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Determination of some Heavy Metals in Sea-grass *"Poisdonia oceanica"(L.)* Delile of Eastern Libyan Coast "Mediterranean"

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Abstract

The concentrations of heavy metals (Cr, Co, Zn, Cd, and Pb) were found in the samples of tissues of Sea-grass, *Posidonia oceanica (L.)* Delile, that were collected from eighteen different sites along 820 Km of the coast of eastern Libya on the Mediterranean sea (the first site is about 500 km to the east of Alexandria of Egypt). These samples were collected from the following 18 sites (east to west): Tobrouk, Ras-Etteen, Derna, Ras-Lehlal, Sousa, QasrLibya, Tulmaitha, Deryana, North Benghazi, Alssabri, Family Village (Qaria), Nairowz, Nakheil, Geminis, Sultan, Zuitina, Al-Briga and Ras-Lanouf. The technique used by this study was Flame Atomic Absorption Spectrometry (model novAA300). This study shows that elevated concentrations of Zn, Co, and Pb are found in most samples; particularly, those were collected near the discharge points of city sewages effluent and the power station sites. The concentrations of Cr and Co were very low in all the samples, except for those were collected near the city of Benghazi. The statistical analysis (one-way ANOVA) indicates that the Sea-grass" *Posidonia oceanica"(L.)* Del. tissues have different levels of metal bioaccumulation, which might be used as a bio monitors for trace metals. The higher values of MPI are recorded for BR and TP that is 121.18 and 124.29, respectively. Perhaps, the high values of MPI for these two sites are due to the high elevated values (387.56) µg /g and (186.40) µg/g of Chromium for both sites (BR & TP). The least values of MPI are obtained for the locations SP, ZU and RH (20.16, 20.96 and 22.20 µg\g), respectively, and this may be explained by the low levels of the five heavy metals (Cr, Co,Zn,Cd and Pb) in these sampled sites.

Keywords: Sea-grass; Metal bioaccumulation

Introduction

The major source of surface water pollution includes effluent discharges by industries, atmospheric depositions of pollutants and occasional accidental spills of toxic chemicals. Trace metals are regarded as serious pollutants of aquatic environment because of their toxicity. The persistence of their difficult biodegradability and their tendency to concentrate on aquatic organisms. They enter the marine environment through atmospheric and land-based effluent source [1,2]. There is currently a great interest in the use of living organisms as in aquatic ecosystem [3]. Given that the method used previously does not provide sufficient information on the bioavailability of the metals present in the environment. In the Mediterranean Sea, the endemic seagrass, *Posidonia oceanic (L.)* Delile, has been used as a metal bio indicator for several over decades [4,5]. Leaves *of P. oceanica* can give an indication of the metal concentration in the environment, a short time period (months) with good accuracy [6]. On the contrary, sheaths, which gave an indication of changes over long time periods (decades), seem to be less sensitive to variations in the metal concentration in the environmental. The use of *P.oceanica* as a bio indicator of water quality in relation to implementation of the water frame work directive [7-9]. The state of health of *P. oceanica* meadows is good indicator of the ecological status of a particular coastal water body. Therefore, *P. oceanica* has been proposed as a biological quality elements (BQES) for Mediterranean coastal water. Considerable work is being currently under taken to develop classification tools and metrics that would allow use of *P. oceanica* as a BQES for WFD (Water Frame work Directive). The *P. oceanica* eco-system is particularly threatened by anthropogenic coastal pollution and bio indication of heavy metal contaminations have already been used as such in the Mediterranean and elsewhere [10-12]. Thus, the aim of this study is to evaluate the state of metal contamination of the Benghazi coast in Libya metal contamination of the Benghazi coast in Libya using *Posidonia.*

Materials and Methods

Sampling and sample preparation

Seagrass Posidonia oceanica samples were collected in the summer of 2009, from 18 stations located along Eastern Libyan "Mediterranean" (Eastern of Libyan Coast; Figure 1). Dirt and foreign herbs from sea grass samples was removed and washed with deionized water to remove marine sediment, soil and others impurities. All sea grass samples were placed in a drying oven at about 65°C until most of the liquid has evaporated, then the temperature was increased to 80°C. Sea grass samples were placed in desiccators for about 48 hrs and then they were ground by a mill–Machine.

Trace metals analysis

Hundred milligrams of each samples was weighed, transferred into 25 ml beaker, dissolved in (8 ml 65% nitric acid) by heating to 70°C on a hotplate for about 8 hrs and the solution was then cooled, 2 ml of 30% hydrogen peroxide was added and heated again for another 4 hrs at 70°C, then filtered and diluted to the mark [13]. All samples solution were analyzed using Flame Atomic Absorption Spectrometer (FAAS), with detection limit of 0.0007 mg L^{-1} for Cr, 0.0013 mg L^{-1} for Co, 0.0009 mg L^{-1} for Zn, 0.0015 mg L^{-1} for Cd and 0.0023 mg L^{-1} for Pb. Good

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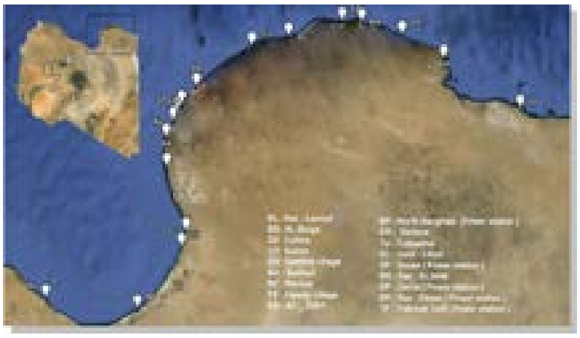

Figure 1: Map of eastern Libyan coast.

overview on sample preparation for atomic spectroscopic analysis was recently published [14]. Calibration standards solutions series were prepared from standard solutions of 1000 mg L^{-1} (Stock solution), to compare the total metal content at the different locations. The metal Pollution index (MPI) to compare the total metal content at the different stations, was used, it is obtained with the following equation: MPI=$(Cf_1 \times Cf_2 \ldots\ldots\ldots\ldots Cf_n)^{1/n}$; where Cf is the concentration of the metal n in the sample. For our study area, which is the multiplication of heavy metals concentration with their number

Statistical analysis

An explorative statistical analysis was carried out for all concentration values measured in all samples, and data were compared with other measures presented in the literature. The explorative parameter are mean value, range, standard deviation, relative standard error and 95% confidence interval of mean (Lower bound and Upper bound), and the results were analyzed using one - way analysis of variance (ANOVA) to examine statistical significantly of difference in the mean concentration of chromium, cobalt, zinc and lead metals ($P<0.05$). The mean concentration of cadmium metal shows no significantly ($P>0.05$), when determined in sea grass "Posidonia oceanica"(L.) Defile sample. Major species correlation matrices (ELOro) was used and showed a clear relation between locations and heavy metals (Cr, Co, Zn, Cd and Pb) (Table 2 data included as supplementary). There is strong relation between cobalt and chromium and zinc locations and lead metal (significance), and medium relation between cadmium and chromium, lead and zinc (significance), weak relation between locations and chromium, cobalt, zinc and cadmium.

Results

Determinationof metals concentration in seagrass "*Posidonia oceanica*" (L.) Defile

The mean concentration of heavy metals (Cr, Co, Zn, Cd and Pb) in *P. oceanica* samples from (18) sites in different location of Eastern of Libyan Oil Crescent are listed in Tables 1.1-1.6 (Data included as supplementary), respectively, the mean concentration of heavy metals were characterized by the following parameters: Mean, standard deviation and relative standard deviation of the trace metal concentration in *P. oceanica* are presented.

Discussion

This study was focused on the pollution by heavy metals, the study area extend about 820 Km along the eastern Libyan coast (Mediterraneansea); form Tobrouk city at the east to Ras-lanouf in the west. Seagrass "*Posidonia oceanica*" (L.), the sea plant known to be as a bio-indicator was chosen because of it is an ability to concentrate heavy metals.

This study have been proved that most expected contaminated sites were polluted with all the heavy metals (Cr, Co, Zn, Pb), with the exception of cadmium, all metals gave a significant indicator values and the average value was higher than the background level for each element. The values of MPI which represents the metal pollution index level, and that equal to an average of all heavy metals concentrations of this study multiplied by their number (five metals) were elevated in some sampling sites (TP, BR, SA, NA, DP, RP, RL, BP) (124.9, 121.18, 72..04, 59.86, 58.94, 51.88, 46.24, 43.68), respectively. The samples (TP, DP, RP, BP) were collected near power stations that uses heavy fuel oil, liquid fuel oil and fuel gas.

Wang et al. [15] states that the first two types of fuel contain zinc, (HFO: 1445 $\mu g/m^3$), (NG: 1479 $\mu g/Nm^3$), and lead: (HFO: 35.5 ng/m^3). These prove the leakage of such fuel into sea, in addition, the machines coolant oil that need to be changed may discarded without treatment into sea. The metal pollution index MPI values were found to be lower than that of previous samples, and it be calculated for the samples (SP, ZU, RH, TU) to be 20.16, 20.96,22.20,27.95, respectively. In order to support our results, a data function system was applied to link between the five heavy metals and their collection sites, this relation shows very strong link between (the sites and Pb metal, Cr and Co metals, Cr and Zn metals, Zn and Co metals), where their correlation values were (0.455**, 0.617**, 0.580**,0.529**), respectively. However, the correlation value was medium for Cr and Cd metals, Zn and Pb metals, that was found to be (0.356*, 0.297*), respectively, the weakest correlation value were recorded between the sites and the Cr, Co, Zn and Cd metals.

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