

A Preliminary Exploration of Heavy Metal Contamination within *Avicennia marina* in the United Arab Emirates

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Abstract

Mangrove forests within the United Arab Emirates are being heavily exposed to anthropogenic contaminants due to pollution and urbanization. However, there is very limited research pertaining to this subject and the extent to which such mangroves can take up and store heavy metals is still unclear. In this research study, the concentrations of zinc, copper, lead and chromium in the grey mangrove *Avicennia marina* were measured. Samples were taken from five different sites within the capital city and tested using Flame Atomic Absorption Spectrophotometer (FAAS) for the presence of heavy metals. The total concentrations of selected heavy metals in the mangrove leaves were compared to the general heavy metal concentration for plant. The general heavy metal concentration for plant was based on the heavy metals concentrations measured in the mature leaf tissue of various plant species. The comparison showed that the total concentrations did not exceed the general concentration. Nevertheless, the fact that the leaves which are the least bioaccumulative part of the mangrove warrants further investigation over a longer period of time and sampling from roots and sediments to determine whether heavy metal contamination within the mangrove ecosystem is a possibility.

Keywords: Heavy metal contamination; *Avicennia marina*; Mangrove; Anthropogenic

Introduction

A rising level of heavy metals has been reported in mangrove sediment biotas globally. This could be indicative of the high level of polluting activities caused by human influence through anthropogenic contaminants [1-8]. As heavy metals cannot be biologically degraded, they get transferred and eventually concentrated into mangrove tissues from sediments, posing a threat to this plant and other organisms within the same ecosystem through food chain interaction [9,10]. Mangroves play a crucial role in maintaining a dynamic ecological balance in coastal and marine environments [1-8]. For instance, a mangrove habitat provides breeding and nursery grounds for many aquatic species and contributes to the stabilization of adjacent coastal landforms against cyclones and tidal waves [2]. Worldwide, there are 59 different mangrove species with one only *Avicennia marina*; grey mangrove; being endemic to the United Arab Emirates (UAE) [3]. This cosmopolitan species which grows through many coastal areas, such as Eastern Africa, the Arabian Gulf, and Indo-Melanesia is characterized by its tolerance to extreme and harsh environmental conditions [3,5]. Numerous studies have demonstrated a greater tolerance by *Avicennia marina* to various metals when compared with other mangrove species. This quality has enabled researchers to utilize particularly this mangrove species as a bio-indicator of heavy metal pollution to obtain quantitative information regarding the quality of its environment [4,10]. Nevertheless, not enough research investigations have been conducted in the UAE, thus emphasizing the need for more research in this area.

The heavy metals which have been typically associated with the pollution of mangrove forests and swamps are lead, zinc, copper, mercury, nickel, chromium, cadmium, manganese and magnesium [1,11,12]. Some are essential plant nutrients, such as manganese and zinc, and are found to be more abundant than the other metals due to high natural background levels. Others, like nickel and mercury, are non-essential and are therefore considered as pollutants [1]. However, elevated concentrations of essential and non-essential heavy metals, collectively, indicate a negative human input in the mangrove

environment. One study revealed high lead levels in the mangrove sediments of Abu Dhabi, the capital of the UAE [3]. This was attributed to the massive urbanization developmental projects which have detrimental impacts in terms of solid wastes, oil spills, and the high rate of gas combustion. Interestingly, not many studies monitor the same combination of heavy metals within mangrove ecosystems, though the two metals that are almost always monitored by investigators are zinc and lead [1-3].

Mangrove sediments often act as natural sinks for heavy metals as they have a high capacity to preserve heavy metals from freshwater rivers, tidal waters, and storm water runoff [13]. Other fauna and flora in the mangrove environment do not possess the mechanisms used by mangrove plants to regulate the uptake of heavy metals. Therefore, heavy metal levels that are too low to induce a negative effect on mangroves may be just sufficient to harm another species. Lead, at excessive levels, could cause death to many organisms and it could be extremely toxic at even low levels. Cadmium is another substance that poses a threat to animal species, as ingesting trace quantities of it can jeopardize the organism's physiology, health, reproduction and survival [11]. Some researchers have experimented with acute exposure to chromium on fish. Their research focused on chromium in particular as it can readily cross-cellular membranes in aqueous solutions, making this heavy metal one of the most dangerous on aquatic fauna [14]. Acute exposure to chromium had been shown to cause degenerative changes in the histology of kidney, liver and gills tissues; the kidney's renal tubules were atrophied, the liver hepatocytes experienced a degenerative

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necrotic condition, and the gills were severely injured [14].

Mangrove areas in the UAE along with other coastal habitats have been recently subjected to recreational development, industrial installations, and urbanization in general. Studies that have been carried out previously in the UAE have revealed that there are many discarded materials disposed around mangroves [3]. These materials include automobiles, batteries, transformers and tires. Wastewater and oil spills have also been among the anthropogenic inputs that mangroves have been subjected to. The imminent consequence of these activities is the accumulation of heavy metals in sediments and within plant tissue. This could in turn lead to bioaccumulation effects along the food chain [3]. The aim of this study is to conduct a preliminary investigation of contamination in mangrove ecosystems within Abu Dhabi by measuring the level of four different heavy metals (zinc, copper, lead and chromium) in the leaves of representative mangrove habitats of Abu Dhabi leaves from five different sites.

Methodology

Study sites and sampling methodology

The study sites were the mangrove areas in five different locations within Abu Dhabi: the Musaffah channel, Eastern corniche, Saadiyat Island, Al Samaliyyah Island, and Yas Island (Figure 1). The mangroves on Saadiyat Island were used as a control because the habitat is protected to some extent with minimal level of urbanization, while the other areas—namely, Al Samaliyyah and Musaffah channel—are predicted to be contaminated due to the abundance of developmental projects. Among all five selected sites, Al Samaliyyah Island has been subjected to intensive anthropogenic inputs (i.e. construction work) for the longest time, while Musaffah is considered the industrial hub of Abu Dhabi city, and therefore rich with chemical residues [6]. From each of the five sites, a sample of 16 leaves was obtained from three randomly selected mangrove plants located within 5 meters of the coastline. These plants were all of good health and measured 2 to 3 meters in height.

Heavy metal analysis by Flame Atomic Absorption Spectroscopy

Extraction: Mangrove leaves were collected (within a one week period in April 2011), wrapped with aluminum foil and kept at 4°C until transported to the laboratory. The sample preparation procedure was adapted from the methods described by Nazli and Hashim [15]:

the leaf samples were washed with distilled water to remove surface contaminants before being placed in an oven at 157°C to dry overnight. Meanwhile, 100 ml of concentrated HNO₃, 300 ml of HCL and 600 ml of distilled water were combined in a volumetric flask to produce a nitric acid-hydrochloric acid dilute at 1:3 ratios. When they have sufficiently dried, the leaves were removed from the oven and grinded to fine particles using a pestle and mortar. The electronic balance was used to weigh 0.1 grams of the grinded leaf sample to be digested in 10 ml of the nitric acid-hydrochloric acid dilute in a 50 ml beaker over a hotplate. A thermometer was used to ensure the solution and leaf mixture has reached a temperature of 80°C. The digested solution was filtered through a Whatman filter paper on a Buchner funnel that was fixed above a side arm flask. Vacuum tubing was attached to the side arm flask and a running water tap to create a vacuum that would enhance the filtration of the digested solution. Using a pipette, the filtrate was transported to a volumetric flask and completed to 100 ml with distilled water. The sample solution was stored in a fridge (maintained at a temperature of 4°C) until it underwent the heavy metal analysis through air/acetylene Flame Atomic Absorption Spectrophotometer (Agilent Technologies). Three sample solutions were produced from each mangrove leaf sample.

Heavy metal analysis

Metal analysis was carried out on the resultant digests using FAAS, with the use of prepared standards (run before each batch) to determine sample concentrations. To ensure precision of FAAS results, three replicates of each sample were run to ensure measured absorbencies were consistent. Standard solutions were prepared for each of the four heavy metals by dissolving the salts of these metals in distilled water [15]. For Zinc, the solutions contained 0.5 ppm, 1 ppm, and 1.5 ppm. Solutions of 2 ppm, 5 ppm, and 20 ppm were prepared from lead. The Copper solutions were of 2 ppm, 4 ppm, and 6 ppm, while those of Chromium contained 2 ppm, 5 ppm, and 10 ppm. This was done to create a calibration curve that provides a correlation between the concentration of the chemical and the rate at which the atoms are absorbed [15]. This in turn helps in producing an accurate measurement of the heavy metal content in the sample solutions. In order to carry out heavy metal analysis, the suction tube extending from the FASS was first inserted into a blank solution consisting of 1 ml HCl and 99 ml distilled water. The tube was then inserted in the three standard solutions of a heavy metal to create a calibration curve before being inserted in the sample solution. The heavy metal content was recorded on the machine software. The measurement µg/g was in microgram (of heavy metal) per gram (of mangrove leaf tissue).

Results and Discussion

The concentrations of the four heavy metals in the five different selected sites are shown in Table 1. The highest concentration value observed was that of zinc at 3.873 µg/g in Saadiyat Island. This value was followed closely also by zinc in Yas island (3.857 µg/g) and in Eastern Corniche (3.181 µg/g). Zinc concentrations within mangrove leaves in Musaffah and Al Samaliyyah were significantly lower. The concentrations of the other metals were all below 0.12, and were, therefore displayed in a bar graph separate from the one displaying zinc. Lead concentrations are shown to be significantly higher than those of copper and chromium in Yas, Saadiyat, and Eastern corniche. The mangrove leaves in Musaffah channel and Al Samaliyyah contained lower trace metal levels than the rest of the sites. Copper was most abundant in the Eastern corniche (0.023 µg/g), while chromium existed in the highest concentrations in Al Samaliyyah island (0.019

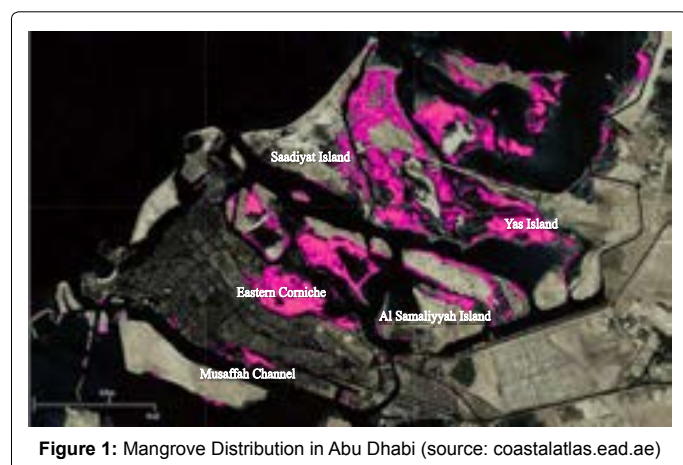


Figure 1: Mangrove Distribution in Abu Dhabi (source: coastalatlas.ead.ae)

Site	Copper	Lead	Chromium	Zinc
Yas	0.009 ± 0.003	0.099 ± 0.014	0.015 ± 0.003	3.857 ± 0.216
Musaffah Channel	0.005 ± 0.001	0.020 ± 0.006	0.013 ± 0.002	0.111 ± 0.005
Al Samaliyyah	0.005 ± 0.002	0.010 ± 0.002	0.019 ± 0.005	1.293 ± 0.078
Eastern Corniche	0.023 ± 0.007	0.090 ± 0.003	0.005 ± 0.001	3.181 ± 0.192
Saadiyat	0.005 ± 0.002	0.108 ± 0.013	0.004 ± 0.0008	3.873 ± 0.232
Average Concentration	0.0094 ± 0.0077	0.0654 ± 0.0455	0.0112 ± 0.052	2.463 ± 1.684

Mean values ± standard deviation (n=3)

Table 1: Heavy metal concentrations (µg/g dry weight) in mangrove leaves.

µg/g). Although a higher level of all tested heavy metals was expected for Al Samaliyyah and Musaffah channel due to the abundance of developmental projects, the results indicated the opposite. The high zinc concentrations could be attributed to high natural background levels in the selected sites. More leaf samples should therefore be collected to confirm any conclusions. Moreover, variations within sites may be attributed to effects of biological and physical phenomena, such as salinity changes, wind and waves which could lead to bioturbation, re-suspension and erosion that are known to affect the metal concentrations in surface sediments [1,16]. The mean concentrations for each of the heavy metals across all selected sites were also recorded in Table 1. Zinc is shown to be the most abundant metal (2.463 µg/g), while lead ranks as the second most abundant heavy metal on average. It is observed that the mean lead level is almost 6 folds higher than the mean concentrations of copper and chromium.

However, the mangrove leaves from all sites contain zinc in a much higher concentration than all the other metals, with a maximum concentration of 3.88 µg/g. This is in concordance with other studies which demonstrated that zinc is a highly mobile metal which could accumulate in plant leaves in great quantities [4,15]. The concentrations of lead are the second highest, and are followed by chromium then copper. The fact that the leaves of *Avicennia marina*, being the least bioaccumulative part of the plant, reflected the presence of heavy metals, could mean that higher concentrations are present in the roots and the surrounding sediments [16,17]. Further investigation into the presence of heavy metals in mangrove roots and sediments is hence needed before conclusions are to be made. The total concentrations of selected heavy metals in the mangrove leaves were compared to the general heavy metal concentration for plants. The general heavy metal concentration for plant was based on the heavy metals concentrations measured in the mature leaf tissue of various plant species. The comparison showed that the total concentrations did not exceed the general concentration, which ranged from 20 to 400 µg/g for the metals of concern [18].

The concentrations of various metals in the plant tissue differ from one part of the plant to another. Mangrove roots appear to have similar metal concentrations to the sediments, while mangrove leaves have significantly less accumulated trace metals in their tissue [10]. It is believed that certain species are able to actively avoid the uptake of metals, regardless of how high the metal concentrations are in the sediments. Exclusion of ions, cell wall immobilization, and barriers at root epidermis are some of the plant tolerance mechanisms used against heavy metals. It has been reported that very low heavy metal concentrations accumulated in leaf tissues because most absorbed heavy metals accumulated in stem and root tissue [10]. So far, root tissue has been recognized as the most accurate part of the mangrove to use as a bio-indicator for heavy metal pollution. Studies carried out in unpolluted areas in Australia have showed that mangrove leaves

have very little, almost insignificant, amounts of non-essential heavy metals [10]. In India, Panama, and Hong Kong, mangrove forests are placed near areas under intense development and industrialization; thus, heavy metal concentrations have been reported to be several folds higher than they are in Australia [1,10].

Moreover, the availability of heavy metals in mangrove sediments to plants is influenced by sediment characteristics such as pH, cation exchange, redox conditions and chlorine content. Further study is needed to investigate these characteristics in order to demonstrate whether contamination of sediments with heavy metals in fact has occurred. A research study has revealed high lead levels in the grey mangrove sediments of the United Arab Emirates most likely as a result of massive expansion of developmental construction projects. The vast developmental growth with emphasis on recreational reshaping of coastal beaches has subjected mangroves to discarded contaminants which could have lead to the sedimentation of heavy metals within plant tissue [3]. Research investigations of the status of heavy metal pollution in grey mangrove habitat biota within the Red Sea coastal areas of Saudi Arabia have also documented a very high concentration particularly for copper and chromium [17]. Similarly in India and Hong Kong, the intense development and industrialization have posed an ecological threat to the nearby mangrove forests which have revealed elevated levels of heavy metals that exceed sediment quality guidelines particularly with lead [1,11,12]. It has been predicted that the levels of lead within mangrove sediments in the Gulf region and others could be increasing in the coming few years due to impacts of oil spills and the higher rate of fuel consumption [3,7,8].

In conclusion, the health of mangrove habitats has the potential to become jeopardized by heavy metal contamination; therefore mitigation efforts must be made to prevent the issue from escalating. This preliminary study provides implications in terms of directing environmental protection and mitigation efforts to the areas where they are most needed. Future studies are needed to provide a better and more comprehensive investigation of heavy metal mobility, bioaccumulation and ecotoxicology within the indicator mangrove species by collecting more samples and profiling for different metals within the mangrove plants and sediments over a long period of time. Temporal accumulation relationships could provide valuable insights into the conservation of mangrove ecosystem within the UAE.

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