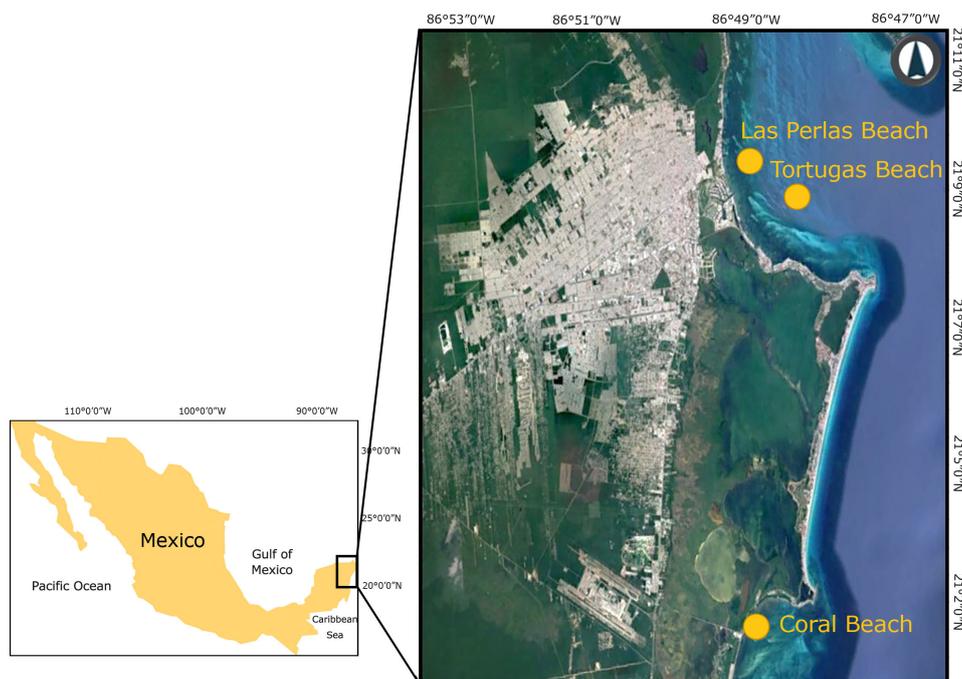


Figure 1. Sample sites: Las Perlas Beach, Tortugas Beach and Coral Beach, in Cancun, Quintana Roo, Mexico; map made using Google Earth© 2019 / Sitios de muestreo Playa Las Perlas (A), Playa Tortugas (B) y Playa Coral (C), en Cancún, Quintana Roo, México, Mapa realizado en Google Earth© 2019

Table 1. List of algal samples obtained in the study area, identified according to *Sargassum* load at each locality / Listado de las muestras de algas obtenidas en el área de estudio, determinadas según la carga de *Sargassum* para cada localidad

Species	Code	Position	Site	<i>Sargassum</i> load
<i>Sargassum fluitans</i>	1	floating	Tortugas Beach	low
"	2	floating	Las Perlas Beach	medium
"	3	floating	Coral Beach	high
"	4	shore	Tortugas Beach	low
"	5	shore	Las Perlas Beach	medium
"	6	shore	Coral Beach	high
<i>Sargassum natans</i>	7	floating	Tortugas Beach	low
"	8	floating	Las Perlas Beach	medium
"	9	floating	Coral Beach	high
"	10	shore	Tortugas Beach	low
"	11	shore	Las Perlas Beach	medium

SAMPLE PROCESSING

Samples were transported to the laboratory at Universidad Politécnica de Quintana Roo and separated by species; *S. fluitans* and *S. natans* (Schell *et al.* 2015). They were then kept in refrigeration at 4 °C for 18 h before processing, to avoid oxidation. Samples were washed three times by leaving them in freshwater for 15 min and then draining them for 5 min.

To determine moisture content, algae were spread on blotting paper and 200 g of sample was weighed in a porcelain container and dried in an oven for 5 h at 60 °C. Once dry, the sample was kept to constant weight and weighed; humidity percentage was 85%.

For elemental analysis, 50 g of washed sample was frozen, and put on a freeze dryer (Christ beta 2-8, Germany) for 24 h, crushed in an agate mortar and sieved (particle size <0.15 mm). Subsamples of 4 g were homogenized, and 3.5 g were prepared for elemental analysis (Tejeda *et al.* 2006).

The pellets were analyzed in triplicate by means of Rigaku NEX QC energy dispersive X-ray fluorescence spectrometer (EDXRF) with palladium x-ray tube, silicon drift detector (SDD), close-coupled Cartesian geometry optical kernel and four secondary target excitations. The elements were quantified by the fundamental parameter's method using RPF-SQX® software. Average values and standard deviations were obtained by means of STATGRAPHICS version 5.0 software (STSC, Rockville, MD, USA).

RESULTS

In this study, the site with the largest number of algae was Coral Beach, particularly the species *Sargassum fluitans*. The load of floating and shored *S. fluitans* and *S. natans* was highest in Coral Beach followed by Las Perlas Beach and Tortugas Beach (Table 1).

Analysis of *S. fluitans* and *S. natans* samples by EDXRF detected the presence of 21 elements. Ca, Na, K and Cl presented the highest concentration in all *Sargassum* samples, at an order of magnitude higher than Mg, S, Sr, and Si, and two orders of magnitude higher than Al and P. Elements considered as trace were present in the following order: I > Fe > As > Mn > Rb > Ti > Zn > Cu > Ni > V > Cr (Tables 2-4).

Table 2. Average concentration (mg kg⁻¹) and standard deviation of macroelements in *Sargassum* biomass at each locality studied / Concentración promedio (mg kg⁻¹) y desviación estándar de macroelementos en la biomasa de *Sargassum* para cada localidad estudiada

Macroelement	Tortugas Beach		Las Perlas Beach		Coral Beach	
Ca	56,250	± 1,344	69,550	± 1,043	64,400	± 2,201
Na	39,700	± 2,449	51,300	± 2,879	45,100	± 2,608
K	32,750	± 525	46,800	± 898	37,700	± 352
Cl	15,550	± 1,856	21,300	± 2,354	25,639	± 2,195

Table 3. Average concentration (mg kg⁻¹) and standard deviation of minor elements in *Sargassum* biomass from the three beaches studied / Concentración promedio (mg kg⁻¹) y desviación estándar de elementos minoritarios en la biomasa de *Sargassum* de las tres playas estudiadas

Microelement	Tortugas Beach		Las Perlas Beach		Coral Beach	
Mg	8,185	± 117	8,320	± 191	9,550	± 157
S	6,220	± 684	7,665	± 489	8,940	± 700
Sr	2,065	± 52	1,810	± 163	2,170	± 41
Si	1,450	± 357	2,085	± 379	1,500	± 405
Al	817	± 99	1,175	± 58	1,070	± 201
P	682	± 72	985	± 61	882	± 67

Table 4. Average concentration (mg kg⁻¹) and standard deviation of trace elements in *Sargassum* biomass, normal geochemical range and Mexican standard values (DOF 2007)¹ / Concentración promedio (mg kg⁻¹) y desviación estándar de elementos traza en la biomasa de *Sargassum*, rango geoquímico normal y valores de referencia de la Norma Oficial Mexicana (DOF 2007)¹

Trace element	Tortugas Beach		Las Perlas Beach		Coral Beach		Normal geochemical range	Mexican standard
As	49.3	± 2.1	98.7	± 8.3	45.5	± 2.2	5-40	22
Zn	8.5	± 0.6	12.2	± 0.4	8.6	± 0.4	25-200	--
Cu	7.2	± 0.5	7.5	± 0.6	6.8	± 0.4	60	--
Ni	5.2	± 0.5	6.4	± 0.5	5.6	± 0.4	2-100	1,600
V	4.6	± 0.4	5.3	± 0.5	5.7	± 0.5	--	78
Cr	4.8	± 0.5	4.7	± 0.5	5.3	± 0.5	--	280
I	139	± 23	148	± 25	141	± 15	Not reported	Not reported
Fe	166	± 22	147	± 41	177	± 47	Not reported	Not reported
Mn	29	± 7	37	± 12	30	± 10	Not reported	Not reported
Rb	25	± 2	32	± 1	27	± 1	Not reported	Not reported
Ti	17	± 7	18	± 6	15	± 4	Not reported	Not reported

DISCUSSION

Galán-Huertos & Romero-Baena (2008) propose geochemical concentrations of elements As, Cd, Cu, Mo, Ni, Pb, Se and Zn considered normal in soils, however these reported parameters are different from those in the Official Mexican Standard (NOM 147, DOF 2007)¹ which stipulates the criteria for characterizing and determining remediation concentrations, and remediation criteria for soils contaminated by As, Ba, Be, Cd, Cr⁶⁺, Hg, Ni, Ag, Pb, Se, Ta, V and their inorganic compounds (Tables 5-7).

Analyzing the average concentration of As, Cr, Cu, Ni, V and Zn in the *Sargassum* from the three beaches under study, it is observed that only arsenic exceeds the NOM-147 (DOF 2007)¹ criteria (Tables 6 and 7). The average arsenic concentrations were 49, 99 and 45 mg kg⁻¹ from Tortugas, Las Perlas and Coral beaches respectively; these concentrations are higher than the total reference concentration for residential, commercial, and agricultural land use stipulated in the Mexican normativity, and they exceed the maximum concentration of 40 mg kg⁻¹ considered normal in soil (Galán-Huertos & Romero-Baena 2008, Fernández *et al.* 2017, DOF 2007)¹.

Table 5. Comparison of average concentration (mg kg⁻¹) of elements in *Sargassum* from the Mexican Caribbean coast / Comparación de la concentración promedio (mg kg⁻¹) de elementos en *Sargassum* del Caribe mexicano

Element	Rodríguez-Martínez <i>et al.</i> 2020	This study	Element	Rodríguez-Martínez <i>et al.</i> 2020	This study
Ca	70,040	63,400	Fe	< 3	116
K	19,666	24,440	V	< 3	5
Cl	22,350	16,883	Cu	< 6	7
Mg	6,537	8,685	Zn	< 5	9
S	14,363	7,608	Na	Not reported	55,367
Sr	1,890	2,015	I	Not reported	109
Si	1,767	1,582	Ti	Not reported	13
Al	206	1,021	Ni	Not reported	5
P	327	850	Cr	Not reported	3
As	80	54			
Mn	71	25			
Rb	56	25			

Table 6. Normal and anomalous geochemical concentrations of some trace elements according to Galán-Huertos & Romero-Baena (2008) / Concentraciones geoquímicas normales y anómalas de algunos elementos traza según Galán-Huertos & Romero-Baena (2008)

Trace element	Normal range (mg kg ⁻¹)	Abnormal concentrations (mg kg ⁻¹)
As	<5-40	≤2,500
Cd	<1-2	≤30
Cu	60	≤2,000
Mo	<1-5	10-100
Ni	2-100	≤8,000
Pb	10-150	≥10,000
Se	<1-2	≤500
Zn	25-200	≥10,000

Table 7. Total reference concentrations (CR_T) by land use, maximum recommended concentration by Mexican standard (DOF 2007)¹ / Concentraciones de referencia totales (CR_T) por uso de suelo, concentración máxima recomendada por la Norma Oficial Mexicana (DOF 2007)¹

Polluting element	Agricultural / Residential / Commercial use (mg kg ⁻¹)	Industrial use (mg kg ⁻¹)
As	22	260
Ba	5,400	67,000
Be	150	1,900
Cd	37	450
Cr	280	510
Hg	23	310
Ni	1,600	20,000
Ag	300	5,100
Pb	400	800
Se	390	5,100
Ta	5.2	67
V	78	1,000

¹DOF. 2007. Norma Oficial Mexicana NOM-147-SEMARNAT/SSA1. 2004. Que establece criterios para determinar las concentraciones de remediación de suelos contaminados por arsénico, bario, berilio, cadmio, cromo hexavalente, mercurio, níquel, plata, plomo, selenio, talio y/o vanadio. Diario Oficial de la Federación, Secretaría de Gobernación, México. <http://www.dof.gob.mx/nota_detalle.php?codigo=4964569&fecha=02/03/2007>

However, these concentrations are to be expected since levels of arsenic in marine flora and fauna are higher than those present in continental systems; generally, the concentrations are between 5 and 100 mg kg⁻¹. Usually marine algae present the highest arsenic concentrations; reaching values between one thousand and ten thousand times higher than the arsenic concentration in the water (Francesconi 2010).

Results obtained for *Sargassum* from Tortugas Beach, Las Perlas Beach and Coral Beach generally agree with those reported by Rodríguez-Martínez *et al.* (2020), who estimated the concentrations of 28 different elements in *Sargassum* tissue collected from the Mexican Caribbean coast. This was to be expected since *Sargassum* that arrives along Mexican Caribbean coastline comes from the same north equatorial stream of the Sargasso Sea (Table 5).

Minority elements in algal biomass were Mg, S, Sr, Si, Al and P. Concentration of S was found in an interval between 6,220 and 8,940 mg kg⁻¹ in the three sampling sites (Table 3). Reussi-Calvo *et al.* (2006) conducted experiments with the application of S in agricultural soils to improve protein yield in wheat grain (*Triticum aestivum L.*). Treatments with doses of 15 kg ha⁻¹ for conventional tillage systems and direct sowing increased the yield to 5,328 kg ha⁻¹, while fertilization increased the yield to 4,748 kg ha⁻¹ of protein in wheat grain, thus presenting a feasible alternative to improve the sulfur-deficient soils of Quintana Roo.

The soils from Quintana Roo presented a P concentration between 0.74 and 4.44 mg kg⁻¹ (Ramírez Silva *et al.* 2015)², which are considered low according to Council on Soil Testing and Plant Analysis (CSTPA) of the United States criteria, which states that a soil is classified as poor if the concentration of phosphorus is less than 5.5 mg kg⁻¹, medium between 5.5 and 11 mg kg⁻¹ and rich if greater than 11 mg kg⁻¹ (Borges-Gómez *et al.* 2007); therefore, it is important to consider the rational application of brown algae to improve the quality of soils in the state since brown algae are rich in P with a concentration of 682, 882 and 985 mg kg⁻¹ at the Tortugas, Coral and Las Perlas beaches, respectively.

Algae samples analyzed contain trace elements such as I, Fe, Mn, Rb and Ti (Table 4). Due to their low concentration, they do not pose a risk to plants grown in treated soils from Cancun in Quintana Roo.

Average concentration of arsenic in the *Sargassum* of the three sampling sites was 54 mg kg⁻¹, and although this concentration exceeded the limit of the Mexican standard and the normal geochemical range (Table 2), it does not necessarily represent a toxicological risk to plants. Due to the similarity of arsenate (AsV) and phosphate (P), marine organisms such as macroalgae may bioaccumulate inorganic arsenic from seawater and transform it into less toxic organic compounds like arsenosugars and fat-soluble species (Francesconi & Edmonds 1996, Francesconi 2010).

Up to 15 dimethylated arsenosugars (AsAz) have been identified in seaweeds. The most common are dimethyl arsinoribosides; when algae die, the AsAz are transformed into methylated compounds of moderately low toxicity such as trimethylarsine oxide, but not inorganic As. Therefore, the arsenic present in *Sargassum* has very low toxicity, being not toxic to mammals including humans and could be used by the industry for growing ornamental plants (Borak & Hosgood 2007, Uneyama *et al.* 2007).

Of the elements detected in *Sargassum* biomass, P and K are considered primary nutrients and are essential for plant growth; Ca, Mg and S are considered secondary nutrients and are applied when there is a deficiency in the soil. Considering that Ca and K concentrations range between 3.27% and 6.9% and for P, Mg and S between 682 mg kg⁻¹ and 9,550 mg kg⁻¹, *Sargassum* could be considered a suitable raw material for producing a biofertilizer with a mixture of primary and secondary nutrients (Zodape 2001, Bula-Meyer 2004, Soto-Jiménez *et al.* 2019).

The addition of seaweeds as biofertilizer favors the absorption of trace elements in plants, due to properties of the polysaccharides which form soluble compounds when they combine with elements such as Mn, Fe, Co, Ni, Cu, and Zn, so *Sargassum* provides nutrients and favors bio absorption of micronutrients present in the soil (Metting *et al.* 1990, Zodape 2001, Sangha *et al.* 2014, Soto-Jiménez 2019).

These prospective studies should serve as a guide for compost preparation to reduce concentration of metals that exceed the criterion values. Reducing the concentrations of these metals can prevent potential public health problems and pollution.

²Ramírez-Silva JH, A Cano-González, Y Aguilar-Duarte, G Ramírez-Jaramillo, VM Loeza-Deloya. 2015. Comportamiento del fósforo en suelos mecanizables dedicados a maíz en el estado de Quintana Roo, México. XXVI Reunión Científica Tecnológica, Forestal y Agropecuaria Tabasco, La innovación tecnológica para la seguridad alimentaria, Universidad Juárez Autónoma de Tabasco, Tabasco, pp. 55-60.

The main proposed use for *Sargassum* is as a biofertilizer for ornamental plants that would enhance their growth and development, benefiting the local and regional ornamental plant industry.

Future studies are proposed to carry out the same analysis on samples of floating *Sargassum* obtained from high seas. This comparison would establish whether algae bioabsorb elements after arriving on the beaches, since macroalgae have been reported and proposed as environmental bioindicators (Bula-Meyer 2004).

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