Original Research

An Investigation of Sediment Pollution in the Anzali Wetland

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Received: 3 February 2012
Accepted: 23 May 2012

Abstract

The heavy metals extent and anthropogenic pollution sources in the Anzali Wetland in the southern coast of the Caspian Sea were the main focus of this research. The area of this study is 193 km^2. This wetland has ecological importance as it hosts migratory birds in the southwest Caspian Sea. The heavy metal pollution study as well as some major element determination studies were carried out on the collected core sediment samples from the wetland and the its related major river sediments. Concentrations of Al, Ca, Fe, K, Mg, Na, Mn, P, and Ti, and trace elements such as Li, Ba, Sr, As, Cd, Cr, Co, Cu, Mo, Ni, Pb, V, Zn, Bi, and S were measured and analyzed using ICP-MS. Statistical analyses of cluster and principal component were carried out on these geochemical data. The results showed that the Hendekhale and Shijan sections of the Wetland were the most polluted, whereas the Siakishom section was the least polluted. The results also revealed As, Cd, Cu, Co, Ni, and Mo elements in the Siakishom section and As, V, Pb, Cd, Co, Ni, Mo, Bi, Cr, and Zn in the HendeKhaleh section and As, Cd, Bi, Cu, Mo, Ni, Pb, and Zn in the Shijan section have anthropogenic pollution sources. However, V, Cr, and other selected elements had natural sources. Agricultural activities in the related watersheds were hypothesized as significant contributors of the pollution in the sediments of main parts of the wetland. For future studies, it is recommended to partition the collected sediment samples into coarse, medium and fine particle sizes so that the sources of pollution would be more precisely determined.

Keywords: Anzali Wetland, cluster analysis, principal component analysis, heavy metals, sediment pollution

Introduction

The Anzali Wetland is registered on the Ramsar Convention Accord in 1975, and it is located on the southeast coast of the Caspian Sea and in northern Iran. This wetland is one of the most ecologically important wetlands among the 22 internationally preserved wetlands in Iran, according to this convention. The total area of the wetland is estimated to be 200 km^2 with an estimated length, width, and depth of 30 km, 3 km, and 2.5 m, respectively. The wetland is located at about 20 km to the north of the largest and most populated city on the southeast coast of the Caspian Sea, namely Rasht city. Unfortunately, the wildlife and their biodiversity in the wetland, especially in the eastern sections, is in great danger. The wetland is currently receiving mass and energy flows of 11 midsize catchments and their rivers originating from the northern mountains with relatively steep slopes toward the wetland [1]. These river systems are used for irrigating paddy lands over their courses to the wetland, implying that residues of pesticides, fertilizers, and residen-

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tial sewage are inevitably being transferred into the wetland [2]. Moreover, different wastes from industrial complexes located in the north of the wetland are exacerbating the pollution problem that seems to be a major source of heavy metals pollutions in the wetland [3-5]. Different land use practices in surrounding catchments have been reported to be likely as an additional source of heavy metals concentration [6]. It is expected that heavy metals concentration may increase through water-exchange processes between surface and subsurface sediments being carried by water [7]. Previous studies have reported that heavy metal pollution of Cd, Pb, Cu, Zn, and Ni was traced in the wetland [8].

The current research is concerned with the extent of heavy metals and the effects of anthropogenic sources related to pollution in most of the wetland. The study was undertaken using core sampling, chemical analysis, and subsequent cluster and principal component statistical analysis. However, it must be noted that the variation of heavy metals to the wetland sediments, particularly those that might have been produced from industry and traffic within the last few decades, has not been considered in this study. Therefore, the objectives of this study were to not only investigate the extent and variation of heavy metals in the wetland important sections and sources of metal pollution, but also to look at them as affected by the cumulative effects of the past few decades.

Location Description of the Anzali Wetland

The wetland's watershed consists of 3,500 km^2 located between coordinates of 48º 45' to 49º 42' eastern latitude and 36º 55' to 37º 32' northern longitude. About 2,000 km^2 of the watershed is geomorphologically categorized as pediment and alluvial plains with Quaternary sediments that are north of the watershed, and the rest is mountains consisting of pretertiary, paleogen to neogen formations with some intrusive bodies. The wetland consists of 4 major relatively-distinct sections respectin to depth, physico-chemical properties and ecosystem. Nine major river systems flow into the wetland, among which the Pirbazar River in the east of the wetland is the most polluted. A previous study undertaken by Sharifi [9] showed a salinity gradient extended into the wetland by a distance of 10 km from where the wetland is connected to the Caspian Sea. It is believed that such a salinity gradient may affect the sedimentation processes in this section of the wetland.

Methods and Materials

The river sediments from 11 sites before the sediments entering the wetland were collected using a grab sampler. Sediment cores from 7 sites in the wetland were collected using PVC-tubes. The collection process was undertaken with caution in order for the samples to be true representatives of the wetland sediments (Fig. 1). As shown in Fig. 1, sediment samples of B1, B2, B3, and B4 were taken from the western section, B8 was collected from the eastern part, B9 was taken from the central part, and B10 was taken from the southern section of the wetland. Core samples were sectioned to 0-5, 5-10, 10-20, and 20-50 cm increments. After air drying and sample preparation (e.g. screening of the bulk sediment samples), chemical analysis was carried out for major elements (Al, Ca, Fe, K, Mg, Na, Mn, P, and Ti) and minor elements (S, Li, Ba, Sr, As, Cd, Cr, Co, Cu, Mo, Ni, Pb, V, and Zn). The samples were analyzed using ICP-MS with ME_ME61 standard techniques. Cluster and principal component analyses were carried out on the data using SPSS 16.

Results and Discussion

The wetland could be divided into 4 major sections, based on the receiving sediments from the upper sub-watersheds. As a result, the data analysis was undertaken separately for each of these sections. The results of sediment

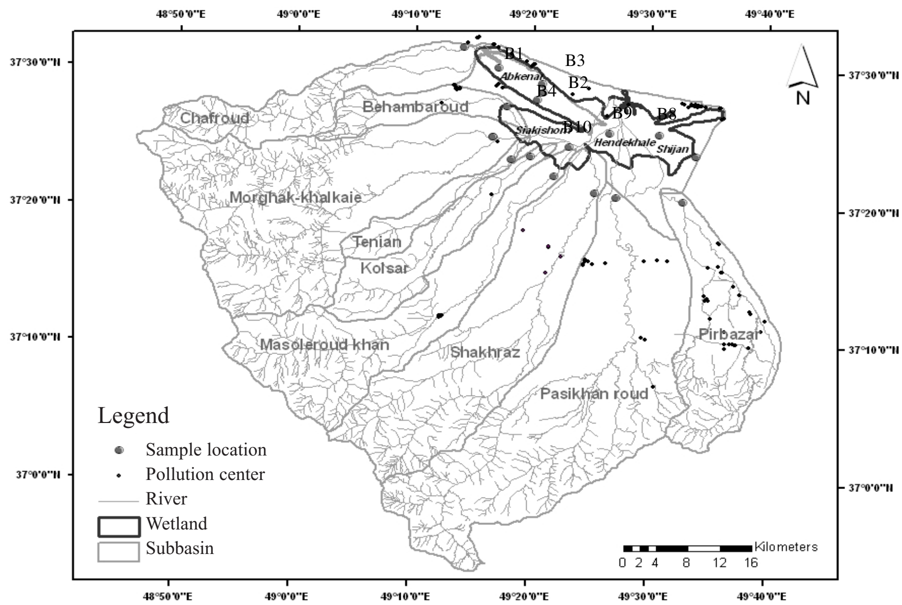


Fig. 1. Sampling sites of the river system and the Anzali Wetland.

Table 1. Elemental analysis of extracted sediment from the Anzali wetland (minor element in ppm and major elements in %).

	ppm							
	Co	Cd	Bi	As	Sr	S	Ba	
	20.97	0.25	0.27	12.49	263.12	16984.78	423.91	
	Cr	Mo	Cu	Zn	V	Pb	Ni	
	98.72	3.28	54.58	109.83	121.33	22.87	68.22	
%								
Ti	P	Na	Mn	Mg	K	Fe	Ca	AL
0.39	0.08	0.86	0.14	1.54	1.95	4.9	2.73	7.5

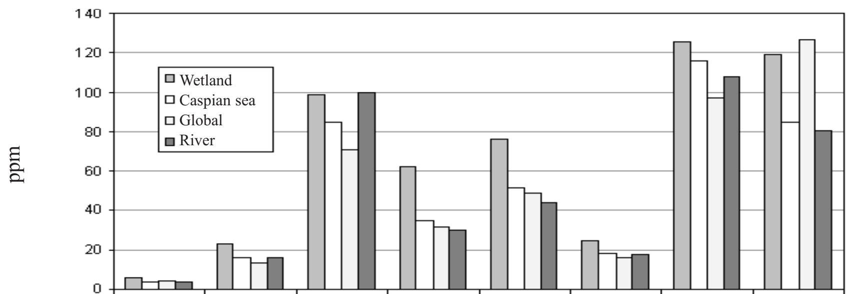
analysis are shown in Table 1. As seen, the results generally revealed a relatively high concentration of heavy metals accumulation in the wetland. The heavy metal concentration results were compared with the mean values of these elements observed in the Caspian Sea, the world, and the river sediments pouring into the wetland (Fig. 2). As shown in Fig. 2, the mean concentrations of Cu, Ni, Co, Cd, V, and Pb of the wetland samples were relatively higher than those of the Caspian Sea, the world, and the Anzali River systems. However, only the mean values of Zn and Cr concentrations from the wetland were slightly lower, as compared with those of the Anzali River systems and world mean values.

When the comparison was made between the concentration values measured in the wetland and those observed in the wetland river systems, the result showed a general increase in heavy metal concentrations in the wetland. Therefore, the fortification ratio of each element should be calculated in order to analyze the extent of possible pollution or abnormal accumulation that is made by these elements in the wetland sediments. The higher concentration values of these elements in the wetland under study had anthropogenic as well as geological sources [10]. Our results also showed the Anzali wetland is no exception in this respect. To further elucidate element sources, cluster analysis and principal component analysis were used for separating human and geologic source differences among the observed concentration values.

Cluster Analysis

Cluster analysis basically intends to cluster geochemical data with similar genesis. As shown in Fig. 3, three main clusters are presented as the technique is used to average linkage within the groups as they are rescaled cluster combined for the Siakishom section of the wetland.

The first cluster with the highest distance includes Al, K, Mg, Zn, Fe, Cr, Ni, Co, Ba, V, Ti, Bi, Pb, Cd, and Ca elements. This cluster consists of elements with geological origin. In contrast, other elements such as Mn, S, and P with the lowest distance and possible agricultural origin create the second cluster. These elements (Mn, S, and P) may be related to the use of paddy soils in extensive rice cultivation in this watershed. Elements of Mn and S could be reduced in the paddy soils of the surrounding watersheds, and in combination with P are absorbed by fine sediments during erosion processes and reach the wetland. The third cluster belongs to As, Na, Mo, and Cu with an intermediate distance as compared to the other two clusters. These elements (As, Na, Mo, and Cu) have anthropogenic sources with industrial and residential origin. In general, As, Na, Mo, and Cu, Mn, S, and P elements have anthropogenic sources, but the major elements such as Al, Ca, Mg, Fe, and some of the race elements mainly have geologic origin. Concentration value of heavy metals such as Cd, Pb, Cu, Zn, and Ni in different sections of the Anzali did not show any seasonal dif-



	Cd*20	Co	Cr	Cu	N	Pb	V	Zn
Wetland	5.70	22.50	98.43	62.34	75.94	24.48	125.63	118.97
Caspian sea	3.20	15.90	85.20	34.70	51.60	18.00	116.00	85.30
Global	4.00	13	71	32	49	16	97	127
River	3.18	16.10	99.64	29.87	43.65	17.75	107.64	80.73

Element

Fig. 2. The mean values of heavy metals of the core samples from Anzali wetland as compared with those of the Caspian Sea, the world, and the Anzali river systems.

ferences [8]. Further research in this context has been done [11] and it reveals that heavy metals such as Cu, Pb, Zn, Ca, and Cr had significant accumulation in the eastern section of the Anzali Wetland. Meanwhile, none of these studies made any distinction among the natural and geological and man-made sources, and the present study is more focused on the locations of the heavy metals concentration. But it also makes a distinction among the sources using discriminative techniques such as cluster analysis.

Cluster analysis in Abkenar (Fig. 3) shows that only Cu and Mo have natural sources, and Zn has the highest correlation with terrestrial elements. The close correlation between As and S indicates that the As element has been transferred in the sulfide phase [2, 12]. As most heavy metals in the Abkenar section are located in the branches of terrestrial elements with natural sources, man-made contamination is expected to be less in this part of the wetland. The presence of As, P, Na, Mn, Cu, Mo, S, and Sr in a branch is probably due to the contamination of the wetland from agricultural sources, particularly the use of chemical fertilizers and herbicides in paddy fields.

Cluster analysis of sediments in Siakishom (Fig. 3) indicate that, apart from As, Cd, Cu, Co, Ni and Mo, other heavy metals have natural origins. The high correlation between Na and P elements possibly indicates heavy pollution by detergents that are produced by domestic sewage in urban areas. The presence of AS and S elements together demonstrates the transport of As in the sulfide phase. Most detergent pollution is reported and seen in the Siakishom section. Also, in this section, contamination of the sediments results from use of fertilizers and agricultural pesticides due to the presence of As, Na, P, Sr, Ca, Mo, and S in a cluster [13].

The results of cluster analysis show that all of heavy metals except Cu have man-made sources in the Hendekhale section. The presence of Cd and Pb on a branch may show pollution caused by worn tires that could been directly carried by air and settle in the wetland. The close correlation of Mo and S in a cluster indicated the transportation of Mo with S within the transported sediments. The presence of Ba, Cd, Pb, Bi, and Cr in a branch is a sign of a common origin, which in this case (the Hendekhale section) can possibly be due to oil pollution entering the wetland through the shipping channel north of the wetland.

The presence of Co, Cr, and V with terrestrial elements in a branch showed their terrestrial origin in the Shijan section, and heavy metals are linked to man-made sources. The close correlation of P and Na elements is possibly due to detergent use in domestic and residential parts of the wetland. The presence of Ni and Zn elements in a branch can potentially be associated with peeling paint from ships and paint factories on the edge of the wetland. The elements As, P, Sr, Na, Mg, and Ca in a category demonstrate contamination in this part of the wetland caused by the use of fertilizers and herbicides, especially in paddy fields and agricultural land.

In summary, the results showed that As, Cd, Cu, Co, Ni, and Mo elements in Siakishom: As, V, Pb, Cd, Co, Ni, Mo, Bi, Cr, and Zn in Hendekhaleh; and As, Cd, Bi, Cu, Mo, Ni, Pb, and Zn in Shijan all have anthropogenic sources, but other selected elements are linked to natural sources. In this respect, other sections of the wetland were also investigated so that their results show similar trends with some small variations that could be neglected at the present scale of this study.

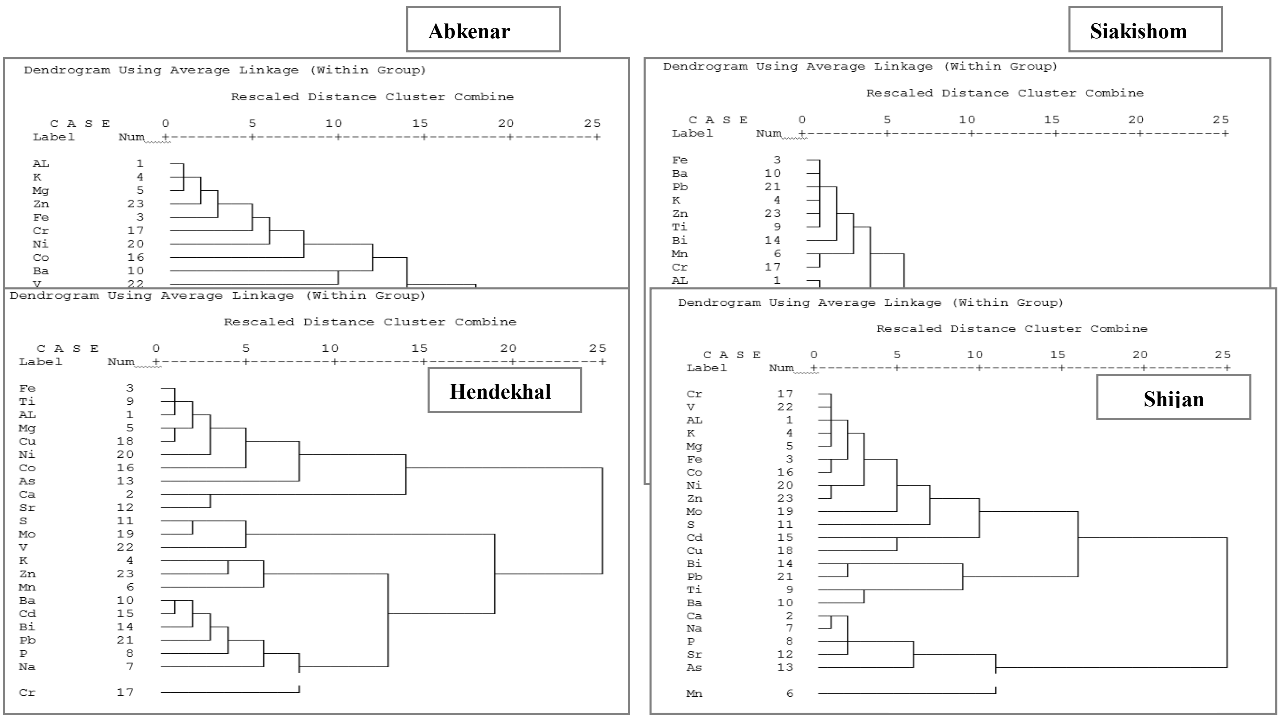


Fig. 3. The results of cluster analysis undertaken in four parts of the wetlands.

Principal Component Analysis

Principal component analysis (PCA) defines a hypothetical relationship among a series of variables, so the main objective of this technique is to reduce the number of main variables defining the existing variation [14] among them. Therefore, in PCA a group of elements that may vary together and have a similar source is determined. The number of columns in the PCA listed table indicates the main factors. In PCA, factors with points more than 0.6 should be selected for interpretation. The Kaiser-Meyer-Olkin (KMO) measure shows the accuracy level of the sampling and as the p-value is closer to zero Barrlett's Test, the result of the PCA is considered to be more precise. A rotated component matrix leads to selection of those elements that are varied together and correlated.

As shown in Fig. 4, there are three groups in the PCA rotated space. In the first group, the variance is estimated to be 30.53% and has the highest rating. The elements of the first group consist of Ni, Cu, and V, which are correlated and rotated together. As this group of elements is related to Ni, they therefore have natural or geological sources. The second group, with a variance of 29.10%, consists of Cd, Zn, Pb, and Cr elements. The lowest variance belongs to the As and Co group, with a value of 18.74%. The elements exited in these three groups have different sources.

Component Plot in Rotated Space

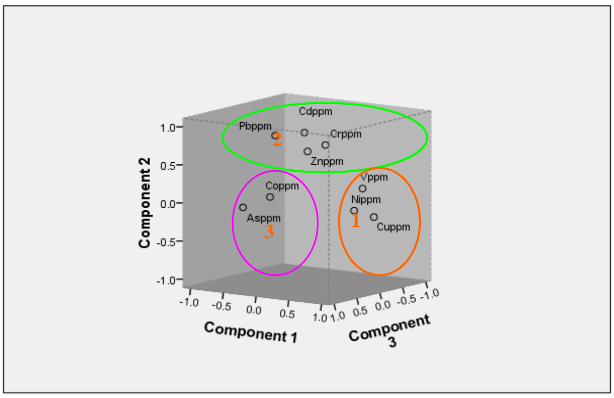


Fig. 4. Component plots for PCA rotated space results.

Component Plot in Rotated Space

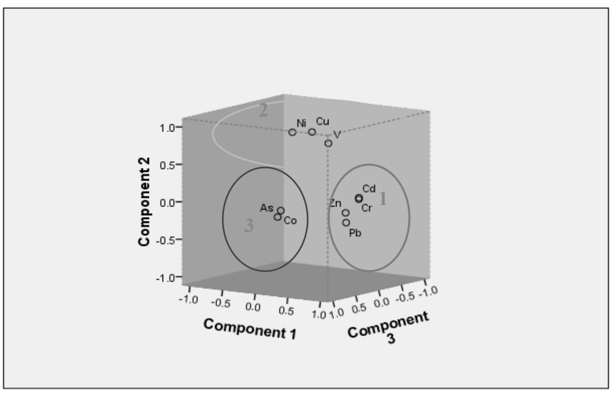


Fig. 5. The effect of normalization with Al on PCA rotated space results.

The application of normalization technique, using Al element, could significantly change the elements in the first and second groups. Normalization with Al element considers the effect of size in the interpretation [15]. In this case, normalization has improved the p-value so that it decreased variance from 30.53% to 34.04% in the first group with Cd, Zn, Pb, and Cr elements (Fig. 5). The second group, consisting of Ni, Cu, and V, has reached a variance of 23.38% after normalization. However, no change has been seen in the elements of the third group after normalization. It is quite clear that the normalization technique has made a significant shift in the elements correlated together. Therefore, the normalization impact is considerable and should be taken into account once the samples are fractioned for elemental analysis and more importantly in future studies, the samples should be partitioned into at least three size groups so that normalization works better.

Conclusions

In this study statistical analysis by clustering technique revealed that in the Abkenar section of the wetland As, Mo, and Cu; in Siakishom As, Cd, Cu, Co, Ni, and Mo; in Hendekhaleh As, V, Pb, Cd, Co, Ni, Mo, Bi, Cr, and Zn; and in Shijan As, Cd, Bi, Cu, Mo, Ni, Pb, and Zn have anthropogenic pollution sources. However, V, Cr, and other selected elements have natural sources. In sections such as those of Abkenar, Siakishom, and Shijan, the agricultural activities have significant contribution to the pollution causes, and hence controlling efforts should be directed toward these activities.

The particle size effect of the samples should be considerable as it takes into account once the samples are fractioned for elemental analysis for heavy metals. Elements such as Ni, Cu, and V are concentrated in fine-sized sediments and they are correlated with Al, and therefore they have geological origin. Elements such as Cd, Cr, Zn, and Pb are more likely concentrated in the coarser sediments. Pollution control measures should be focused on these elements and related human activities, inducing them to reduce sediment pollution. Increasing sample numbers in Hendekhale and Shijan sections is strongly suggested and, finally, phytoremediation [16] is recommended for pollution reduction in the wetland, as the environment is suited for such practices.

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