Comparison of Arsenic Adsorption Efficiency between Macroalgae and Seagrass on the Shorelines of Jazan Province, Saudi Arabia

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The aim of this study was to measure consequences of the arsenic pollution released from a sewage treatment plant into the seawater in Jazan province in the southwest of Saudi Arabia. The impact of the release of arsenic on the ecosystem is the adsorption of arsenic by sea plants. To do so, samples were collected alongside a distance of seven kilometers from the treatment plant. The algae samples: *Sargassum* sp., *Cladophora* sp., and *seagrasses*: *Halodule uninervis* and *Cymodocea rotunda* were digested in nitric acid, and the assays of arsenic levels were taken by ICP-AES according to EPA methods. The results showed that algae are more efficient than seagrass with absorbing arsenic. Also, the treatment plant was not the only source of arsenic contamination, as ships and boats were adding more arsenic to the ecosystem.

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Keywords: Adsorption; Arsenic; Macroalgae; Seagrass; Sewage treatment; Pollution; Boats; Bioremediation; Flouting paints; Alginate acids and fucoidans

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INTRODUCTION

Marine ecosystems have been a sink of contaminants that are released by anthropogenic activities. Trace elements, for example, could break through soil to the sea (Zaho *et al.* 2016). Heavy metals can reach sea ecosystems through both surface and subsurface water (Monory *et al.* 2014). Pollutants also can be transported by the air to the aquatics (Gajbhiye *et al.* 2016). The arsenic metalloid is one of several pollutants that can move to different environments including marine ecosystems by taking similar trajectories and increase above the permissible level 0.01 mg/L (Kumari *et al.* 2017). A study by Abadi *et al.* (2018) in the Caspian Sea shows that several contaminants including arsenic reach Gorgan Bay that borders Caspian Sea and that these accumulate as a result of being near agricultural, industrial, and commercial centers. Arsenic in marine environments occurs in different inorganic and organic chemical forms such as arsenate, arsenite, and methylated arsenic (Wang *et al.* 2022).

In general, arsenic is toxic to plants. This is especially the case for As-sensitive plants, for which it causes root growth inhibition (leading to death), reactive oxygen species generation, energy flow disruption (since it replaces phosphorus in energy production in plant cells), chlorophyll contents and photosynthesis rate inhibition, and photophysical distortions (Meharg and Hartley-Whitaker 2002; Iriel *et al.* 2015). Aquatic animals are exposed to arsenic, which results in arsenic poisonous effects. Fish cells exposed to sodium arsenite are affected with cytotoxicity (Seok *et al.* 2007). In addition, the exposure to As is associated with oxidative stress and a decrease of antioxidant enzymes activities in fish, such as *Clarias batrachus* and in polychaete *Laeonereis acuta* (Ventura-Lima *et al.* 2007). Antioxidant responses have been shown in zebrafish *Danio rerio* upon exposure to arsenic for two days (Ventura-Lima *et al.* 2009).

Bioremediation using economically feasible and environmentally friendly means has been employed in efforts to remove pollutants from water. Thus, to reach such a goal, bio-removal methods have been shown to be promising for the removal of heavy metals from water (Kumar *et al.* 2015; Gonçalves 2021; Ahmed *et al.* 2022). Aquatic plants have shown themselves to be effective adsorptive agents for heavy metals in water (Dong and Yung 2022). Both marine and freshwater algae were investigated in wastewater polluted with Cu, Pb, Zn and Cd, and it was found that both types of algae are effective for heavy metals mitigation (Utomo *et al.* 2016). It has been reported that some cyanobacteria such as *N. linckia* and *Oscillatoria* spp. are able to remove Zn and Cd from water (El-Enany and Issa 2000; Azizi *et al.* 2012). Not only is microalgae useful for toxicants removal, but also macroalgae is practical. *Sargassum hystrix*, *S. natans*, and *Padina pavonia* were found effective in removing Pb from aqueous environments, with the priority to *Sargassum* sp. (Jalali *et al*. 2002; Siyal *et al.* 2018). The algae *Sargassum* sp. was found to be effective for absorbing each of Cr, Pb, and Cd (Yu *et al.* 2014). Therefore, these plants can be used as indications of metal(loids) contaminated environments. The aim of the current study was to measure the arsenic contamination in Jazan shorelines. At the same time, the distribution of metal pollutants in the plants was used as evidence to look for the source of the contamination. The study examined two major groups of marine plants, macroalgae and seagrasses, and compares them regarding their storage of arsenic.

EXPERIMENTAL

Samples Collection

The samples of macroalgae and seagrasses were collected near a sewage treatment plant on the shoreline of Jazan province in the Red Sea, Southwestern Saudi Arabia. The sampling was taken at different distances from the plant, shown in Table 1. The distance from treatment plant to the last point was divided into eight sampling points, and the total distance was eight kilometers. Then, sampling was randomly chosen from those points, as shown in Tables 1 and 2. Sampling was completed in March 2022.

Table 1. Samples of Algae and Distances from Treatment Plant

Sample No.	Distance from the Treatment Plant (km)	Species
1	2	*Sargassum* sp.
2	2	*Sargassum* sp.
3	4	*Sargassum* sp.
4	4	*Sargassum* sp.
5	7	*Sargassum* sp.
6	7	*Sargassum* sp.
7	2	*Cladophora* sp.
8	2	*Cladophora* sp.
9	7	*Cladophora* sp.
10	7	*Cladophora* sp.

Table 2. Samples of Seagrasses and Distances from Treatment Plant

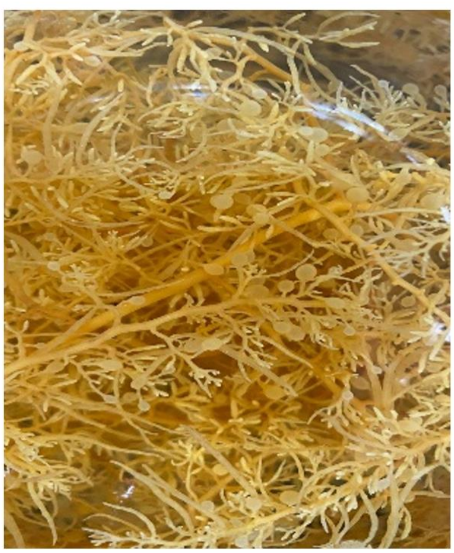
Sample No.	Distance from the Treatment Plant (km)	Species
1	4	*Halodule uninervis*
2	4	*Halodule uninervis*
4	5	*Halodule uninervis*
5	5	*Halodule uninervis*
6	7	*Halodule uninervis*
7	7	*Halodule uninervis*
8	5	*Cymodocea rotunda*
9	5	*Cymodocea rotunda*

Samples Identification

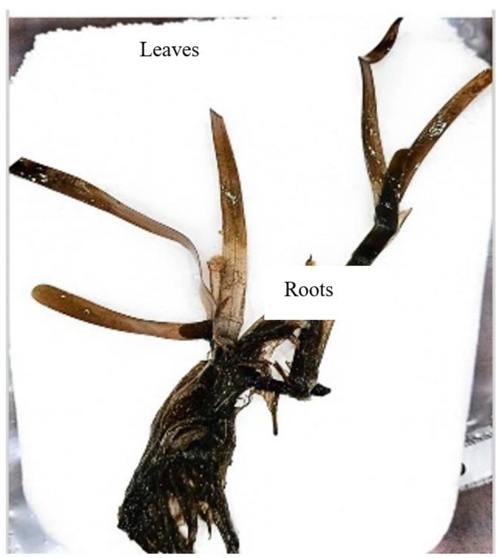
Both macroalgae and seagrasses were identified based on the taxonomic keys, and voucher specimens were deposited in the Jazan University Herbarium. Algae is characterized as a non-vascular, non-flowering, and delicate plant, whereas the sea grasses are vascular, flowering, and resilient plants (Table 3).

Table 3. Morphological and Anatomical Differences between Macroalgae and Seagrasses

Macroalgae	Seagrasses
Not differentiated into root, stem, and leaves	Well-demarked root, stem, and leaves
Non-vascular plants	Vascular plants
Flowers are absent Plant body is soft and delicate	Flowers present Plants are strong



a. *Sargassum* sp.



b. *Cymodocea* sp.

Samples Preparation

The samples randomly collected from the area were carefully and deeply washed with tap water, then rinsed with deionized water. After that, the samples were marked and placed in an oven at 40 °C until the weights of each sample had been stable.

Chemical Analysis

For acid digestion, 20% of each sample was taken to be powdered. The grinder was cleaned with alcohol wipes after each sample to avoid mixing and cross-contamination. According to ICP-AES (Method 3050B), one gram of the dry weight (DR) was taken from each sample into a tube, then concentrated nitric acid (65% HNO_3) (2.5 mL conc.) and 10 mL of concentrated hydrochloric acid (pure 35 to 38% HCL) (7.5 mL conc.) were added to the sample. Then, the filtration process was carried out, in which the samples were filtered using Filter Paper 40 Ashless Diameter of 125 mm. For each sample, the filter was washed with 5 mL of hot HCl and 20 mL of reagent water. The solution was placed back into a tube with 5 mL of HCl. Three replicates per each sample were taken, and the averages were calculated. Quality assurance was required for the lab where blank tubes were prepared, a standard for arsenic used (catalog No. 01969-100ML-F, Sigma Aldrich), and duplicate QC digests were made using certified reference material (Apple leaves NIST 1515).

RESULTS

The average values of arsenic in the analyzed marine plants are presented in Table 4. The important result is that algae accumulated more arsenic than that of grass.

Table 4. Average Values of Arsenic (ppm) in Both Groups of Algae and Seagrass

Sample No.	Distance	Marine Plant Species	Average as Value (ppm)/DW	St. Deviation
1	2	*Sargassum* sp.	3.07	0.98
2	2	*Sargassum* sp.	2.75	0.11
3	4	*Sargassum* sp.	2.83	0.01
4	4	*Sargassum* sp.	2.72	0.05
5	7	*Sargassum* sp.	5.35	1.3
6	7	*Sargassum* sp.	5.06	0.17
7	2	*Cladophora* sp.	2.16	0.89
8	2	*Cladophora* sp.	2.35	0.09
9	7	*Cladophora* sp.	4.96	1.01
10	7	*Cladophora* sp.	2.84	0.7
1	4	*Halodule* sp.	0.27	0.09
2	4	*Halodule* sp.	0.21	0.07
4	5	*Halodule* sp	0.16	0.04
5	5	*Halodule* sp.	0.2	0.02
6	7	*Halodule* sp.	1.02	0.41
7	7	*Halodule* sp.	1.33	0.15
8	5	*Cymodocea* sp.	0.17	0.58
9	5	*Cymodocea* sp.	0.17	0.05

For *Sargassum* sp, and *Halodule* sp, the average values of arsenic seemed to increase as the distance from the plant treatment increased. However, *Cladophora* sp and *Cymodocea* sp showed no clear pattern.

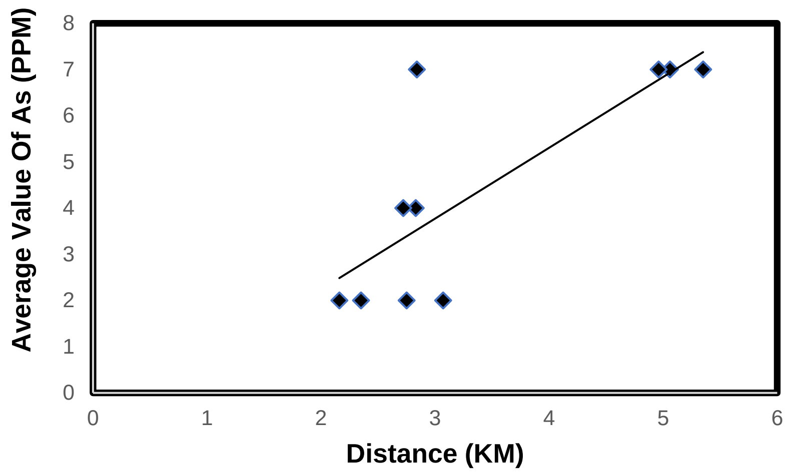


Fig. 1. The average value of arsenic in algae in relation to the distance from the sewage treatment plants. It seems that the average value of As increased as the distance from the treatment plant increased (r = 0.78, p = 0.006)

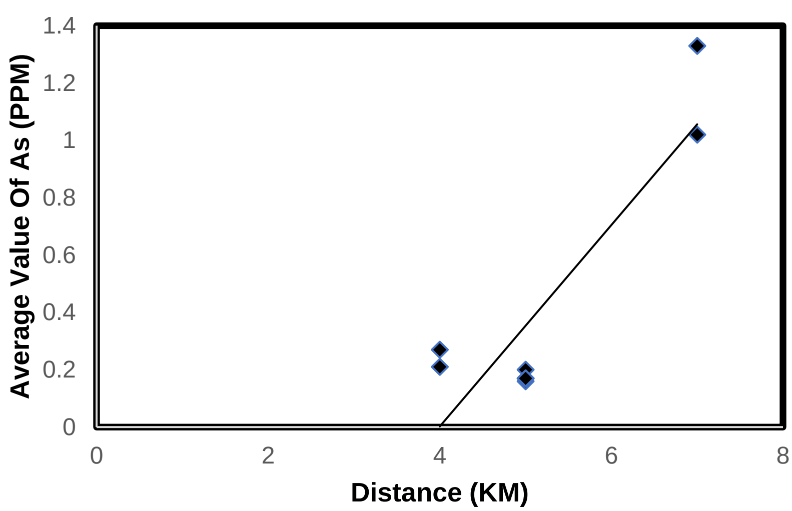


Fig. 2. The average value of arsenic in seagrass in relation to the distance from the sewage treatment plants. It seems that the average value of As increased as the distance from the treatment plant increased (r = 0.88, p = 0.003)

DISCUSSION

Sewage water is a source of arsenic (Tavares *et al.* 2012), and that is why sea plants in this study were found with arsenic in their tissues. Macroalgae and seaweeds are sources of both organic and inorganic arsenic such as arsenite, arsenate, dimethylarsinic acid, monomethylarsonic acid, and arsenocholine. The toxicity has been found to increase with concentration in its various inorganic forms (Ma *et al.* 2018)

The comparison between the two types of plants shows that algae in this study adsorbed more arsenic than grasses. The behavior of algae in collecting more arsenic might be related to specific physiological aspects of algae, as shown in Table 4. It was found that in the spring season, algae regulate an increasing uptake of phosphorus, which synchronously regulate the uptake of arsenic at high levels, since the absorption of both elements is correlated (Hellweger *et al.* 2003). However, that could be a physiological aspect of seagrasses as well, since phosphorus is required for most plants.

Both *Sargassum* sp. and *Cladophora* sp. had the highest arsenic values of 5.35 and 4.96, respectively, as listed in Table 4. The increase of arsenic contents in the algae tissues can be attributed to the existence of more than one type of binding sites of arsenic by the algae tissues (Shigeki *et al.* 1984). In a previous study, Sargassum was found with a high arsenic uptake capacity, since it has high contents of alginate acids and fucoidans in the cell wall structures (Saldarriaga-Hernandez *et al.* 2020). Fucoidans is a type of polysaccharide with structures of high portions of L-fucose and sulfate ester groups (Li *et al.* 2008). Both the acid and the polysaccharide in brown algae are responsible for the high capability of *Sargassum* to be a strong absorbent of heavy metals in water (Ortiz-Calderon *et al.* 2017). *Cladophora* sp. is a green alga, but it seems to take up arsenic as much as *Sargassum* does, as shown in Table 4. It might have the same biological structure in the cell wall that enables it to absorb arsenic at high percentages.

It was expected that the arsenic contents in the plants would increase as the distance from the sewage plant decreased. However, it seems that the contents of arsenic increased in plants as the distance from the treatment plant increased, as shown in Figs. 1 and 2. The concentrations of arsenic in the plants at the 7 km distance from the treatment plant was almost double that of 2 km for each of *Sargassum* sp., *Cladophora* sp., and *Halodule* sp. Thus, there must be another arsenic source than the sewage treatment plant. The area, which is called Marjan salva beach, has been used for the anchorage of ships. Thus, the source of arsenic in the area must be either from 1) the boats themselves, 2) from the terrestrial areas, or 3) from both sources together.

If the source of arsenic is terrestrial, then the chemical contaminants and trace elements may be driven from the terrestrial neighboring areas to the shorelines and rapidly deposited into the sediment rocks (Zhao et al., 2016), then extracted and dispersed in the water by heavy boating (Kennish 2002).

Another suggestion is that the materials used in boat manufacturing are a source of arsenic contamination, such as antifouling paints (Ivče *et al.* 2020). Therefore, the source of the arsenic within a 7-kilometer distance seems to be due to ship manufacturing materials, where those materials are released into the water by the force of erosion by water movement around the boats' surfaces.

Therefore, the high values of arsenic in this sampling point could be due to the following: accumulative amounts of arsenic raised by boating mechanical pressure on sediment rocks; arsenic originating from sewage treatment plants; and the chemical structure of boats' manufacturing materials.

CONCLUSIONS

1. The contamination by arsenic on shorelines could come from several sources, and the awareness of such risk should be increased. The community must hold more monitoring and assessment efforts of shorelines.
2. Boating manufacturing and maintenance operations should be evaluated for the release of paint materials. Efforts are needed to develop environmentally friendly surface treatments for boats, and such treatments need to pass through more restrictive regulations.
3. Algae are more efficient in accumulating arsenic in their tissues than grass. The difference can be explained based on their specific biological structure that allows for more physiological efficiency in accumulating arsenic. Thus, *Sargassum* sp. and *Cladophora* sp. can be utilized in aquatic bioremediation activities. Specifically, they can be utilized for more stabilization of arsenic that is released into the shorelines.

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