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Preliminary investigation into the chemical composition of the invasive brown seaweed *Sargassum* along the West Coast of Ghana

Gloria Naa Dzama Addico* and Kweku Amoako Atta deGraft-Johnson

CSIR-Water Research Institute, P.O. Box AH 38, Achimota, Ghana.

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The arrival of the invasive brown seaweed *Sargassum* in the Western Region of Ghana was first reported in 2009. This impacted negatively on biodiversity, tourism and the livelihoods of the coastal communities. The objectives of the study among others were to identify and determine the nutritional and toxicological contents of the seaweed. Twenty four samples collected from 6 zones along the Western Region were analysed. Nutritional and toxicological analyses were carried out using an Atomic Absorption Spectrophotometer (AAS) 900T. Results of the study indicated that the *Sargassum* samples analyzed contained low concentrations of nitrogen. However, nitrogen utilized by plants, namely, nitrate and ammonia were very high, together with phosphates. This makes the *Sargassum* a good source organic fertilizer. However, the high concentrations of toxic heavy metals in the *Sargassum* defeat this assertion. Heavy metals have implications in both the growth and metabolic activities of plants. Most heavy metals, especially arsenic and lead are carcinogenic and are capable of causing skin, lung, liver and bladder cancers and miscarriages. Indiscriminate domestic and industrial wastes disposal, oil and gas activities, mining and high shipping traffic may have contributed to the heavy metal concentrations in the seaweeds.

Key words: Seaweed, *Sargassum*, nutrients, toxins, health.

INTRODUCTION

Invasion of the brown seaweeds *Sargassum* species on the beaches and in estuaries in the coastal regions of Ghana especially the Western Region was reportedly first recorded in 2009. Since then there have been several other invasions which have impacted negatively on biodiversity, tourism and the livelihoods of coastal communities especially the fisher folks whose lives are dependent on the fishing industry.

Sargassum belongs to the Phylum Ochrophyta, class Phaeophyceae and constitutes a distinct taxonomic group due to their morphological, anatomical and physiological complexities. It is the most diverse genus of marine macrophytes (Xie et al., 2013), including 265 genera and roughly about 1500 species worldwide.

*Corresponding author. E-mail: Naadzama443@hotmail.com. Tel: 0248114068.

Sargassum spp. are known to have a broad geographical distribution from Central America, through Australia, New Zealand, Asia, Europe and Africa (Guiry and Guiry, 2011). *Sargassum* is highly tolerant to environmental parameters such as desiccation, full sunlight and variations in salinity and temperature. This enables it to occupy a broad range of habitats from the upper intertidal, mainly rock pools to the sub tidal and substrata from exposed rock to Eel-grass beds. The *Sargassum* spp. normally all reproduce sexually except for the halopelagic *Sargassum natans* and *Sargassum fluitans* which reproduce only by fragmentation (Dawes and Mathieson, 2008; Rogers, 2011).

In Ghana, two indigenous species of *Sargassum* have been recorded, namely *Sargassum vulgare* C.Agardh 1820, occurring in the intertidal zone and *Sargassum filipedula* C.Agardh 1824 which occurs on the offshore reefs.

The species *Sargassum* invading Ghana is believed to originate from the "Sargasso Sea" situated in the Western Atlantic tropical region of the Northern Hemisphere (Szechy et al., 2012). It is encircled by a gyre formed the Gulf Stream, The North Equatorial Current and the North Atlantic Drift (Luning, 1990).

Seaweeds are marine resources of various economic uses. The economic importance of seaweeds or algae lies on its utilization as a source food and in the pharmaceutical and medicine industries. For example *Sargassum* is known to form about 10% of the average diet in Japan where it is eaten raw as salad or cooked in coconut milk (Oyesiku and Egunyomi, 2014). It is also used as in Chinese medicine as an expectorant for bronchitis and to treat laryngitis, hypertension, infections, fever and goiter (Hou and Jin, 2005). The major products derived from the utilization of seaweeds are agar, alginic acid, also called alginin or alginate, fucoidan and carrageenan (McHugh, 2003; Namvar et al., 2013). Fucoidans are sulphated polysaccharides unique only to brown algae such as the *Sargassum* that have been found to have anti-tumor, anti-metastatic, anti-viral, anti-coagulant and anti-bacterial properties in laboratory trials (Khotimchenko, 2010).

Seaweeds are exported either in their raw forms (fresh or dried seaweeds) or in processed forms (carrageenan and kelp powder). They also provide energy to grazers and contribute immensely to the benthic detritus food chain. The seaweed beds also form important habitat for fishes and invertebrates. They are also known to be useful indicators of climate change and can be used to determine the diversity patterns and especially for planning conservation and sustainability of inshore marine resources (John and Lawson, 1991; Bolton et al., 2003).

Recently, several authors have published studies on the chemical composition of the *Sargassum* including their nutrients and heavy metal content. This is because of the usually heavy invasions and the need to put it to some economic use. Sudharsan et al. (2012) worked on seaweeds, including *Sargassum* and *Padina*. They observed these brown seaweeds were more tolerant to Zinc and recorded the highest level of zinc. Oyesiku and Egunyomi (2014) also did proximate analysis and chemical composition analysis especially nitrogen, phosphorous and potassium on *Sargassum* samples found offshore in Ondo State, Nigeria. Manivannan et al. (2009) reported that the brown algae *Padina gymnospora* showed the maximum content of mineral composition such as copper, chromium, iron, lead, sulphur, and calcium content than other seaweed. Nazni and Deepa (2015) also recently looked at minerals and heavy metal present in five selected red seaweed of South Coast Region of Tamilnadu with the aim of evaluating the minerals and heavy metals present in the seaweeds present in the south coastal line. They concluded that seaweeds are a potential source of essential minerals which can be used to promote good health.

The objectives of this study were to identify the invasive *Sargassum* on the coast of Ghana and to determine the chemical composition in order to promote its use as food or fertilizer to improve the livelihood of the coastal communities.

MATERIALS AND METHODS

Study area

Samples (24) collected offshore and onshore at low tide at specific locations along the coast of the Western Region of Ghana delineated into 6 zones (Figure 1).

Identification of *Sargassum*

The Seaweeds samples were identified using keys described by John et al. (2001, 2003). The Brown alga *Sargassum* spp. was identified in all the samples from the 6 zones, whilst the rest of the algae were only identified from zone 6 samples.

Chemical analysis of *Sargassum* spp.

Thirteen chemical parameters were analyzed. These were grouped in two major components; nutritional and toxicological parameters. The nutritional parameters were nitrogen, phosphate, ammonia, nitrate and potassium. The toxicological parameters were copper, zinc, iron, lead, cadmium, mercury, arsenic and chloride.

Preparation of seaweed sample for chemical analysis

Samples were washed under a jet of tap water and rinsed with distilled water to remove any minerals particles and organisms attached to the seaweed.

Principle

Heavy metals in plants are measured in a digest obtained by treating samples with an acid mixture made from concentrated nitric

Figure 1. Map of the study area in the Western Region of Ghana.

acid, concentrated sulphuric acid, and perchloric acid (Anderson and Ingram, 1989; Maiti, 2003).

Analytical procedure

Dried sample weighing about 1.0 g were placed into a 125 ml Erlenmeyer flask which has been previously washed with acid and distilled water. Ten milliliters of Ternary mixture (20 ml $HClO_4$: 500 ml HNO_3: 50 ml H_2SO_4) were added under a fume hood. The contents were thoroughly mixed and heated gently at low to medium heat on a hot plate under a perchloric acid fume hood. Heating was continued until dense white fumes appear (that is, fumes of sulphuric acid). After the mixture was heated strongly for half a minute, it was allowed to cool and 40 to 50 ml distilled water was added, boiled for half a minute on the same plate at medium heat. The solution was then cooled again and filtered using Whatman filter paper (No. 42, 9 cm) and made up to 100 ml in a Pyrex volumetric flask. Make up to the mark with distilled water. The solution was stored for heavy metal determination. Analysis was carried out using an Atomic Absorption Spectrophotometer (AAS 900T). Table 1 shows the various wavelengths used in the analysis.

Table 1. Wavelengths used in the AAS 900T for the determination of each metal.

Parameter	Wavelength
Mercury	253.7
Arsenic	242.8
Cadmium	228.8
Lead	283.3
Iron	248.3
Zinc	213.9
Potassium	766.5
Copper	324.8

RESULTS AND DISCUSSION

Identification of *Sargassum*

The Brown alga *Sargassum* spp. was identified in all the 24 samples from the 6 zones. *Sargassum* spp. identified using physical characteristics (in the identification guide courtesy of Dr. Jim Franks and the University of Southern Mississippi Gulf Coast Research Laboratory, Figure 2b) were not known to occur naturally in the Gulf of Guinea and especially Ghana. These were *S. fluitans* and *S. natans* (Figure 2).

The two identified species of *Sargassum*, namely, *S. fluitans* and *S. natans* are Holopelagic remaining free-floating through their entire life cycle. They reproduce vegetatively and never attach to the sea floor during their life cycle. Thus, they do not need a holdfast, an organ at the base of the seaweed that attaches the weed to a surface. In West Africa, three *Sargassum* spp. have been identified. These are *Sargassum cymosum* C.Agardh 1820 occurring mainly in Serra Leone and Gabon with *Sargassum filipendula* C. Agardh 1824 occurring in

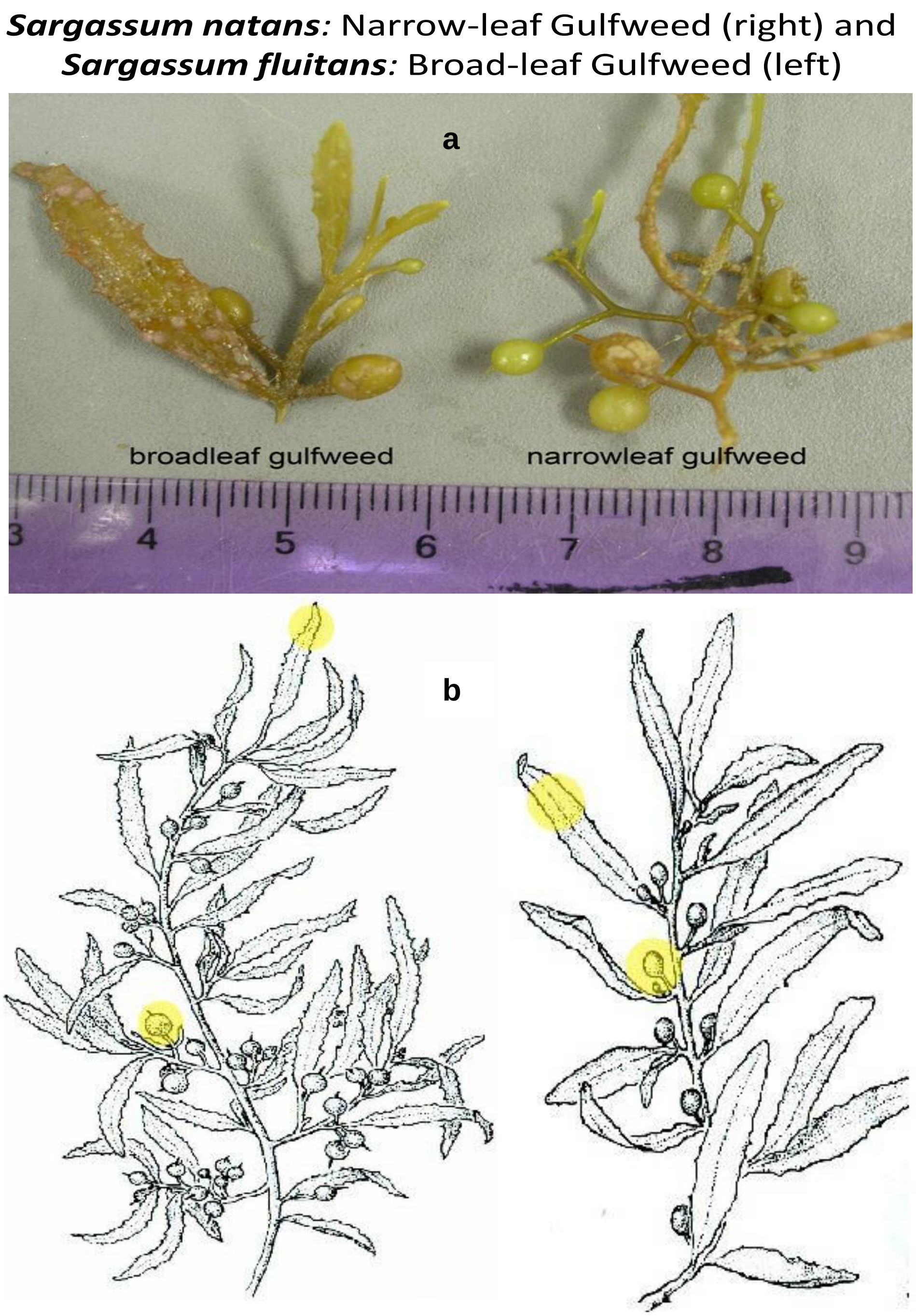

Figure 2. (a) S*argassum fluitans* and *Sargassum natans*; (b) *Sargassum natans* (Pods – usually tipped with spikes or small leaves; Leaves – long-stalked, narrow) and *Sargassum fluitans* (Pods – usually not tipped with spikes or small leaves; Leaves – short-stalked, broad).

Ghana and Gabon, whilst the third *S. vulgare* C.Agardh 1820, the most common, is found from Senegal to Gabon.

As reported in Ghana, only *S. vulgare* found usually growing attached to inshore rocks and *S. filipendula* found usually growing attached under water offshore reefs.

Chemical analysis

The results of the chemical analysis of the *Sargassum* (Tables 2 and 3) were broken down in two broad sections; nutrients and heavy metals. The nutrients are among the elements known as essential nutrients needed for normal plant growth. Essential nutrients must be

Table 2. Concentrations of nutrients (mg/kg) recorded in the Invader *Sargassum* species from the various sampling zones along the coast of the Western Region, Ghana.

Parameter (ppm)	Zone 1 /onshore	Zone 2 /onshore	Zone 2	Zone 2 /onshore	Zone 3 /onshore	Zone 3 /onshore	Zone 3 /onshore	Zone 5	Zone 6 /onshore	Acceptable limits (ppm)
	Half Assini	Egbazo	Assiama	Asunda	Atuabo	Miemia	Axim/Agyan	Africa Beach	Essipon	
Nitrogen (N)	0.67	0.87	0.84	0.95	0.87	1.04	0.62	N/A	0.62	1 to 6
Phosphate $(PO_4)_2$	1.02	1.37	1.53	1.16	0.83	1.43	1.52	N/A	1.55	0.05 to 1
Amonia $(NH_4)_3$	460.8	878.4	568	354.4	734.4	424.8	741	N/A	554.4	1 to 6
Nitrate (NO_3)	208.8	201.6	180	187.2	410	237.6	288	N/A	216	1 to 6
Potassium (K)	2.28	1.88	1.42	0.72	2.48	2.41	1.08	N/A	1.86	0.3 to 6

Table 3. Concentrations of heavy metals (mg/kg) recorded in the Invader *Sargassum* species from the various sampling zones along the coast of the Western Region, Ghana.

Parameter (ppm)	Zone 1 /onshore	Zone 2 /onshore	Zone 2	Zone 2 /onshore	Zone 3 /onshore	Zone 3 /onshore	Zone 3 /onshore	Zone 5	Zone 6 /onshore	Acceptable limits (ppm)
	Half Assini	Egbazo	Assiama	Asunda	Atuabo	Miemia	Axim/Agyan	Africa Beach	Essipon	
Copper (CU)$^{++}$	27	27	28	30	29	36	24	N/A	22	20 to 100
Zinc (Zn)	79	16	37	57	100	44	22	N/A	37	100 to 400
Iron (Fe)$^{++}$	1413	1952	5910	1209	1530	1226	2284	N/A	2550	10 to 100
Lead (Pb)$^{++}$	248	329	169	105	225	335	190	N/A	86	30 to 300
Cadmium (Cd)$^{++}$	102	95	119	78	97	111	98	N/A	80	37
Mercury (Hg)$^{++}$	1	1	1	2	1	1	1	N/A	2	1 to 3
Asemic (As)$^{++}$	27.3	13	17	53.5	53.5	20	36	28.8	24	5 to 20
Chloride (Cl)$^{+}$	1353.2	1240.4	1353.2	225.54	61	1353.2	22.54	N/A	830.14	0.05 to 3

specific and cannot be replaced. A heavy metal is defined as a metallic element which is toxic and has a high density, at low concentrations can excite some biological processes, but at threshold concentrations becomes toxic (He et al., 1998).

Nutrients

The results of nutrient analysis (Figure 3) of the samples showed they contain a low concentration of nitrogen. However, plants utilized nitrogen in the form of nitrate (NO_3) and ammonia (NH_4) which occurred in very high concentration, together with phosphate (Table 2). Potassium a key element for plant growth was relatively high falling within the range expected in plants (0.3 to 6 ppm) (Peters and Laboski, 2011). This will facilitate the potential use of *Sargassum* as an organic fertilizer or manure. Oyesiku and Egunyomi (2014) also recommended the use of *Sargassum* as fertilizer after obtaining a good percentage ratio of N-P-K of 1-10-3. However, further enhancement of nutrient levels by addition of big slurry, chicken droppings or cow dunk will be needed. High nutrient in water bodies are associated mainly with domestic wastes both liquid and solids, industrial pollution, agricultural waste waters including inorganic fertilizer.

The nutrition content and utility of the seaweed

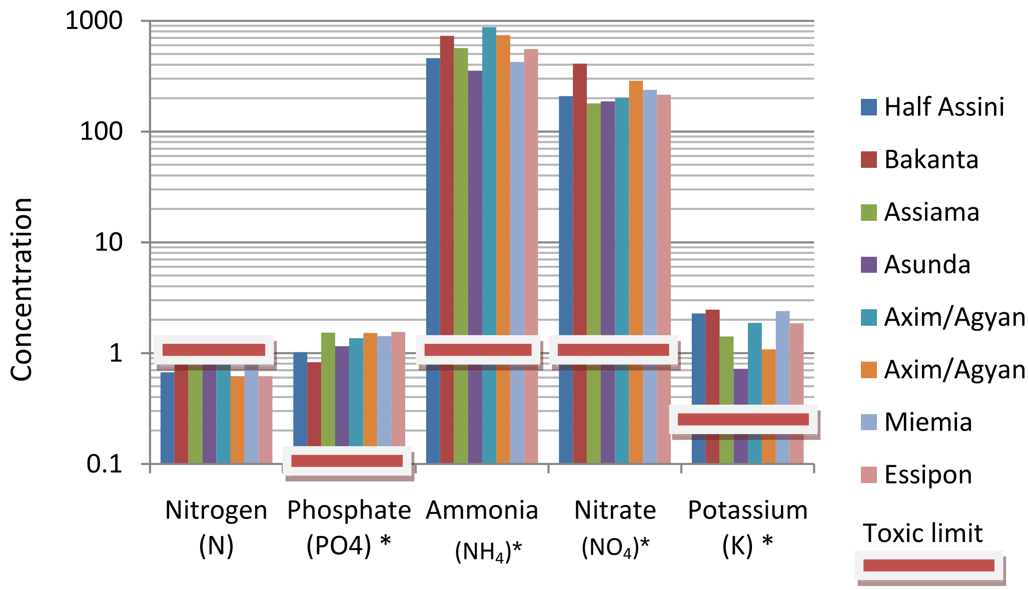

Figure 3. Histogram of the concentrations of nutrients (ppm) measured in the *Sargassun* samples analysed.

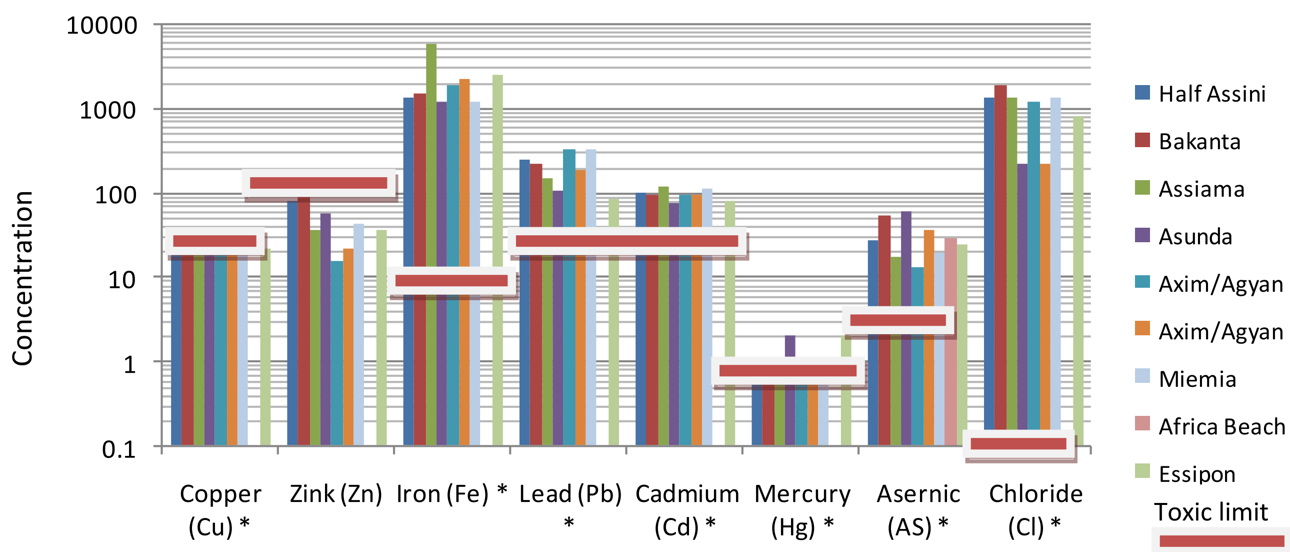

Figure 4. Histogram of the concentrations of heavy metals (ppm) measured in the *Sargassun* samples analysed.

cannot be considered alone without incorporating the results of the heavy metal concentrations found in all the samples evaluated in this study.

Heavy metals

Heavy metals being non-biodegradable can accumulate at various trophic levels through the food chain and can cause human health problems (He et al., 1998). In humans, these metals build up in living tissues and thus increase the dangers they pose by causing physical distress and life threatening illness such as damage to vital body systems ((Sudharsan,et al., 2012). Seaweeds are excellent agents for filtering heavy metals such as zinc, cadmium, copper, nickel and iron from the sea. Seaweeds are able to accumulate these metals from their environment into body cells to as much as 4,000 to 20,000 times more than in the surrounding waters (Sudharsan et al., 2012).

As noted in Figure 4, the concentrations of heavy metals from the evaluated samples are all broadly the same. The minimum acceptable limit of these heavy metals in plants is shown by the red bars. From the analysis, six (Cu, Fe, Pb, Cd, Hg and As) out of the seven heavy metals measured were found to be in the toxic range (Kabata-Pendias, 2001). Only zinc was found to be below the toxic range. Sudharsan et al. (2012) reported that zinc was moderately absorbed by seaweeds and seagrasses. Veroy et al. (1980) explained that the ability for uptake of heavy metals in any species was based on the nature of their cell wall and polysaccharides. Other factors may be due to competition and the ability by the metals to bind with such polysaccharides which has been reported to be preferential (Paskins-Hurlburt et al., 1976). This may explain the low concentration of zinc as compared to the other metals.

Quari (1976) reported that red seaweeds have more ability to uptake these metals when compared to brown and green seaweeds. Heavy metals have implications in both the growth and metabolic activities of plants and humans. Sathya and Balakrishnan (1988) have reported that Cadmium even at very low concentrations can cause physiological disturbance like protein, carbohydrate and pigment concentration. Cadmium levels above 20 ppm in seaweeds have been designated for polluted environment (Lozano et al., 2003). In our current studies, a higher cadmium range of 78 and 119 ppm were recorded across the sampled locations. High Cadmium concentrations have been attributed to influx of domestic sewage and content of local gold bearing rock formations.

According to Al-Abdali et al. (1996), calcium carbonate ($CaCO_3$) in rock formation contains much cadmium impurities. In addition, steel used in port and industrial facilities contain cadmium coatings which can end up in surrounding waters. In a study conducted by Lozano et al. (2003), cadmium was reported to be more concentrated in red and brown seaweed than green seaweed. *Sargassum* is a brown alga and this may explain the high cadmium concentration recorded in the plant in this study.

Copper which also fell within the toxic range is an essential micronutrient in plants but at high concentrations can affect photosynthesis and lead to de-pigmentation as well as depressing growth in plants (Sathya and Balakrishnan, 1988).

Organisms which accumulate contaminants in their tissues can be used to assess the health of coastal environments, including their presence, levels and changes in contaminants. Seaweeds are such organisms which have been used as bio-monitor of heavy metals (Al-Homaidan, 2007; Kamala-Kannan et al., 2008).

It is possible that the sources of Pb, Fe and As all of which fell in the toxic range (Table 3) could be coming from the same source as many studies have shown a strong correlation between these three metals (Santos-Santos et al., 2006). These sources may include paints, dyes, certain fertilizers, metals and pesticides as well as industrial wastes. Combustion of fossil fuels and oil pollution could also account for the high concentrations of these three metals. Nazni and Deepa (2015) recorded high levels of lead in five seaweeds and attributed it to combustion of fossil fuels and oil pollution. The Western Region has for a long time been a hub of the gold industry and the coastal areas are at the terminus of the inland drainage system from renowned mining locations as Prestea, Tarkwa and Obuasi. It is now also the hub of oil exploration and drilling activities and all efforts must be made to thoroughly investigate the sources of these heavy metals so as to be clear as to where they originate.

Most heavy metals, especially arsenic and lead are carcinogenic and are capable of causing skin, lung, liver and bladder cancers. Low levels of arsenic are suspected to cause nausea and vomiting, damage to blood vessels and sensations (pin and needles) in the hands and feet. Exposure to high levels of lead can lead to damage of the kidney and brain. In pregnant women, it can lead to miscarriages and in men can damage the organ responsible for sperm production (Centre for Hazardous Substance Research, Kansas State University, Issue 15th March, 2009).

Iron recorded the highest concentration of 5,910 ppm at Essiama (Zone 2) (Figure 4). The air dried sample was taken from a wire fence, which is another likely source of the iron. Ali et al. (2011) had earlier also reported iron to be the highest in their study of seaweed species in the Strait of Hormuz, Iran. As mentioned earlier, accumulation of metals in seaweed depends on the type of polysaccharides in the seaweed and since various elements have different electronegativity, these can affect the type of metals to be taken actively, hence, the high uptake of iron by *Sargassum*.

Studies by Abdallah and Abdallah (2008), reported that variation of concentrations of metals in seaweed species from different sampling locations may be related not only to different metal levels, but also to factors such as tidal range, temperature, salinity regimes, dissolved nutrients, tissue type, age of plants, its nutritional history and the geological structure of the study area.

In this study, the highest concentrations of copper, lead and cadmium were all recorded in zones 2 and 3 (Table 3 and Figure 4) and Miemia (an important tourists hub situated in a cove west of Cape). Three points has the highest concentrations of all three metals out of all the locations sampled. Although, zones 2 and 3 stand out for having the highest toxic levels of these three metals, it should be noted that insufficient sampling of zones 4, 5 and 6 prevents further conclusions to be drawn as to whether the highest observed toxicity is focused on the western half of the study area, although intensive mining and industrial activity is associated with this area. Ali et al. (2011) recorded similar trends in an area with intense human and industrial activities. Gold mining is very much associated with these types of heavy metal load in the water which can travel down river into the sea. Seabed trawling by offshore fishing vessels may lead to agitation and mixing of the sediments with the overlaying waters, which increase the heavy metals load in the water and hence make them available for uptake by the seaweed for example the *Sargassum*.

Conflict of interests

The authors have not declared any conflict of interest.

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