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Green Algae as Bioindicators of Heavy Metal Pollution in Wadi Hanifah Stream, Riyadh, Saudi Arabia

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Abstract: Anthropogenic activities around the main stream of Wadi Hanifah may lead to a considerable increase in the heavy metal loading of the stream. The two filamentous green algae *Enteromorpha intestinalis* (Linnaeus) Nees and *Cladophora glomerata* (Linnaeus) Kutzing were collected from three sites along the valley and used to determine the heavy metal concentrations in the main stream. The dried algal samples were digested using appropriate acids and the concentrations of manganese (Mn), copper (Cu), Zinc (Zn), Arsenic (As), cadmium (Cd) and lead (Pb) were measured in the aliquot samples using Inductively Coupled plasma-Optical Emission spectrometer (ICP-OES). High burden of manganese, copper and arsenic were detected at all sites indicating a high degree of pollution by these elements. The levels of zinc, cadmium and lead were within the expected limits for uncontaminated areas. *E. intestinalis* could be used as an excellent indicator for manganese, zinc and arsenic pollution, whereas *C. glomerata* may be used as an excellent indicator for copper, cadmium and lead pollution in this area. The stream runs through the city of Riyadh and serious efforts should be considered to decrease the heavy metal levels in this fragile and valuable habitat.

Key words: Accumulation · Heavy metals · Macroalgae · Freshwaters · Saudi Arabia

INTRODUCTION

Macroalgae have been used extensively to measure heavy metal pollution in freshwater and marine environments throughout the world (e.g. [1-5]. They are used as bioindicators because of their distribution, size, longevity, presence at pollution sites, ability to accumulate metals to a satisfactory degree and ease of identification [1,4,6]. It is preferred to measure heavy metal levels in bioindicators organisms rather than measuring the concentrations in water and/or sediment samples [7,6].

In recent years, several species of the green algae *Enteromorpha* and/or *Cladophora* have been utilized to measure heavy metal levels in many parts of the world. In Europe, for example, many studies have been conducted using these two species as bioindicators of heavy metal contamination. The European countries include Bulgaria [8], Croatia [9], Greece [10], Ireland [6], Italy [11], Poland [12], Spain [13], Turkey [7] and United Kingdom [14]. Other parts of the world include, for example, Argentina [15], Australia [16], Canada [17] and New Zealand [18].

In Saudi Arabia, three studies only have been published about the accumulation of heavy metals by green algae [19] used several species of green, brown and red algae to measure many heavy metal levels in the Saudi coast of the Red Sea. Recently, [20] used the green algae *Chaetomorpha aerea*, *Enteromorpha clathrata* and *Ulva lactuca* to measure the levels of iron, nickel, copper, zinc, cadmium and lead in three sites on the Saudi coast of the Arabian Gulf. The levels of nickel were determined in twelve species of green, brown and red algae collected from Dammam area on the Saudi coast of the Arabian Gulf [21].

Luxuriant growth of green algae has been reported from different freshwater bodies in Saudi Arabia [22,23]. This study is the first one to use the green algae of the inland waters of Saudi Arabia as indicators of heavy metal pollution. The main objective of this investigation is to measure the levels of manganese, copper, zinc, arsenic, cadmium and lead in the filamentous green algae *E. intestinalis* and *C. glomerata* of Wadi Hanifah main stream and whether or not these two species can be used as heavy metal indicators in this part of the world.

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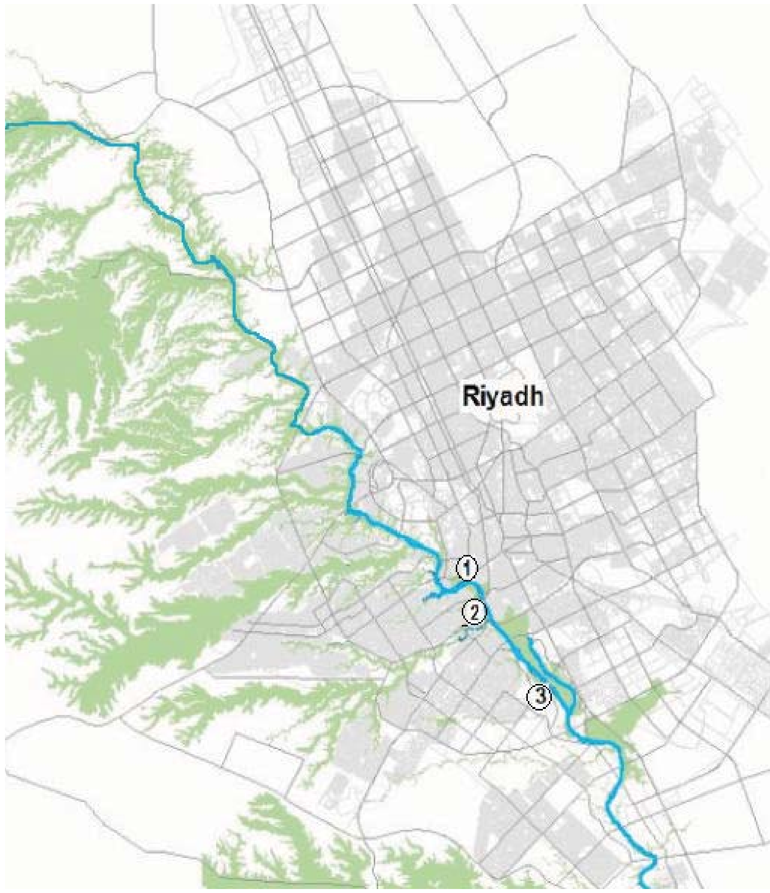

Fig. 1: Map of Wadi Hanifah showing sampling sites

MATERIALS AND METHODS

Study Area: Wadi Hanifah is one of the most important natural landmarks in the central region of Saudi Arabia. The valley runs for a length of 120 kilometers descending from the town of Sodoos in the northwest of Riyadh to the open desert in southeast of the capital. It covers a drainage run-off area of more than 4,000 square kilometers. In addition to the capital Riyadh, several towns and villages lie along the valley and they include Oyainah, Jobailah, Diriyah, Irqah and Al-Hayir. A discharge of 400,000-600,000 cubic meters of ground water, rainwater and industrial waste and domestic sewage water reaches the valley every day. The continuous flow of water has created a unique natural habitat that supported a luxuriant growth of algae and other aquatic plants.

Sampling Procedure: Algal and water samples were collected in triplicates from three sites along the water stream within the city of Riyadh (Fig. 1) using 5 liter polyethylene acid-washed bottles during the months of February and March of 2009. The samples were transferred to the laboratory in refrigerated boxes where they cleaned with distilled water and identified. They were air dried at 90°C and then used in the analysis.

Analytical Methods: Exact weights of each alga (500 mg dry weight) were placed into acid washed digestion tubes. Twenty five ml of concentrated analar grade nitric acid (BDH, England) was added to each tube and the contents were evaporated to near dryness. After cooling, 20 ml of double distilled deionized water was added to each tube and the contents were filtered through 0.45 µm Millipore filters. The solutions were then transferred to 25 ml acid washed volumetric flasks and the volumes were completed to 25 ml with double distilled deionized water [18, 10, 21]. The concentrations of manganese, copper, zinc, arsenic, cadmium and lead were measured in the aliquots of algae using Inductively Coupled Plasma-Optical Emission Spectrometer (Optima 4300 DV).

Statistical Analysis: One-way analysis of variance (ANOVA) was used to evaluate the inter-specific significance between algal metal accumulation and between metal levels in different sites with p= 0.05.

RESULTS AND DISCUSSION

Several species of filamentous green algae were collected during this study and *E. intestinalis* and *C. glomerata* were chosen to conduct this investigation due to the fact that they were collected from all sites during all field expeditions. Their proliferation is probably attributed to the elevated levels of nutrients which prevailed in the stream and to the high concentrations of total dissolved solids (TDS) which varied between 1,250 and 2,714 mg L^{-1} during the course of this study (Al-Homaidan, unpublished data). The species of *Enteromorpha* and *Cladophora* are known to grow in freshwaters and marine habitats [17, 11, 14, 12, 24] and they are used all over the world as indicators of heavy metal pollution in both habitats [1, 10, 13, 7, 16, 6, 20, 8].

The mean concentrations of all metals and their ranges in *E. intestinalis* and *C. glomerata* are presented in Tables 1 and 2. The average concentrations of manganese in *E. intestinalis* (regardless of sampling site) ranged from 84.49 to 339.29 µg g^{-1} dry weight (Table 1). For *C. glomerata* these values varied between 100.25 and 259.33 µg g^{-1} dry weight (Table 2). Such high concentrations are not usually encountered in these algae in unpolluted waters and much lower values have been reported by other workers from different countries (e.g. [13, 7, 12, 8]. These high concentrations of manganese indicate that there is a high degree of pollution by this element in this area and domestic sewage, which is discharged to the stream, is probably the main source of this problem [10] have attributed the high levels of manganese in the algae of the Thermaikos gulf, Greece to the discharge of wastewater from houses to the waters of the gulf.

The average concentrations of copper in the two algae varied between 28.23 and 71.76 µg g^{-1} dry weight (Tables 1 and 2). The highest average value of this metal in *E. intestinalis* (44.65 µg g^{-1} dry weight) was lower than the lowest value in *C. glomerata* (55.06 µg g^{-1} dry weight). These high levels of copper are much higher than what is expected for uncontaminated freshwaters [25] reported the range 10-100 µg g^{-1} dry weight as typical of attached plant species inhabiting polluted waters. Similarly, [10] have considered that a range of 20 to 70 µg g^{-1} dry weight in *Enteromorpha* as a characteristic of contaminated sites. Several sources of pollution are expected for the high levels of copper in Wadi Hanifah stream. These include the excessive use of algicides (e.g. copper sulphate) to control algal growth in the stream. Cu-based fungicides are also used extensively to control fungal pathogens in the agricultural areas around the wadi.In addition to this and as in the case of manganese, domestic sewage is probably a main source of copper pollution in the area.

Table 1: Mean ±SD (range in parentheses) of heavy metal concentrations in the thalli of *E. intestinalis* in µg g^{-1} dry weight

	Sites		
Metal	1	2	3
Mn	267.48 ±230.97 (121.95 - 533.80)	339.29 ±122.52 (224.37 - 468.20)	84.49 ±60.68 (15.25 - 128.43)
Cu	28.23 ±24.64 (5.67 - 54.53)	44.65 ±33.47 (12.13 - 79.00)	33.82 ±13.50 (21.80 - 48.43)
Zn	30.66 ±6.24 (23.50 - 34.90)	35.37 ±3.42 (32.28 - 39.05)	24.94 ±2.50 (22.80 - 27.68)
As	54.10 ±12.78 (39.55 - 63.51)	69.29 ±19.37 (54.92 - 91.32)	49.14 ±8.29 (39.87 - 55.83)
Cd	0.25 ±0.33 (0.05 - 0.63)	0.64 ±0.72 (0.20 - 1.48)	0.33 ±0.20 (0.15 - 0.55)
Pb	2.48 ±1.39 (1.18 - 3.95)	3.77 ±4.15 (1.02 - 8.55)	4.58 ±1.14 (3.52 - 5.78)

Table 2: Mean ±SD (range in parentheses) of heavy metal concentrations in the thalli of *C. glomerata* in µg g^{-1} dry weight

	Sites		
Metal	1	2	3
Mn	259.33 ±175.93 (155.17 - 462.45)	210.79 ±109.68 (138.28 - 336.97)	100.25 ±45.99 (47.15 - 127.38)
Cu	71.76 ±36.15 (30.02 - 92.82)	66.48 ±26.18 (44.75 - 95.55)	55.06 ±72.07 (13.18 - 138.28)
Zn	23.54 ±8.75 (14.90 - 32.40)	24.12 ±12.34 (14.32 - 37.98)	23.82 ±9.51 (17.77 - 34.78)
As	8.13 ±8.99 (2.32 - 18.48)	7.71 ±5.15 (4.03 - 13.60)	3.38 ±0.54 (2.80 - 3.88)
Cd	0.61 ±0.33 (0.33 - 0.97)	0.81 ±0.57 (0.15 - 1.18)	1.08 ±0.56 (0.68 - 1.72)
Pb	6.15 ±3.28 (2.40 - 8.48)	6.14 ±2.82 (3.57 - 9.16)	4.30 ±2.60 (1.40 - 6.42)

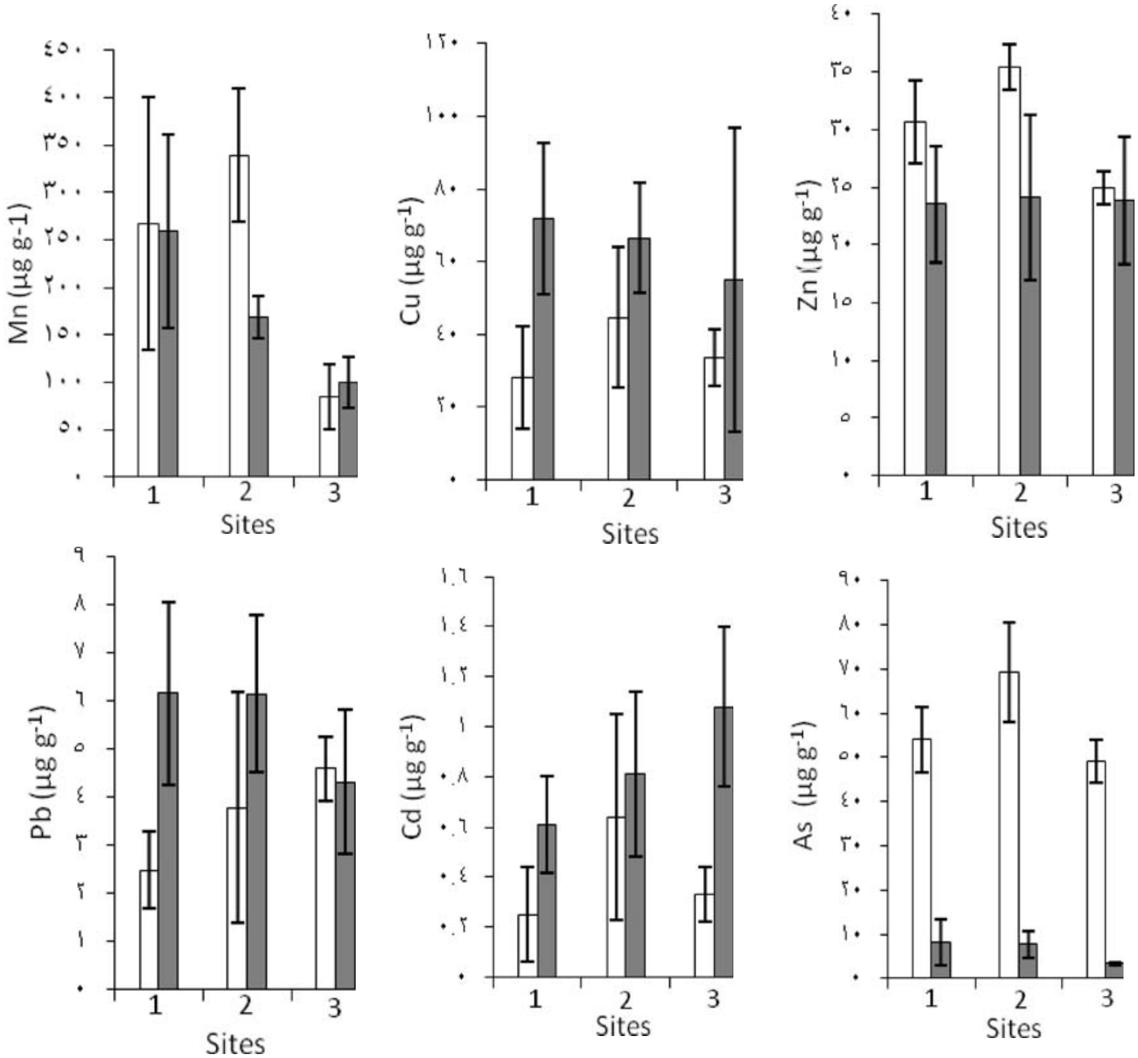

Fig. 2: Mean concentrations of metals in the thalli of *E. intestinalis* (☐) and *C. glomerata* (■) in µg g^{-1} dry weight; bars represent the standard error

Zinc mean values in the two green algae of Wadi Hanifah stream ranged from 23.54 and 35.37 µg g^{-1} dry weight (Tables 1 and 2). The average concentrations of this metal in *E. intestinalis* and *C. glomerata* were 30.32 and 23.83 µg g^{-1} dry weight, respectively. These levels are within the expected limits for uncontaminated freshwaters. It has been reported that the average zinc residues in plants collected from polluted waters are within the range of 100 to 500 µg g^{-1} dry weight [25]. In other studies, it has been indicated that the values for *Enteromorpha* in contaminated waters varied between 95 and 130 µg g^{-1} dry weight [26,18,10]. By comparing the findings of this study with other investigations it can be said that there is no zinc pollution in the study area.

The mean concentrations found for Arsenic in *E. intestinalis* varied between 49.14 and 69.29 µg g^{-1} dry weight with an average of 57.51 µg g^{-1} dry weight (Table 1). Much lower concentrations were detected for *C. glomerata* and they did not exceed 13.60 µg g^{-1} dry weight (Table 2). There is a very limited number of studies about the ability of these two algae to accumulate arsenic. [16], have measured the concentration of this metal in *Enteromorpha* sp. and *Cladophora* sp. which were collected from an aquaculture pond in Australia. They reported concentrations ranging from 5.43 to 10.73 µg g^{-1} dry weight for the former species and 3.06 and 3.94 µg g^{-1} gdry weight for the latter one. A mean concentration of 7±2 µg g^{-1} dry weight was reported in the green alga *Ulva rigida* which was collected from the Venice Lagoon, Italy [27]. By comparing the findings of this study with the results of the other limited studies we can conclude that there is a high degree of arsenic pollution in the stream. Several sources of contamination are expected and they include pesticides, herbicides and fungicides which are widely used in the area. In addition, domestic sludge and nearby tannery may contribute to this problem.

The average concentrations of cadmium ranged between 0.25 and o.64 μg g^{-1} dry weight for *E. intestinalis* (Table 1). For *C. glomerata* these values varied between 0.61 and 1.08 μg g^{-1} dry weight (Table 2). The mean values of this metal (regardless of sites) were 0.41 μg g^{-1} dry weight for the former and 0.83 μg g-g dry weight for the latter. It has been reported that algal samples containing lower than 2 μg g^{-1} dry weight can be considered not polluted [28]. In three brown algae collected from unpolluted area of the United Kingdom, cadmium concentrations varied between 0.15 and 0.43 μg g^{-1} dry weight (Moore and Ramamoorthy, 1984). In brief, we do not think there is a cadmium pollution problem in the study area.

The mean concentrations detected for lead for *E. intestinalis* were from 2.48 to 4.58 μg g^{-1} dry weight (Table 1). For *C. glomerata* they fluctuate between 4.30 and 6.15 μg g^{-1} dry weight (Table 2). A concentration of <7 μg g^{-1} dry weight has been reported for *Enteromorpha* from the uncontaminated Gulf San Jorge, Argentina [15]. Very low concentrations of this element (<3 μg g^{-1} dry weight) were also reported for several green, red and brown algae from a low polluted station at the Turkish Coast of the Black Sea [7]. A concentration of < 10 μg g^{-1} dry weight has been considered as a border line between contaminated and uncontaminated species [28]. We can conclude that the lead contents of the algal specimen studied were within the expected limits of uncontaminated areas.

Finally, a comparison between the ability of *E. intestinalis* and *C. glomerata* to accumulate the different metals at all sites is shown at Fig. 2. From this figure we can say that both species can be used successfully to assess the heavy metal levels in freshwater and brackish water environments. *E. intestinalis* was an excellent indicator for manganese, zinc and arsenic levels, whereas *C. glomerata* was an excellent indicator for copper, cadmium and lead concentrations. The mean metal levels with standard errors in each alga at all sites are shown in Fig. 2. Interspecific comparisons between metal levels in the three studied sites showed, in most cases, significant differences between these sites indicating that there are many sources of pollution in the area.

CONCLUSIONS

High levels of manganese, copper and arsenic were found in the two algae at all sites. Anthropogenic discharges, including domestic, industrial and agricultural discharges are probably responsible for this problem. The levels of zinc, cadmium and lead were within the expected limits of uncontaminated waters. Both algae can be used as bioindicators of heavy metal pollution in the area. *E. intestinalis* can be used as a good indicator of manganese, zinc and arsenic pollution, whereas *C. glomerata* can be utilized as an indicator of copper, cadmium and lead contamination. Wadi Hanifah stream runs through the city of Riyadh and considerable efforts must be performed to reduce the contamination levels in this unique and fragile habitats.

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