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Determination of some heavy metals in seagrass "*Poisdonia oceanica*"(L.) Delile of Benghazi Coast in Libya "Mediterranean"

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ABSTRACT

The heavy metals (Cr, Cd, Zn, Co, and Pb) concentrations were determined in Seagrass Poisdonia oceanica (L.) Del. Tissues. Samples that collected from five sites along 30Km north and south of Benghazi, the second largest city in Libya, [Northern sea of African coast (Mediterranean)]. The technique used for the analysis was Flame Atomic Absorption Spectrophotometer (model novAA300).The study shows that an elevated concentration of Zn, Cd, and Pb were found in most samples particularly those collected near the discharge point of city sewages effluent, and the north Benghazi power station site. The concentration of Cr and Co was very low in all samples except for those collected near the city. Statistical analysis (one-way ANOVA) indicated that the Seagrass Poisdonia oceanica (L.) Del. tissues had different levels of metal bioaccumulation and might be used as a biomoniotors for trace metals.

Keywords: Sample preparation, FAAS, Mediterranean, Seagrass, *Poisdonia oceanica*, Marine pollution.

INTRODUCTION

The major sources of surface waters 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. Their persistence, their difficult biodegradability and their tendency to concentrate in 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 pollution biomonitors in aquatic ecosystem.[3] Given that the methods used previously does not provide sufficient information on the bioavailability of the metals present in the environment, Bioaccumulation of heavy metal in fresh water fishes was reviewed by [4] In the Mediterranean Sea, the endemic seagrass *Poisdonia oceanica* (L.) Delile has been used as a metal bioindicator for several decades.[5] Leaves of P. Oceanica can give an indication of the metal concentration in the environment over a short time period(months) with good accuracy. 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.[1,6] Use of P. Oceanica as a bioindicator of water quality in relation to implementation of the water frame work directive. The state of health of 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 Framework Directive).[7,8]The P. Oceanica ecosystem is particularly threatened by anthropogenic coastal pollution and bioindication of heavy metal contaminations and have already been used as such in the Mediterranean and elsewhere.[7,9,10]Thus, the aim of this study is to evaluate the state of metal contamination of the Benghazi coast in Libya using Posidonia Oceanica as a bioindicator .

MATERIALS AND METHODS

A. Sampling and sample preparation

Seagrass *Poisdonia oceanica* samples were collected in the summer of 2009, from 5 stations located along the Benghazi coast in Libya" Mediterranean" (Fig.1). Dirt and foreign herbs from seagrass samples was removed and washed by using distilled deionized water to remove marine sediment, soil and others impurities [11]. All seagrass samples were placed in a drying oven at about 65 C^0 until most of the liquid has evaporated , then the temperature was increased to 80C^0, Seagrass samples were placed in a desiccators for about 48 hrs. then they were ground by a mill- Machine.

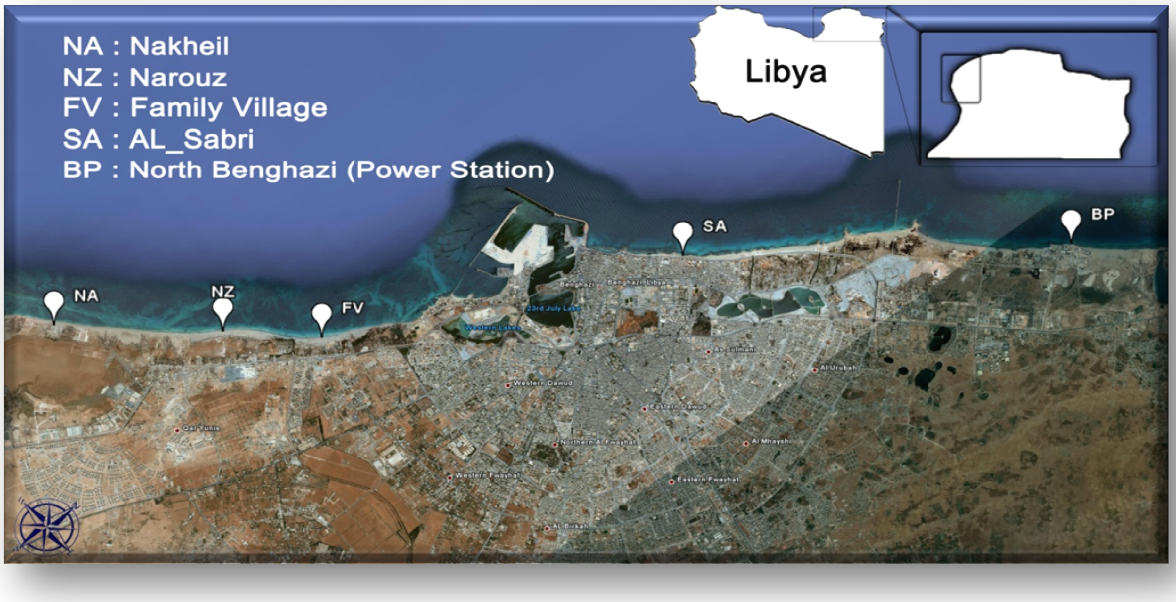

Figure (1): map of Benghazi coast in Libyan

B. Trace metals analysis

Hundred milligrams of each sample was weighed in a 25ml beaker, dissolved in (8 ml 65 % nitric acid) by heating to 70 C^0 on a hotplate for about 8 hrs**.** and the solution was then cooled, 2ml of 30% hydrogen peroxide was added and heated again for another 4 hrs**.** at 70 C^0. The filtered solutions were analysed using *Flame Atomic Absorption Spectrometer*(FAAS)*(model novAA300).*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. An overview was recently published on the preparation of samples for Flame[12] and Flameless[13]Atomic Absorption techniques.The standard addition method was performed, and calibration standards series were prepared from standard solutions of 1000 mg L^{-1} (Stock solution).

To compare the total metal content at the different stations, the metal Pollution index (MPI) defined by Usero et al was used. It is obtained with the following equation:

MPI = $(Cf_1 \ x \ Cf_2 \ \ldots\ldots\ldots\ldots Cf_n)^{1/n}$; where *Cf* is the concentration of the metal *n* in the sample. In this It's represented by the multiply action of heavy metals concentration with their numbers.

C. 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 analysed 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**) but mean concentration of cadmium metal shows no significantly**(P>0.05)**when determined in seagrass " *Poisdonia oceanica* "(L.) Delile samples. Major species correlation matrices (ELOro) in table (3.7) to was used clear relation between locations and heavy metals (Cr, Co, Zn, Cd and Pb) 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

Determination of metal concentration in seagrass samples

The mean concentration of heavy metals (Cr, Co, Zn, Cd and Pb)in P. Oceanica samples from twelve sites in different location of Benghazi coast in Libya are listed in tables (1), (2), (3), (4) and (5)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**.**

Table (1): Statistical treatment of chromium data using ANOVA

Location	Sample number	Mean concentration(µg\g)	Minimium	Maxmium	Standrad Deviation	RSD%	95% Confidnence interval for mean	
							Lower Bound	Upper Bound
BP	2	108	102	114	8.48528	7.851	31.7628	184.2372
SA	2	337.5	213	462	176.06959	52.14	0	1919.42
FV	2	0.67	0.54	0.8	0.18385	19.4	0	2.3218
NZ	3	0.74	0.65	0.8	0.07937	10.67	0.5428	0.9372
NA	3	0.72	0.58	0.8	0.12166	16.8	0.4178	1.0222

Table (2): Statistical treatment of cobalt data using ANOVA

Location	Sample number	Mean concentration(µg\g)	Minimium	Maxmium	Standrad Deviation	RSD%	95% Confidnence interval for mean	
							Lower Bound	Upper Bound
BP	2	31.65	26.2	37.1	7.70746	24.35	0	100.8988
SA	2	35.255	9.51	61	30.40893	86.24	0	362.3762
FV	2	21.775	8.25	35.3	19.12724	62.1	0	193.6264
NZ	3	7.0533	6.3	7.54	0.66161	9.375	5.4098	8.6969
NA	3	6.6767	5.3	7.5	1.19985	17.95	3.6961	9.6573

Table (3): Statistical treatment of zinc data using ANOVA

Location	Sample number	Mean concentration(µg\g)	Minimium	Maxmium	Standrad Deviation	RSD%	95% Confidnence interval for mean	
							Lower Bound	Upper Bound
BP	2	113.85	96.05	131.65	25.173	22.1	0	340.0202
SA	2	180.85	110.9	250.8	98.92424	54.69	0	1069.649
FV	2	174.175	164.45	183.9	13.75323	2.283	50.6072	297.7428
NZ	3	52.7667	11.5	85.7	37.79541	71.62	0	146.6557
NA	3	72.5833	57.9	88.4	15.28155	21.05	34.6219	110.55448
Range	(52.76 - 180.85)							

Table (4): Statistical treatment of cadmium data using ANOVA

Location	Sample number	Mean concentration (µg\g)	Minimium	Maxmium	Standrad Deviation	RSD%	95% Confidnence interval for mean	
							Lower Bound	Upper Bound
BP	2	32.485	10.52	54.45	31.0632	95.62	0	311.5768
SA	2	39.5525	39.12	39.99	0.61872	1.562	33.9935	45.1115
FV	2	41.205	40.05	42.36	1.63342	3.963	26.5293	55.8807
NZ	3	35.5733	33.59	37.46	1.93681	5.442	30.762	40.3846
NA	3	75.0767	32.5	159.9	73.45935	97.84	0	257.5598
Range	(32.48 -75.07)							

Table (5): Concentration of lead in seagrass"P. Oceanica"(L.) Delile by using ANOVA

Location	Sample number	Mean concentration (µg\g)	Minimium	Maxmium	Standrad Deviation	RSD%	95% Confidnence interval for mean	
							Lower Bound	Upper Bound
BP	2	16.69	16.27	17.11	0.59397	3.553	11.3534	22.0266
SA	2	28.49	26.95	30.03	2.17789	7.641	8.9224	48.0576
FV	2	22.865	20.48	25..25	3.3729	14.75	0	53.1693
NZ	3	21.7333	14.1	32.63	9..68645	44.56	0	45.7958
NA	3	55.5867	34.48	66.55	18.28351	32.88	10..1679	101.0054
Range	(16.69 - 55.58)							

Table (6) : The trace metals concentration in seagrass"*Poisdonia oceanica*" (L.) Delile

Location	Mean concentration of heavy metal µg/g					MPI
	Cr	Co	Zn	Cd	Pb	
BP	108	31.65	113.8	32.48	16.69	43.68
SA	337.5	35.25	180.8	39.55	28.49	72.04
FV	0.67	21.77	174	41.2	22.86	41.55
NZ	0.74	7.05	52.76	35.57	21.73	31.07
NA	0.72	6.67	72.58	75.07	55.58	59.86
Range	(0.67 - 337.5)	(6.67 - 35.25)	(52.76 - 180.0)	(32.48 - 75.07)	(16.69 - 55.58)	

Table (7): correlation matrix for major species and trace elements in "Seagrass P.Oceanica" (L.) Delile

Major species correlation matrix

Locations	*Cr*	*Co*	*Zn*	*Cd*	*Pb*
Locations					
Correlation Coefficient			***1***		
Sig-(2-tailed)					
Cr					
Correlation Coefficient			***-0.137***	***1***	
Sig-(2-tailed)			***0.374***		
Co					
Correlation Coefficient			***0.360***	***0.529****	***1***
Sig-(2-tailed)			***0.815***	***0.000***	
Zn					
Correlation Coefficient			***0.190***	***0.580****	***0.617****
Sig- (2-tailed)			***0.903***	***0.000***	***0.000***
Cd					
Correlation Coefficient		***0.188***	***0.297****	***0.184***	***0.292***
Sig-(2-tailed)		***0.222***	***0.050***	***0.231***	***0.055***
Pb					
Correlation Coefficient	***0.445****	***0.249***	***0.251***	***0.356****	***0.095***
Sig-(2-tailed)	***0.002***	***0.103***	***0.100***	***0.018***	***0.539***

*** Correlation is significant at the 0.01 level (2-tailed).*
** Correlation is significant at the 0.05 level (2-tailed).*

DISCUSSION AND CONCLUSION

From table (1), it is noticed that the concentration of chromium in most sites were the low values and below the background level (0.67ppm) . Only for the locations (SA and BP) the levels of this metal was very high compared with other samples sites of our study. The elevated concentration of chromium in the site BP Benghazi power station (108 µg\g) can be explained as a result of the contamination of these site with the heavy fuel oil (HFO) which used in all of the three power stations from which the samples were collected. The average chromium concentration of the SA sample that belong to Al-Sabri beach was very high (337.50 µg\g), the only logic interpretation of this value is the high quantity of sewage effluent in this area, despite of domestic sewage, small factories, painting mixing shops and Hospitals discards their wastes into these beach it is noticed also that there is a stinking odour in the area. The average concentration of this metal in all of other sites (FV , NZ and NA) (0.74, 0.72 and 0.67) µg\g respectively. From table (2) it is noticed that high concentration of cobalt inlocations (SA, BP and FV) (35.25 , 31.65 and 21.775 µg\g respectively) all other sites were slightly contaminated with cobalt and the values were high the background level (6.676µg\g).From tables (3) , (4) and (5) the zinc , cadmium and lead concentrations in our study sampling sites was found that this metals level was higher than the background level (52.76, 32.48 and 16.69 µg /g) respectively. The zinc, cadmium and lead concentrations in the sites (SA,FV, BP and NZ)were (180.85, 174.17,113.85 and 72.58)µg\g, (NA, FV, SA and NZ) were (75.07, 41.20, 39.55 and 35.57)µg\g and (NA, SA, FV and NZ) were (55.058, 28.44, 22.86 and 21.73)respectively. The location SA contain high concentrations of zinc, cadmium and lead although there is no power stations near this site, but the location lies in Al-Sabri beach which contaminated with domestic sewage effluent and effluent from Hospital, (7th October and Al-jamhoria Hospitals had a medical laboratory) that discards their wastes to sea beach in addition to domestic and workshops discharge wastes[14]. It is useful to mentioned her that heavy fuel oil containing up to 0.15 µg/m^3 chromium. fuel oil (HFO) contain zinc concentration of about 1445 µg/m^3 and natural gas fuel (NG) of 1479 µg/Nm^3 zinc, oil contains 7.2 to 148 µg/L of zinc and HFO contain lead up to 5.35 ng/m^3[15], pesticides or Herbicides that contains quantity of cadmium which may reaches (3µg/g) in such compounds and pesticides contain concentration of lead of 120 µg/g.[16].

Although the locations of the Family Village (FV) samples were far away from city centre, they contains an elevated concentration of zinc, cadmium and lead this may also be explained as a result of sewage discharge point from domestic industrial areas and from Quirsha sewage treatment plant. The (Family village (Qaria),(Nakheil), (Narouz), (Benghazi power station) locations appear to be the least contaminated sites and lies within the background level.

The average value of chromium, cobalt, zinc, cadmium and lead respectively in samples of P. Oceanica in the Corsican coastline site (Mediterranean) is (0.89, 2.54, 0.45, 0.34 and 3.37) µg\g, the average values in the North Corsica is (0.74, 7.73 ,15, 0.65 and 7) µg\g, the gulf of Naples (southern Italy) is (0.65, 0.98 ,0.45, 0.88 and 0.32) µg\g and Venezuelan costal is(0.60 ,3.92, 0.25, 0.86 and0.25)µg\g.[14,17-19,]

The high values of MPI for the sites (SA and NA) (72.04, 59.86) respectively can be attributed to the high levels of Cr, Co, Zn {(SA: 337.50, 35.25, 180.85) µ*g\g* ; while for the site NA ,it's may due to the high levels of Cd &Zn metals (NA: 75.07 µ*g\g* , 72.58 µ*g\g*) and the value of MPI sites(BP and FV) (43.68 and 41.55) respectively can be attributed to the high levels of {BP: (Cr = 108, Co = 31.65, Zn = 113.8) and FV: (Zn = 174)}.

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