

GEOCHEMICAL FRACTIONATION AND RISK ASSESSMENT OF HEAVY METALS IN ANZALI WETLAND, IRAN

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Introduction

Metals present in sediments have a significant impact on the health of aquatic ecosystems. Since the environmental behavior of metals in sediments depends heavily on their chemical forms and affects their toxicity for organisms, concentration measurement of metals cannot solely provide sufficient information in terms of their mobility, bioavailability and potential risks to marine ecosystems. This calls for chemical partitioning studies to reach the source and type of transplants. Among different parts of geochemical sediments, labile fractions are the result of metals entrance due to human activities on aquatic environments and the residual fraction as a result of their natural existence in the Earth's crust. Studies show that metals usually have the highest bioavailability in the exchangeable fraction and the lowest in the residual part (Shirneshan et al., 2013; Gu et al., 2014).

Methods

In this study, a minimum of three samples of surface sediments were taken from five parts of the surface layer (0-3 cm) of the wetland using Van vine grab. For the preparation, at first the samples were converted into powder through grinding by the dry stone in the freeze-drier. The preparation of samples for their concentration determination was as follows: 1gr of each dried sample by a mixture of nitric acid perchloridric acid in a ratio of 4:1 digested on the Heating block (140 degrees) for three hours. In order to determine the source of metals in sediments, sequential extraction method, which is one of the simulation methods of releasing metals in natural environments, was used to predict the possibility of the impact of metals on living organisms in aquatic ecosystems. To analyze the concentrations of Cu, Zn, Pb and Cd in geochemical sections of the sediments, the modified method (SET), was implemented (Yap et al., 2002):

- The exchangeable form: sample with 50ml 1M Ammonium Acetate and pH 7 on the shaker for three hours
- The form bound to oxides and hydroxides of iron and manganese: The remaining material from the previous step is acidized with Hydroxylammonium chloride placed on the shaker for three hours
- The form bound to organic matter: The remaining material from the previous step is oxidized with Hydrogen Peroxide in a water bath at 90-95 °C; after cooling down, it is placed on the shaker with Ammonium Acetate
- The residual form: The remaining material from the third step is first placed on the digestive device with a mixture of nitric acid and perchloridric acid in a ratio of 4: at 140 degrees for three hours

At the end of each step the concentration of the metals in the sample sediments were determined using the Atomic Absorption Spectrometry (AAS) and the results were shown in microgram per gram of dry matter.

Results

In order to evaluate the effectiveness of the sequential extraction method, using the comparison of the total of four sections of separated metals with the total concentrations of metals were examined. Recovery range was between 97-103%, indicating the reliability of the test method used. The mean percentages of concentration share of metals in different geochemical parts of the sediments are as follows:

Exchangeable fraction: Pb (0.02) < Zn (1.35%) < Cu (1.42%) < Cd (2.70%)

Bound to Fe/Mn oxides: Pb (0.01%) < Cu (0.17) < Zn (5.36%) < Cd (9.46%)

Bounded to Organic Matter: Cu (12.26%) < Zn (12.50%) < Cd (46.62%) < Pb (94.28%)

Residual: Pb (5.69%) < Cd (41.22%) < Zn (80.79%) < Cu (86.15%)

According to the results of the current study, Cd has the highest share of extractable section of acid than other metals, which indicates its higher potential environmental hazards in comparison to the other metals under study and is consistent with the results of Sakan et al (2013). Due to their large areas, iron and

manganese oxides have high adsorption and have been known as effective phosphating cleaners with a regulatory impact and may provide a sink for heavy metals. The sustainable phases of metals have very low toxicity to organisms in aquatic environments; since the metals in this fraction have been bounded in a crystalline matrix, they are not expected to release into the environment under normal conditions. Cu and Zn have mainly made connections with the residual sections. Significant amounts of Pb in sediments have been bounded to organic matter which in spite of low mobility may become mobile through oxidation of organic matter in prolonged periods of drought or microbiological activities. Organic matter in the sediments probably plays a key role in the control of Pb speciation in sediments under oxide conditions the labile fractions suggest the following descending trend for the metals under study, which agrees with the results of Davutluoglu et al (2011). The percentage of concentrations in labile fractions: Cu (14%) < Zn (20%) < Cd (59%) < Pb (95%). Based on the results obtained from the source determination of the metals under study, Cu and Zn have significantly higher natural sources than anthropogenic ones, whereas Pb has a significantly higher anthropogenic source. Regarding Cd, except for stations 2 and 3, the rest had higher anthropogenic sources compared to natural ones and had a higher percentage of anthropogenic than natural source in general. According to the results of the individual contamination factors (ICF), Cu and Pb had the highest amount in the second station, Zn in the fourth one and Cd in the fifth. Rare metals tend to accumulate in sediments from any source and in hot spot near the entrance and then disperse regionally in lower concentrations. Therefore, the results of global contamination factors (GCF) showed that sediments of the second and fourth stations had the highest amounts of contamination respectively, which is justifiable due to the commute of entertainment boats in these two areas as well as wastewater entrance observed in these two stations. Chemical forms of metals, especially in the exchangeable section, affect their toxicity on the living organisms of aquatic systems. In total, metals existing in the first section have weak bounded and therefore cause greater risk. RAC amounts of metals in sediments of Anzali wetland and results of Yuan et al. (2014) are as the following decreasing trend: The mean concentration of metals in the exchangeable fraction: Cd > Cu > Zn > Pb. The mean concentration of metals in the exchangeable fraction: Cd > Pb > Zn > Cu (Yuan et al., 2014). According to the classification of Risk Assessment Code Cu, Zn and Cd are considered low risk (1-10%) and Pb is evaluated without risk (<1%).

Conclusion

Although the highest concentration percent of metals in the labile fractions belongs to Pb, this metal mainly exists in the form bound to organic matter. Hence, compared to other man-made fractions Pb is of more stability in the environment; This is while Cd shows the highest concentration percent in the exchangeable form and therefore in terms of environmental studies, it can be said that compared to Pb, Cd has a higher risk of transferring the contaminants from the sediments into the food chain which accords with the results obtained from the Risk Assessment Code. It seems, the related rules allow the minimum concentration of Pb in sediments to be more than Cd. Self purifications is among the factors reducing the concentration of heavy metals in natural ecosystems, especially in wetlands, and acts as a sediment trap to protect absorption and prevent the contamination of the Caspian Sea. However, the intensity of human and industrial activities in the catchment pond of the wetland together with the urban and rural areas surrounded by large agricultural landscape, lead to an increase in the concentrations of heavy metals in this natural ecosystem. Accordingly, to determine the state of the environment and carry out the possible measures for the sustainability of these environments the potential for the sustainability of the situation, environmental monitoring and developing the necessary strategies required to reduce local pollution seems necessary.

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