Evaluation of Heavy Metal Pollution in Anzali Wetland, Guilan, Iran

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ABSTRACT

Background: Evaluation of heavy metals as toxic pollutants in environment has a significant importance in environmental pollution studies. surficial sediments of water resources have a high potential in releasing heavy metals to the upper water environment, hence sediment analysis presents guidelines to the authorities for monitoring the environmental systems.

Methods: In this study, total and fractional concentration of eight heavy metals (V, Ni, Cr, Cd, Zn, As, Fe, and Pb) were investigated along different sites of Anzali Wetland in Iran using bulk elemental analysis and sequential chemical extraction techniques respectively. Geoaccumulation index (I_{geo}) and Pollution Index (I_{poll}) were computed and compared in different sites of the wetland, too.

Results: Total concentration of metals in sediment samples found to be in this order: Fe>As>Cr>Zn>Ni>V>Pb>Cd. The speciation data revealed that most metals were bonded in lithogenous fractions that means no pollution. I_{geo} results indicated that the wetland is moderately to highly polluted for Cd and As and I_{poll} results showed that the wetland is moderately polluted for Pb and Cd were applied to metals also to investigate on I_{geo} and I_{poll} results. For V, Ni, Cr, Zn and Fe, cluster analysis confirmed both indices but for As and Pb it confirmed I_{geo} results.

Conclusion: The results of the present study showed that the Anzali wetland is threatened by pollutants related to rivers entering it. So to preserve the environment of the Anzali wetland from deterioration, the main act is to prevent the discharge of wastewater to rivers entering it.

Keywords: Anzali Wetland, Cluster Analysis, Geoaccumulation Index (I_{geo}), Heavy metals, Pollution Index (I_{poll}), Sediment.

INTRODUCTION

In an aquatic environment, sediments have a high contamination capacity especially for heavy metals. In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water and more than 99.9% are stored in sediments and soils (1,2). Because of their toxicity, persistence, and non-degradability in the environment, heavy metals pollution in the aquatic systems is one of the largest threats to their environment that affects directly on flora, fauna and human health. To assess the pollution condition in an aquatic environment, one of the useful methods is the evaluation of metals distribution in bed sediments. This method has been applied by many researchers all over the world. Karbassi, et al. investigated the source of some trace elements on Persian Gulf by the method of cluster analysis as well as chemical partitioning techniques (3). They compared their results with those of mean crust and mean world sediments. Adamo, et al. computed Enrichment Factors (EF) for some metals in twenty surface sediment sites at the port of Naples, Italy to assess the polluting metals and the degree of pollution at each site (4). Their results from sequential extractions revealed that heavy metals pollution is related to anthropogenic sources like shipbuilding activities and petroleum refineries. Karbassi, et al. studied on

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Shefa-Rud riverbed sediments by bulk and chemical partitioning of elements (5). They measured geoaccumulation Index (I_{geo}) and Enrichment Factor and showed that the mentioned values are in a well agreement with results of chemical partitioning data.

Lokeshwari and Chandrappa assessed the level of some heavy metals in water, water hyacinth and sediment samples of Lalbagh tank, Bangalore, India (6).

Geoaccumulation index results revealed that there was moderate input of copper and lead from anthropogenic sources to the tank basin. Priju and Narayana analyzed five heavy metals on sediments of Vembanad Lake in India to understand the pollution levels and the impact on the coastal environment (7). They showed that industrial effluents are major source of metal enrichment in the lagoonal system. Praveena, et al. tried to establish a complete and comprehensive set of sediment quality guidelines by applying numerous sediment quality guidelines on Mengkabong lagoon mangrove sediment in Malaysia (8). They concluded that the most appropriate guideline that meets the prioritization criteria consistent with international initiatives and regulations is interim sediment quality values for Hong Kong. In another research, Praveena, et al. investigated on Mengkabong lagoon mangrove sediments by applying principal components analysis (PCA) and cluster analysis (CA) to interpret information about the sediment and its controlling factors (9). Calculation of geoaccumulation index indicated that the Mengkabong mangrove sediments are having background concentrations for Al, Cu, Fe, and Zn and unpolluted for Pb. Lasheen and Ammar investigated the mobility and the availability of eight heavy metals in sediments from different sites along the Nile River in Cairo district using sequential chemical extraction technique to evaluate their threats to ecological and human health (10). Banat and Howari evaluated the accumulation of six heavy metals in fine-grained sediments from the sediments of the late marshes and swamps of southern Iraq (11). They reported that the concentrations of Co, Zn, Cr and Cu approach the average concentration in the Earth's crust and uncontaminated sediments but Pb, Ni, and Cd are slightly enriched which may reflect anthropogenic effect. It was believed that metals in the study area were derived mainly from the igneous mineral deposits in the Iraq-Iran Mountain range. Mohiuddin, et al. investigated seasonal and spatial distribution of heavy metals in the bed sediments of polluted Tsurumi River in Japan by analyzing ten heavy metals and revealed that Tsurumi River sediments are moderately to heavily contaminate by Zn, Pb and Co base on Pollution Index (I_{poll}) (12).

Nasrabadi, et al. measured total content and four chemical partitioning fractions of ten heavy metals in Haraz River bed sediments in Iran and concluded about its contamination level (13). Yu, et al. investigated the effect of Mo mining activities in western Liaoning, northeast China with geochemical method and showed that Mo tailings ponds deposited along the bank may have a closely relationship with the high levels of these metals in sediments and Mo in sediments may pose a high risk to the local environment (14). Hosseini, et al. determined the concentration of some elements in water and sediment of Shadegan wetland, Iran (15). They measured I_{geo} and I_{poll} Indices and discussed about the wetland metal contamination base on the Indices.

The Anzali Wetland, located on the southern coast of the Caspian Sea in Gilan Province of Iran, is a large complex of freshwater lagoons with extensive reed-beds, shallow impoundments and seasonal flooded meadows. It is internationally known as an important wetland for migratory birds and was registered as a Ramsar site in 1975. The water quality of the wetland is deteriorating due to the inflow of domestic, agricultural and industrial wastewater from neighboring cities. A few researches on evaluation of metal pollutions have been done on Anzali wetland. Pourang measured Lead, Copper, Zinc and Manganese in surfacial sediments of the wetland (16). Results indicated that no distinct relationship existed between heavy metal levels and percentage fine fraction in sediments. Amini-Ranjbar determined the concentrations of Cd, Pb, Cu, Zn and Ni in surficial sediments from eleven sampling sites in the Anzali wetland and statistically proved significant differences among the accumulation of the metals in sediments, while differences were not observed among the seasons (17). To investigate the precipitation of heavy metals in Anzali wetland and evaluate its refining performance, Sartaj, et al. collected sediment samples from fifteen stations including inlets, outlets and some internal locations in the wetland and analyzed them for six metals of Cr, Cd, Pb, Zn, Cu and Ni over a period of six months (18). Their results indicated that concentration of heavy metals decreases with an increase in the distance from delta of rivers entering the wetland. This is due to the role and performance of wetland chemical contents in reducing the pollutants, the self-purification action of wetland as well as precipitation of heavy metals at the beginning of the entries into the wetland. Significant differences between the sampling sites in Anzali wetland from the concentrations of cadmium, copper, and lead in surficial sediment were reported by Pourang, Richardson and Mortazavi (19). The pattern of metal occurrence in sediments exhibited the following order: Cu>Pb>Cd. The mean concentrations of Cd and Pb in the sediments were higher than the global baseline values and world average shale. In the case of Cu, results were somewhat higher than the baseline values but well below the world average shale. Ghazban and Zare investigated on the pollution situation of Anzali wetland by analyzing heavy metals in core sediments of the wetland (20). They measured major elements and trace elements of sediment samples and compared their results with the Caspian Sea and global sediments and showed that the concentrations of heavy metals in wetland sediments are higher.

In this study sediment samples were collected from twelve stations along the Anzali wetland and the concentration of eight heavy metals V, Ni, Cr, Cd, Zn, As, Fe and Pb were measured by total elemental analysis method (21). Tessier Chemical partitioning method was applied to recognize the kind of heavy metal bonds to sediment and to know the background concentration of metals in sediment (22). Geoaccumulation index (I_{geo}) and pollution Index (I_{poll}) were measured and compared with each other. Cluster Analysis was applied to investigate the relationship between different metals and to assess the I_{geo} and I_{poll} results.

Study area and sampling sites

The Anzali wetland is a large complex environment of fresh water lagoons with extensive reed-beds, shallow impoundments and seasonal flooded meadows. It is extremely important as a spawning and nursery ground for fish, and as a breeding, staging and wintering area for a wide variety of waterfowl. It is located in the northern part of Iran, along the coast of the Caspian Sea approximately at north latitude between 37° 25′ and 37° 32′ and east longitude between 49° 15′ and 49 ° 36′. It has a catchment area of 3610 km^2. Approximately 42% of the catchment area is covered by forests. Among the landuse categories, forest has the largest share of 42%, followed by paddy field/farmland (26.7%) and orchard (8.6%) in that order (Figure 1). There are ten major river systems entering the wetland. The annual mean discharge into the wetland is estimated at 76.14 m^3/s. Base on inflowing rivers the wetland can be divided as two zones: the west zone that has only one river inflowing (Zone A) and the southern and eastern zone that has nine rivers inflowing (Zone B)(Figure 2). The average annual of Anzali Wetland watershed is about 1200 mm.

Twelve sampling sites were chosen along the wetland considering the situation of the wetland (low depth marsh areas) and sediment samples were collected. Figure 2 shows sampling sites. Samples were collected using Ekman grab sampler on May 2011. Samples were dried in an oven at 105°C and powdered in an agate mortar. In order to normalize the variations in grain size distributions, the dried sediment samples were sieved to 0.15 mm using sieve No. 150. All chemicals used are from Merck company and all experiments have done in sediment and chemistry laboratory of Water Research Institute, Tehran, Iran.

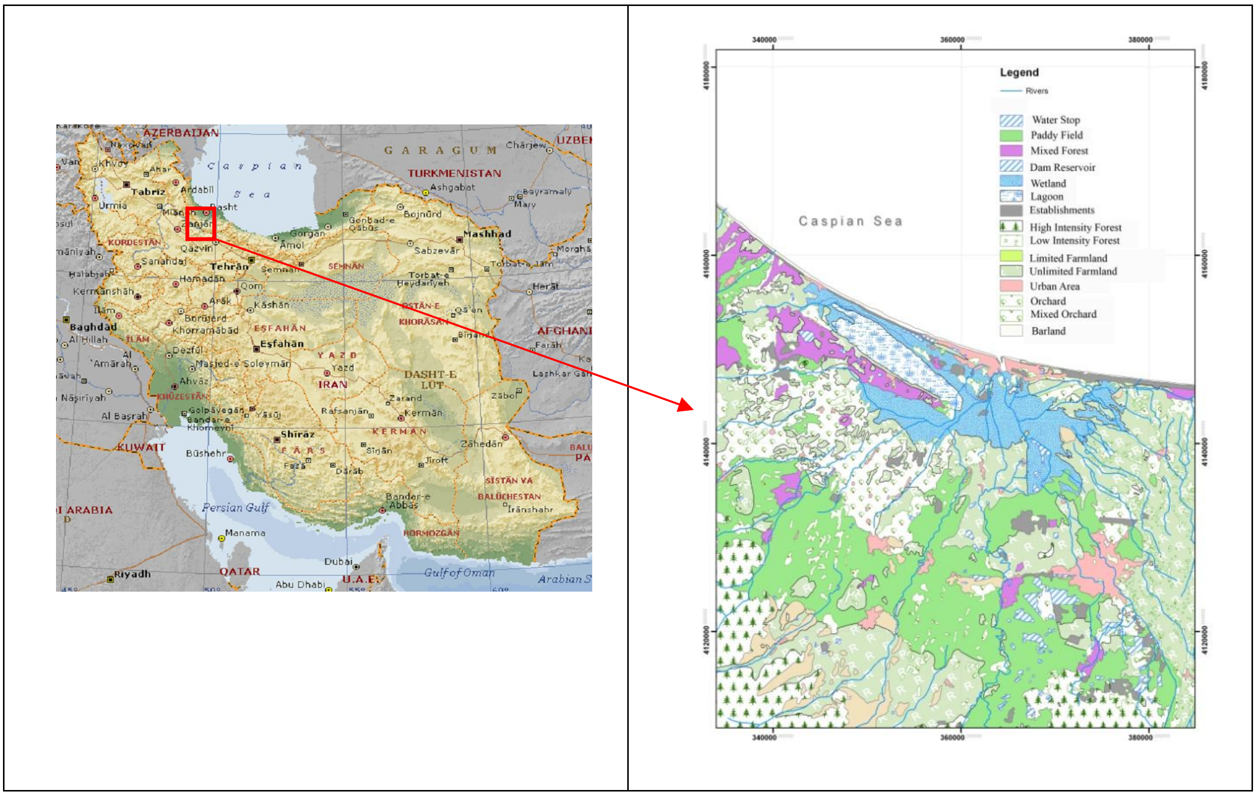

Figure 1. Anzali wetland location and landuse of its basin

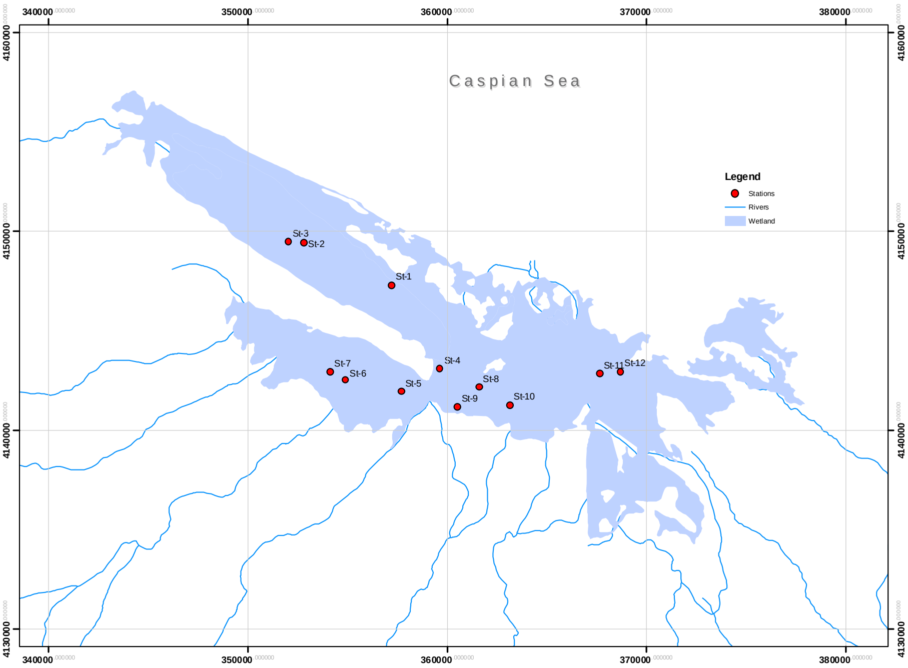

Figure 2. sampling sites

MATERIALS AND METHODS

1. Total elemental analysis

Digestion of organic matter and dissolution of silicates for total elemental analysis was proposed by Sparks, et al. (21). The procedure of the method is described below: 1.0 g of the 100-mesh (0.15mm) sediment was weighed into a 100-mL Teflon beaker and 10 ml of HNO_3 and 10 ml of $HClO_4$ were added. The beaker was covered with a Teflon watch cover and heated at 200^oC for one hour. The cover was removed and heating was continued until the volume became 2 to 3 ml. After cooling the sample, 5 ml of $HClO_4$ and 10 ml of HF were added; Teflon cover put and heated at 200°C until all siliceous materials has been dissolved. Then the cover removed and heating continued until the volume was 2 to 3 ml. The digest cooled, 10 ml of 50% HCl added, Teflon cover put and heated at 100°C for 30 minutes. After cooling the sample brought to 50-mL volume. The solution is then ready for ICP determination (21). The concentrations of heavy metals were determined according to APHA (1998) (23). The analyses of total digestion samples were duplicated.

2. Metals speciation

The metals speciation using sequential extraction proposed by Tessier, Campbell and Bission and modified by Elsokkary and Müller (22,24). Heavy metals have five kinds of bonds so following five operational steps were used for partitioning the heavy metals.

2.1. Fraction I (exchangeable)

One gram dry solid (sediment or sludge) sample was shaken for one hour at room temperature with 8 ml of 1 M magnesium chloride -6 hydrate ($MgCl_2.6H_2O$).

2.2. Fraction II (bound to carbonates)

The residual solid from exchangeable fraction of metals was shaken for 30 minutes at room temperature with 8 ml of 1 M sodium acetate anhydrous ($C_2H_3NaO_2$) and adjusted to pH 5.0 with acetic acid (99.83% $C_2H_4O_2$).

2.3. Fraction III (bound to iron and manganese oxides: (reducible))

The residual solid from carbonate fraction of metals was shaken at 85°C in water bath for five hours with 20 ml of 0.04 M Hydroxylamine hydrochloride ($H_3NO.HCl$) in 25% acetic acid (99.83% $C_2H_4O_2$) (v/v).

2.4. Fraction IV (bound to organic and sulfide)

The residual solid from Fe/Mn-Oxide fraction of metals was shaken at 85°C in a water bath for two hours with 5 ml of hydrogen peroxide (30% H_2O_2). Nitric acid (0.02 M HNO_3) was added to reach the pH of samples to 2 ± 0.2 pH units. Subsequently, a second addition of 3 ml of 30% H_2O_2 was added, and pH was monitored during the experiments. Additional acid was added as necessary to maintain the pH of the samples within 2 ± 0.2 pH units and shaken again at 85°C in a water bath for three hours.

2.5. Fraction V (residual)

Finally, the residual solid from the organic and sulfide fraction of metals was digested with a mixture of HNO_3, HF, $HClO_4$, HCl in (4:1:1:1) ratio, respectively, for three hours in a water bath. The residue dissolved entirely, and it is diluted with 50 ml distilled water.

In each operational fraction step the extractions were conducted in centrifuge tubes (50 ml with cap) to minimize losses of solid materials, and centrifuged at 2000 rpm for 30 minutes. The supernatant was filtered through Whatman No. 4 filter paper, and the residue was washed, shaken with 8 ml of deionized water for 30 minutes, and centrifuged, so it was ready for the next step and the washing was combined with the supernatant of each step (25,26,10). The concentrations of heavy metals in all steps were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Varian 710) according to APHA (1998). The analyses of the sequential extractions procedure were being replicated two times.

3. Geochemical Indices

To quantify the degree of anthropogenic contamination of heavy metals in different ranges of concentration in wetland sediments, index of geoaccumulation, I_{geo} and index of pollution, I_{poll} were used. The index of geoaccumulation (I_{geo}) has been used as a measure of bottom sediment contamination since the 1970s, and numerous researchers have employed it to assess the contamination of soils and sediments. It determines contamination by comparing current metal contents with pre-industrial levels. The content accepted as background is multiplied each time by the constant 1.5 in order to take into account natural fluctuations of a given substance in the environment as well as very small anthropogenic influences. The value of the geoaccumulation index is described by the following equation (27):

$$I_{geo} = Log_2\left[\frac{C_n}{1.5\times B_n}\right] \quad (1)$$

where C_n is measured concentration in sediment mg/kg, B_n is geochemical background value mg/kg and the factor 1.5 is introduced to include possible variations of the background values that are due to lithologic variations. The interpretation of the obtained results is as follows: $I_{geo} \leq 0$ practically uncontaminated, $0 < I_{geo} < 1$ uncontaminated to moderately contaminated, $1 < I_{geo} < 2$ moderately contaminated, $2 < I_{geo} < 3$ moderately to heavily contaminated, $3 < I_{geo} < 4$ heavily contaminated, $4 < I_{geo} < 5$ heavily to very heavily contaminated and $I_{geo} \geq 5$ very heavily contaminated.

I_{poll} was presented as a new developed pollution index by karbassi (2008) to evaluate the pollution intensity of metals in sediments as follows:

$$I_{Poll} = Log_2\left[\frac{B_c}{L_p}\right] \quad (2)$$

where B_c and L_p are indicative of, bulk concentration and lithogenous portion, respectively. Since there was not any need in these evaluations to use the shale metal concentrations, the constant factor (1.5) had been eliminated. Here, chemical partitioning results is substituted for the mean crust and shale levels. The interpretation of the obtained results is like I_{geo}.

In the present study I_{geo} and I_{poll} were adopted to assess the pollution intensity in the wetland sediments.

RESULT

Table 1 shows the results of total concentration of heavy metals in sediment samples and in the earth crust. As Table 1 indicates, mean concentration of elements in sediment samples follows this pattern: Fe>Cr>V>Zn>Ni>As>Pb>Cd. The concentration of Fe varies from 20.30 ppt in St3 to 27.81 ppt in St11. V ranges from 107.6 ppm in St1 to 137.50 ppm in St12. Cr varies from 108.60 ppm in St1 to 145.60 ppm in St 11. Zn varies from 103.20 ppm in St2 to 145.60 ppm in St10. As ranges between 17.30 ppm in St2 to 38.85 ppm in St8. Pb varies from 17.30 ppm in St2 to 29.5 ppm in St11. Ni varies between 86.40 ppm in St2 to 114.00 ppm in St7 and Cd ranges between 250 ppb in St2 to 630 ppb in St10. It can be observed that the concentration of metals in the zone A of wetland (St1 to St3) is lower than the concentration in the zone B (St4 to St12). This concept is related to the rivers inflowing to the wetland. Industrial wastewater from Rash industrial city is discharged to rivers and they inflow to the east zone of wetland as illustrated in Figure 2.

Considering formula 1 and replacing data on Table 1 as C_n and the crust content of elements as B_n gives the value of I_{geo} for metals in each station. The results have been illustrated in Figure 3. Base on I_{geo} classification, As places in class 3 i.e. moderately to heavily contaminated. Cd locates in class 2 in some stations that means moderately contaminated (27). Other metals are located in class 1 and 0 that indicates no pollution.

The result data from chemical partitioning on sediment samples are given in Table 2. Because of high experimental costs two stations from zone A (St1 and St3) and four stations from zone B (St5, St7, St9 and St11) were chosen for chemical partitioning. Step 1 and step 2 (exchangeable and carbonate forms) are the easily assimilable fractions and shows the greatest degree of metal mobility. Step 3 and step 4 (Fe/Mn-oxide and organic and sulfide forms) exhibit some degree of mobility, and the step 5 (residual form) corresponds to the part of the metals which cannot be mobilized. Table 2 indicates that the mean value of lithogenous part of metals in sediments follows this pattern:

Fe(83.29%)>Ni(82.74%)>Cr(70.99%)>Zn(65.95%)>V(65.73%)>As(60.05%)>Pb(50.10

)>Cd(49.84%). Figure 4 compares the lithogenous and anthropogenic (nonlithogenic) percentage of metals in selected stations. It is obvious that the lithogenous part of stations 1 and 3 (zone A) is higher than other stations (zone B). This fact can be observed also by computing I_{poll}. Considering formula 2, and replacing data on Table 1 as B_c and lithogenous data from Table 2 as L_p gives the value of I_{poll} for metals in selected stations. Figure 5 illustrates the results. L_p is calculated in this way: (step4+step5)+0.1(total content)(5).

Figure 5 shows that base on I_{poll}, only Pb and Cd in zone B of the wetland are in class 2 i.e. moderately contaminated and most of metals categorize in class 1 i.e. no pollution. It is pointed out that in both indices, Cd is in class 2 but in I_{geo}, As is in class 3 even though base on I_{poll} it is in class 1 and for Pb, it is in class 1 in I_{geo} but in class 2 base on I_{poll}.

The difference between these indices for selected stations is illustrated in Figure 6. To investigate on this difference the cluster analysis was run on the metals base on data from Table 1. Results have shown in Figure 7. The cluster analysis indicated that there is strong relationship amongst all metals (Pearson coefficient> 0.75) especially between Cr and Pb and both of them with Fe. Because Fe originates from natural sources it can be resulted that Cr and Pb originate from natural sources, too (5). It means cluster analysis confirms I_{geo} for Pb. Figure 7 shows strong relationship between Cd and V so it can be revealed that since V originates from anthropogenic sources Cd comes from anthropogenic sources, too (5). It means cluster analysis confirms I_{geo} and I_{poll} for Cd. As has strong relationship with Ni. Since Ni originates from anthropogenic sources As comes from anthropogenic sources, too (5). It means cluster analysis verifies I_{geo} results. Considering this fact that the discharge of industrial wastewater to the Anzali wetland from input rivers is the most important reason for its contamination, it can be concluded that in the case of Anzali wetland, I_{geo} is more reliable than I_{poll}.

Table 1. Total concentration of heavy metals in sediments of the Anzali wetland and mean crust

Sites	Fe ppt	V ppm	Cr ppm	Zn ppm	As ppm	Pb ppm	Ni ppm	Cd ppb
St1	21.80	107.60	108.60	105.90	17.45	17.30	96.70	280.00
St2	21.50	110.50	112.30	103.20	17.30	19.60	86.40	250.00
St3	20.30	108.60	111.30	106.50	18.60	18.80	94.50	260.00
St4	23.26	123.00	121.50	126.20	32.75	23.40	108.50	480.00
St5	22.43	127.00	125.70	116.50	31.65	27.20	112.00	460.00
St6	25.26	127.30	127.60	120.80	30.90	27.90	106.00	520.00
St7	26.54	129.60	131.00	122.60	35.40	26.70	114.00	450.00
St8	23.00	125.80	125.90	114.20	38.85	25.40	101.10	600.00
St9	23.60	125.30	135.20	123.50	29.10	26.40	107.00	480.00
St10	25.23	132.50	140.30	145.60	31.50	25.30	103.00	630.00
St11	27.81	123.00	145.60	128.00	33.45	29.50	107.00	540.00
St12	25.77	137.50	135.80	138.70	27.90	28.30	106.00	540.00
Min	20.30	107.60	108.60	103.20	17.30	17.30	86.40	250.00
Max	27.81	137.50	145.60	145.60	38.85	29.50	114.00	630.00
mean	23.87	123.14	126.73	120.98	28.74	24.65	103.52	457.50
Mean Crust	51.00	130.00	100.00	70.00	5.00	13.00	80.00	200.00

Table 2. Specification of heavy metals in Anzali wetland sediments

metals	Stations	Fractional Steps					nonlithogenous (%)	Lithogenous (%)
		step1	step2	step3	step4	step5		
Fe (ppt)	**St1**	0.25	0.65	4.3	3.5	14.5	12.4	87.6
	St3	0.20	0.60	4.10	3.50	15.30	10.7	89.3
	St5	1.10	3.10	4.80	5.90	17.60	17.7	82.3
	St7	1.00	3.10	4.50	5.20	16.50	18.4	81.6
	St9	1.20	3.20	5.60	5.10	16.20	21.9	78.1
	St11	1.10	2.50	5.20	5.60	15.80	19.1	80.9
	Mean	0.81	2.19	4.75	4.80	15.98	16.71	83.29
V(ppm)	**St1**	10.50	12.60	22.50	20.60	45.30	30.9	69.1
	St3	11.50	11.30	24.30	21.30	46.50	31.0	69.0
	St5	15.00	16.90	28.50	23.40	48.00	35.8	64.2
	St7	15.00	16.90	28.50	23.40	47.60	36.0	64.0
	St9	13.20	15.60	31.80	22.30	48.50	36.1	63.9
	St11	14.50	16.30	34.10	25.80	51.00	35.8	64.2
	Mean	13.28	14.93	28.28	22.80	47.82	34.27	65.73
Cr(ppm)	**St1**	9.60	11.30	14.60	26.50	52.00	21.1	78.9
	St3	10.50	12.30	15.60	25.40	50.30	23.7	76.3
	St5	16.00	15.40	21.30	30.30	46.30	30.8	69.2
	St7	17.60	16.80	22.60	31.20	45.90	32.5	67.5
	St9	19.80	18.60	25.60	32.10	49.60	33.9	66.1
	St11	19.60	17.90	24.60	33.20	52.30	32.1	67.9
	Mean	15.52	15.38	22.60	29.78	49.40	29.01	70.99
Zn(ppm)	**St1**	11.30	18.60	13.20	23.00	44.20	29.1	70.9
	St3	12.30	16.30	14.50	22.30	46.20	28.6	71.4
	St5	18.60	23.50	16.80	23.50	47.20	35.4	64.6
	St7	21.00	23.50	16.30	24.60	49.60	35.0	65.0
	St9	22.30	25.60	17.50	24.20	44.20	38.9	61.1
	St11	21.30	23.10	19.60	23.20	48.30	37.2	62.8
	Mean	17.80	21.77	16.32	23.47	46.62	34.05	65.95
As(ppm)	**St1**	1.50	4.10	5.10	3.20	10.10	34.6	65.4
	St3	1.90	3.80	5.20	3.60	10.50	33.6	66.4
	St5	4.20	6.80	6.80	4.80	11.30	42.5	57.5
	St7	5.60	6.30	6.50	5.00	12.30	41.5	58.5
	St9	5.30	7.50	6.40	4.90	11.60	43.8	56.2
	St11	5.60	6.70	5.90	4.70	11.00	43.7	56.3
	Mean	4.02	5.87	5.98	4.37	11.13	39.95	60.05
Pb(ppm)	**St1**	2.30	5.30	1.30	3.60	6.70	36.4	63.6
	St3	3.10	5.70	1.50	3.80	7.50	37.7	62.3
	St5	4.80	8.30	1.80	3.50	6.80	49.1	50.9
	St7	5.30	8.50	1.60	3.20	6.90	50.4	49.6
	St9	5.60	8.60	2.20	3.10	5.20	56.4	43.6
	St11	5.20	9.30	3.10	3.20	5.90	55.9	44.1
	Mean	4.80	8.08	2.04	3.36	6.46	49.90	50.10
Ni(ppm)	**St1**	7.10	2.60	11.10	34.50	49.30	9.9	90.1
	St3	8.40	2.50	12.30	34.30	51.20	11.3	88.7
	St5	12.60	5.20	15.60	35.00	53.00	17.5	82.5
	St7	12.30	5.30	15.20	35.20	54.80	16.7	83.3
	St9	13.50	5.60	14.80	32.10	46.20	20.2	79.8
	St11	12.30	6.80	16.80	33.20	48.50	20.5	79.5
	Mean	11.82	5.08	14.94	33.96	50.74	17.26	82.74
Cd(ppb)	**St1**	91.00	21.00	35.00	80.00	65.00	40.3	59.7
	St3	85.00	23.00	36.00	78.00	60.00	41.1	58.9
	St5	135.00	74.00	70.00	90.00	80.00	52.1	47.9
	St7	145.00	65.00	70.00	90.00	80.00	52.2	47.8
	St9	136.00	75.00	83.00	86.00	95.00	51.9	48.1
	St11	154.00	85.00	88.00	90.00	98.00	53.5	46.5
	Mean	131.00	64.40	69.40	86.80	82.60	50.16	49.84

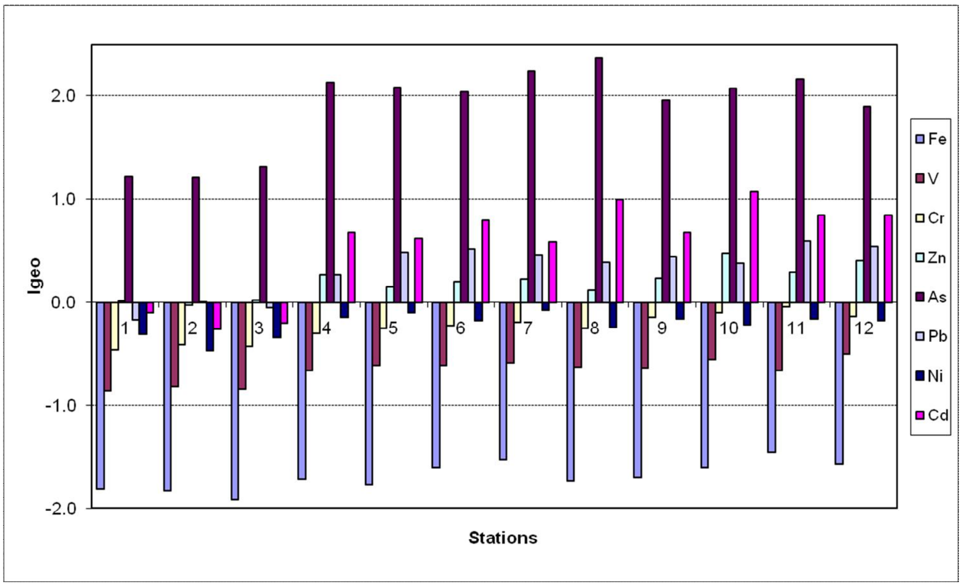

Figure 3. I_{geo} of metals in different sites.

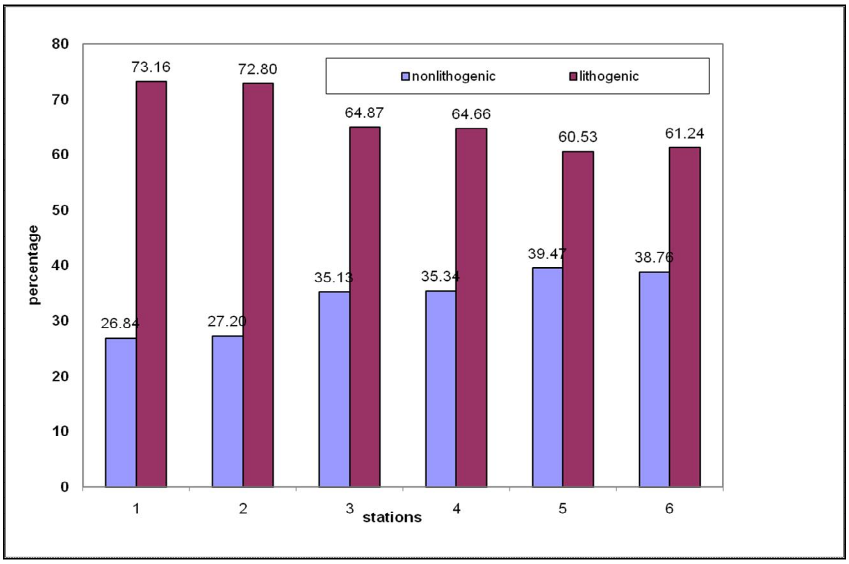

Figure 4. comparison of nonlithogenic and lithogenic part of heavy metals in Anzali wetland

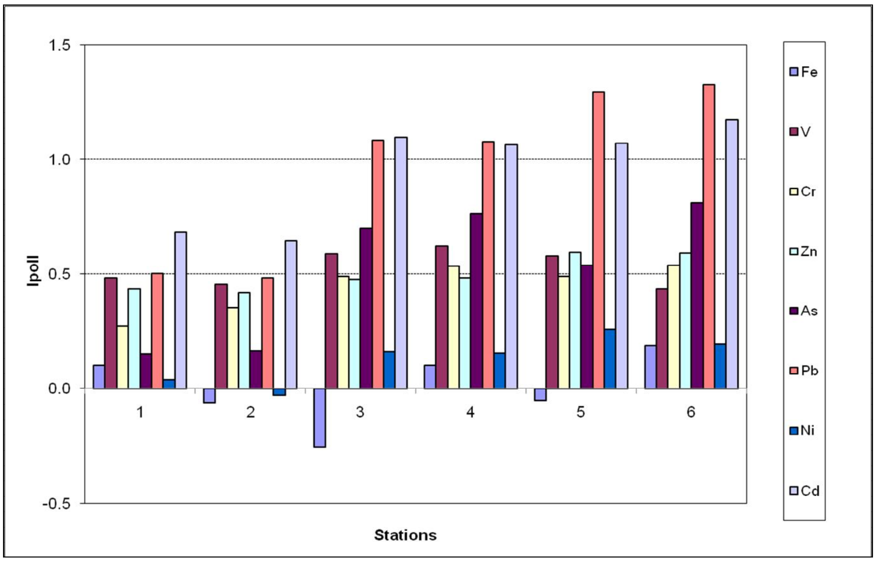

Figure 5. I_{poll} of metals in stations

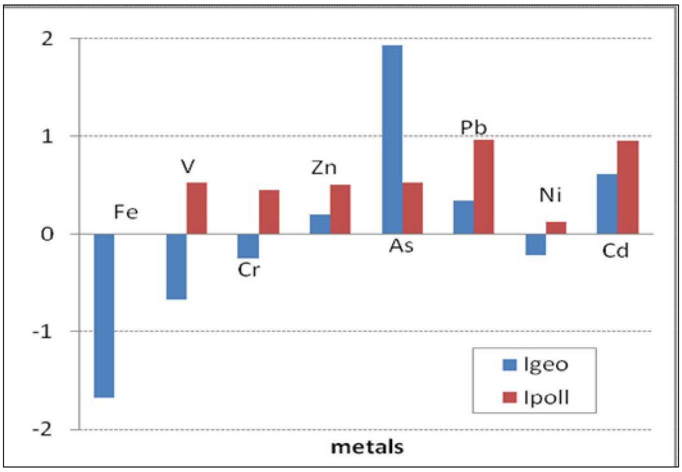

Figure 6. comparison between mean I_{geo} and mean I_{poll}

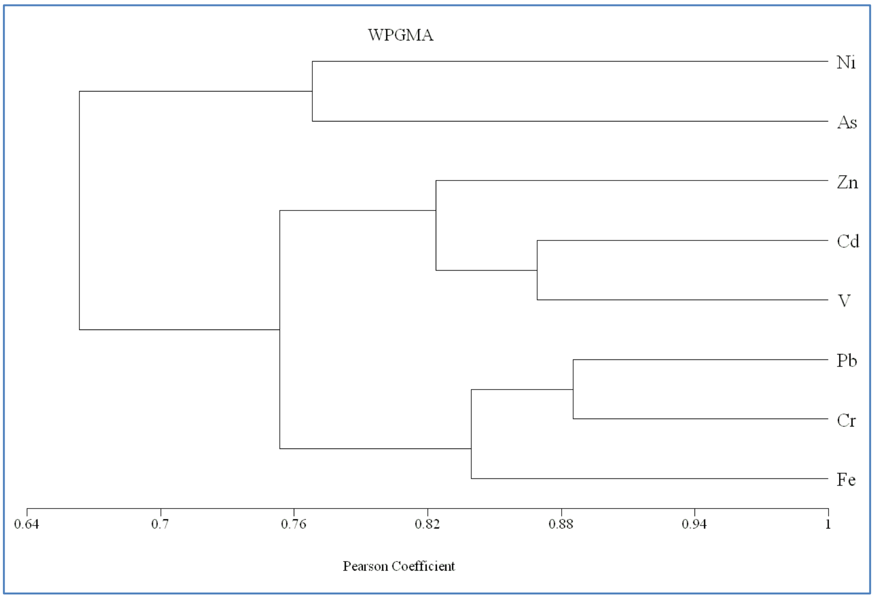

Figure 7. cluster analysis of heavy metals in aAnzali wetland

CONCLUSION

The main objective of this study was to evaluate the contamination of Anzali wetland to heavy metals. To achieve the aim, twelve stations along the wetland were chosen and surfacial sediment samples were collected. Eight heavy metals V, Ni, Cr, Cd, Zn, As, Fe, and Pb were analyzed by total elemental analysis and sequential chemical extraction techniques. Comparing the results of measuring the concentration of mentioned metals with the mean concentration of earth crust showed high contamination level for Cr, Cd, Zn, As, Ni and Pb but to achieve the contamination level of wetland, I_{geo} and I_{poll} as two pollutin indices were computed and compared together. The results showed base on I_{geo}, As and Cd and base on I_{poll} Pb and Cd are pollutants for the wetland. The results of this study showed that I_{poll} index can be effectively applied to show environmental pollution like I_{geo} because it uses background concentrations of metals base on the status of the study area but it is better to check the results by statistical analysis. In this study Cluster analysis was applied. It confirmed the results of I_{geo} and I_{poll} for V, Ni, Cr, Fe, Zn and Cd but for As and Pb it confirmed I_{geo} results. Totally, the results of the present study showed that the Anzali wetland is threatened by pollutants related to rivers entering it because the west zone of wetland that only one river inflows (zone A), the pollution indices have lower magnitude in contrast to the other zone of wetland that nine rivers inflow (zone B). So to preserve the environment of the Anzali wetland from deterioration, the main act is to prevent the discharge of wastewater to rivers entering it.

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