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Ecological risk assessment of heavy metals (Zn, Cr, Pb, As and Cu) in sediments of Dohezar River, North of Iran, Tonekabon city

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ABSTRACT

Sediments of the Dohezar River in Tonekabon contain high levels of heavy metals and therefore, they were chemically analyzed to determine concentrations of these elements. In fact, this research intended to evaluate the ecological risks of the heavy metals As, Pb, Cr, Zn, and Cu in the river sediments. Contamination indices such as enrichment factor and contamination factor, potential ecological risk index for each heavy metal (Ei), and potential ecological risk index (RI) were evaluated. Considering the average concentrations of the heavy metals at all of the Stations, the maximum average for the elements was zinc and the minimum was copper. Therefore, the averages of changes in the concentrations of the elements are Zn > Cr > Pb > As > Cu. Considering calculation of the enrichment factors for the heavy metals according to the EF classification table, the maximum number of Stations (43.02%) with respect to contamination with As were in class 4(moderately severe enrichment). With respect to enrichment of Pb, Zn, Cr, and copper, the rest of the stations with 83.72, 77.91, 86.05, and 69.77%, respectively, were in class 2 (minor enrichment). Considering the high concentrations of the studied elements in the sediments of the region compared to the background value, and based on calculations related to contamination factor, arsenic with the average of 11.9 exceeded the most from the standard limit. It was followed by Pb with 2.2, zinc with 2, Cr with 1.8, and Cu with1.6 (copper exceeding the least from the standard limit). With respect to Ei (the potential ecological risk index for each heavy metal), arsenic was the element with the highest environmental risk. Moreover, with respect to RI (potential ecological risk index), most Stations were in the low-grade range (low environmental risk). This research used statistical studies on correlation coefficients and cluster analysis to find the origin of the heavy metals in the sediments of the region. The low correlation between the heavy metals in the soil can indicate they probably did not have the same source. Moreover, these elements have different geochemical behaviors due to their low correlation. Finally, the kriging method was employed to extract interpolation maps of the spatial distribution for each of the heavy metals.

1. Introduction

Heavy metals are concerning pollutants because they are not biodegradable and, once they reach a certain concentration, are quite harmful to the environment [1]. Sediments are considered significant sources of these pollutants and play an important role in environmental risk evaluation [2]. Sources of heavy metals in the environment include natural resources such as runoff, rock weathering, and river bank erosion [3], and human sources including agricultural activities and liquid waste disposal and discharges of industrial and urban wastewater [4,5,6,7]. Many of heavy metals and suspended particles are carried by seawater, runoff, weather conditions, discharge of wastewater, and by other human and non-human factors and are concentrated in surface sediments because of their low in aquatic environments. Therefore, sediments are considered the main source of heavy metals and other chemical materials [8], and distribution of heavy metals in sediments can act as an indicator to reflect the extent of water pollution [9,10]. Because of their adsorption, hydrolysis, and precipitation, only a small portion of free metal ions can be carried by flowing water and a major part of them is stored in sediments [11]. The pollutants can be released from the sediments when environmental conditions such as electrical conductivity (EC), pH, temperature, sediment particle size, oxidation–reduction potential change in the water or in the sediments and can cause secondary pollution to the water environment [12]. Heavy metals such as arsenic, copper, zinc, chromium, lead, etc., are generally metallic pollutants found in sediments and agricultural soils [13], tidal zones and swamps [14], and water systems and wetlands [15]. Because of adsorption, hydrolysis, and coprecipitation, only a small portion of free metal ions could be taken away by water flows (e.g., flooding or rainfall runoff) and a large quantity of them get deposited in the sediment [11], which endangered human health by food cycle [16]. Certainly, river and lake sediments are not only a storage place for heavy metals but are also considered potential secondary sources of heavy metals in

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water systems [17]. Consequently, the investigation of sediment quality is an essential and prime component of aquatic ecosystem assessment studies [18]. To evaluate accurately accumulation of heavy metals resulting from human and natural sources, enrichment and geo-accumulation indices are used as complementary methods of evaluating the degree of sediment pollution and, finally, the method of evaluating the potential environmental risk is employed to determine the risk level caused by sediment pollution [19,20,21,22,23]. The objectives of this study were to measure the contents and distribution of some heavy metals in surface sediments of Dohezar River. The goals of this research were (1) to evaluate the concentration level and distribution of the heavy metals in the sediment; (2) to accurately quantify the extent of heavy metal pollution using the enrichment factor (EF) and contamination factor (Cf); (3) to assess the potential ecological risk of heavy metals in sediments; (4) to analyze possible sources of heavy metals in sediment using the Pearson correlation analysis, cluster analysis (CA);and (5) present the investigated parameters visually by using GIS based maps. When the location of the study area and the anthropogenic pressure on the system were considered, it can be clearly understood that the investigation of sediment quality and determining heavy metals concentrations in sediment of Dohezar River.

2. Materials and methods

2.1. The study region

Tonekabon with longitude of 55°50′ East and latitude of 36°48′ North, length of about60 and average width of 30 km, and an area of about 2140 km^2, is located south of the Caspian Sea. Because of its proximity to the Caspian Sea, Tonekabon has a temperate northern climate with a considerable amount of rainfall. In the coastal plains of Tonekabon, it usually rains in all the seasons of the year, most of it (almost 70%) in the fall and winter.

Climate has substantial effects on the regime and water network of the related region. There are rapid flows and flood currents upstream of these rivers with substantial riverbed destruction all along the courses of the rivers. Downstream of the rivers, flow rates decline with the flattening of the riverbeds in the plains region, and the rivers flow gently towards east and enter the Caspian Sea. In the past, the sea level was lower and the rivers could flow into the estuaries and easily empty their sediments into the sea. However, the prevailing conditions of today are different. The sea level has risen and roaring waves prevent the rivers from progressing into the estuaries and, hence, riverbed rise with increasing sedimentation in them, with the sedimentation reaching its maximum at the time of flood currents. To have access to the study area, the grade 2 forest road from Tonekabon to the Dohezar heights must be use. After passing the Khorramabad District and moving on towards the Dohezar valley, we will enter the study region.

2.2. Sampling method and sample preparation

According to the map of 1:50,000 topography of the area, the watershed and catchment area were determined. Sampling points were indicated with using the geological map of the region, the rock units that are prone to production of heavy metals, and the land use map. Furthermore, specified points for sampling were scanned to digitization and a list of samples with their coordinates was provided in the UTM system. Sediment sampling was done using sample coordinates and a sampling map and the use of a GPS device.

Samples were taken by dropping 10 cm first of the soil. The region of sampling was the low energy part of the river where the sediments had accumulated. Then from every sampling point were taken 5 kg sample of sediment, after drying was passed of 80 mesh sieve (about 2 mm) then was kept in appropriate polyethylene bags. At 4 °C, the number of samples was recorded on them as label.

After the final control of the label number with the relevant list, samples were sent to the laboratory for analyzing. Process of preparation begins with grinding. After initial homogenization, the samples are powdered in a volume of about 25 cm^3 to about 200 mesh (some parts of this powder are stored for future reference). The powdered samples are digested by solutions of HCL and HNO_3 (in the ratio of 3:1) and they are chemically analyzed using the ICP-Mass (Inductivity couple plasma a mass spectrometry) method. In this study, geochemical samples were sent to the AMDEL Laboratory in Australia for analyzing of some heavy metals (Zn, Cr, Pb, As and Cu) in samples of sediment.

3. Statistical analysis of the data

Data was analyzed using the statistical version 16 of SPSS and correlation analysis and cluster analysis were performed to identify correlational relationships between concentrations of heavy metals in the river sediment samples. The version 10.1 of Geographic Information System (GIS) that is known to be designed to capture, store, manipulate, analyze, manage, and present all types of spatial, geographical or environmental data provides visual summaries of investigated data to make them easy to evaluate in especially environmental assessment studies [18]. Moreover, the kriging method, the spatial distribution of the heavy metals at the various stations was processed and interpolated [24,25,26]. Geostatistical estimation consists of two stages. The first stage involves collecting information and modeling the spatial structure of the variables, and the second stage is estimation of the required variables obtained from the first stage [27].

3.1. The kriging method

Like the weighed moving average method, the kriging method is used to derive predicted values for unmeasured locations by giving weights to the surrounding measured values:

$$Z^* = \sum ʎ Z(x_i)$$

Z^* expresses the spatial value of the variable, and Z(xi) the spatial value of point xi which indicates the importance of the predicted point. Use of this estimator is possible if the distribution of the x variables is normal. Otherwise, the non-linear kriging model must be used, or the distribution of the variables must be normalized [28].

Kriging is the most suitable model for expressing spatial correlation and/or for data, and it is often used in application programs in soil sciences and geology. The kriging method is based on weighted moving averages, which is the best linear unbiased estimator with minimum variance [27].

The predicted values are derived from the values of the measured samples using the weighted average method. This most important and most widely used interpolation method, and is based on basic statistical models and relationships. The raster layer produced in this method shows a very accurate surface. Unlike the IDW method that is a local interpolation method, the kriging method is a global method; that is, all observations made in the region under study are utilized in this method [25].

4. Methods for evaluation of sediment pollution by heavy metals

There are several global methods for evaluating sediment pollution by heavy metals including the geo-accumulation index (Igeo), enrichment factor (EF), and the potential environmental risk index (PERI) methods, each of which has its own various and special merits [29,30,31]. General conditions related to pollution by heavy metals can be identified using the enrichment factor (EF) method that is employed for evaluating concentrations of heavy metals. However, the sources of pollution are recognized with difficulty in this method. Moreover, examination of the results cannot show the chemical activities or bioaccumulation of heavy metals. Therefore, EF is not able to evaluate the

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