Metals Pollution Assessment of Surface Sediment in Anzali Wetland and Their Quality Zonation

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Introduction: Heavy metals are originated from natural or anthropogenic sources. Mining activity, fuel combustion, urban discharge, pesticides, agricultural and industrial activities are considered as the m ain anthropogenic sources of the metals. Generally, more than 90% of the toxic metals load in aquatic systems is bound on solid phase of the aquatic systems such as suspended matter and sediment. Thus, assessment of heavy metals pollution in aquatic sediment is a critical issue that has been studied by many researchers. Anzali International Wetland was registered in Ramsar Convention in 1975 (Ramsar site #40, Wetlands International Site Reference No.: 2IR005). It is located in Guilan Province (between 48°45' and 49°42'E longitude and 36°55' to 37 32'N) and covers 192 Km2 that is considered as the main freshwater coastal wetlands in southern part of the Caspian Sea. Its catchment area with prevalent agricultural activities is about 3610 Km2. Moreover, presence of 41 major factories such as wood and paper mill companies, food industries, metal and related industries, plastics and tires, textile and electrical machines are samples of anthropogenic sources in the study area. In the present study forty one surface sediment samples in January 2011 were collected from Anzali International Wetland to assess metals pollution state and sediment quality zonation. Moreover, metals pollution assessments in the study area were conducted using different existing indices, multivariate analysis approach and GIS tools.
Materials and Methods: The collected samples transferred to the laboratory in sealed plastic bags under 4C. After digestion using HNO3/HCl/H2O2 according to U.S.EPA 3050B test method, total metal (Cu, Zn, Cr, Fe, Mn, Pb, Ni, Cd) contents were determined using Atomic Absorption Spectrometry (Bulck Scientific 21 VGP). Moreover, sediment quality indices such as Modified degree of Contamination (mCd), ecological Risk Index (RI), and Enrichment Factor (EF) were applied to assess metal pollution state. In addition, multivariate statistical analysis was conducted to determine probable sources of metals in the study area and interpret data. The investigation was conducted by Principal Component Analysis (PCA).
Results and Discussion: According to total metals content, the higher mean concentrations of all studied metals (except for Cr) were found compared with those of earth's crust and mean world sediments. Moreover, the minimum content of Zn and Pb are also higher than earth's crust content. Based on zonation maps about metals distribution, the samples with the minimum metals concentration were located in central part and Siahkeshim (Protected area) of the study area where there is no main sources of pollution. Moreover, the higher concentration of Cu, Zn, Cr, Pb, and Cd were determined in eastern and northwestern part of the study area. These parts are affected by river discharges that pass through the more populated, industrialized and higher levels of agriculturalactivities areas. However, no distinguished distribution pattern of Fe, Mn, and Ni were detected. Overall, it could be concluded that central and northern parts of the wetland that are less exposed to the sources of pollution demonstrated to have higher concentrations of Fe, Mn and Ni. Moreover, results of applied aggregative indices such as ecological RI and modified degree of contamination (mCd) revealed higher degree of metals pollution in the eastern part. Fig. 1 depicts metals pollution state based on RI and mCd. In addition, the Cluster Analysis (CA) was applied to heavy metals concentrations in Anzali Wetland to verify probable metals relationship. The CA of variables based on Pearson Coefficient identified five clusters: 1. Cu-Zn; 2. Cr-Pb; 3. Cd; 4. Fe-Ni 5. Mn. The first cluster named A including metals (Cu, Zn, Cr, Pb, and Cd) that exhibited higher degree of enrichment may indicate that they were originated fromanthropogenic sources. However, it seems that Cd might be derived from different anthropogenic sources. The second cluster named B was made by Fe and Ni. It may be concluded that Ni and Fe are originated from same sources, while Mn in cluster C has separate sources. Results of multivariate statistical analysis demonstrated three main principal components with their eigenvalues greater than 0.8. The cumulative variance of the components was about 81% of total variance. The high positive loadings for Cu, Zn, Cr, and Pb, and moderate positive loadings of Fe, Ni, and Cd were extracted in the first component with 46% of total

variance. The loadings level of these two groups was not the same, so it could beconcluded that Fe, Ni, and Cd may be originated from the different sources. In general, high loading values of Cu, Zn, Cr, and Pb in the first component may imply the anthropogenic sources of these metals. The positive loadings of Fe, Ni, and Mn were found in second component with 24% of total variance. This fact may indicate natural sources of theses metals. Cd is dominant element in the third component with 11% of total variance. Results of PCA are depicted in Fig. 2. According to the results of PCA, it can be concluded that the first and the third factors are originated from anthropogenic source like agricultural and industrial activities, and discharge of urban wastewater and leaching from prevalent dumping waste in open space that is considered as the main waste disposal methods in the north of Iran.
Conclusion: In the present study, metals concentrations in surface sediments of Anzali Wetland were determined. Many prevalent and useful indices such as mCd, ecological RI, and EF were applied to assess metals pollution state in the collected samples. Moreover, based on the results of applied indices and total metals content, sediment quality zoning were performed using GIS software. Overall, it could be concluded that aggregative indices such as mCd and RI could assess metals pollution state in surface sediments of the study area in an acceptable manner. According to the obtained results, eastern parts of the Anzali Wetland were more polluted than the other parts of the area. Moreover, concentration of all studied metals except Cr was higher than those in the earth crust.Application of multivariate statistical analysis also revealed that Cu, Zn, Cr, Pb, and Cd may be originated from anthropogenic sources and metals like Fe, Mn, and Ni might be derived from natural sources in the study area.

Anzali Wetland, ecological risk, GIS, heavy metals, multivariate statistical analysis