Evaluating of heavy metal pollution in Amir-Kalayeh wetland using geochemical and statistical analyses
Maryam Zare Khosheghbal and Marjan Esmaeilzadeh

ABSTRACT

Metal pollution in aquatic ecosystems has created concern due to its toxicity, environmental stability and ability to transfer into the food chain, and monitoring the metal source is one way to decrease the environmental impact. The present study aimed to investigate metal concentrations of Al, Fe, Mg, P, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, and Zn, their spatial distribution, origin of the contaminants, contamination factor (CF), pollution load index (PLI), enrichment factor (EF), and geoaccumulation index ($I_{geo}$) in surface sediments of the Amir-Kalayeh wetland. Using statistical methods such as Pearson correlation coefficient, cluster analysis and factor analysis, the natural or anthropogenic origin of these elements was determined. According to the results, As, Cd, Mn, Mo, and Pb have CFs higher than 1, which means they have contaminated the area. In this research, PLI was 0.9, which means the sediments of Amir-Kalayeh wetland are not polluted. The highest EF belongs to Mn and Mo. Determining $I_{geo}$ showed that none of the metals in Amir-Kalayeh wetland are within the pollution range. However, the enrichment of elements in the sediments shows that continuous monitoring and managing of metal pollution source in this wetland is an essential step.

Key words | Amir-Kalayeh wetland, enrichment, geochemical, metal, pollution

INTRODUCTION

The pollution of aquatic ecosystems by heavy metals is a global issue (Bai et al. 2011a; Yi et al. 2011; Gao & Chen 2012). In the third world countries, the lack of accurate equipment for tracking and monitoring water pollution has caused further exposure to the pollutants (Lu et al. 2010). Among aquatic ecosystems, wetlands, due to their unique ecological feature, are of high importance and preserving them is of the highest environmental priority (Bai et al. 2011b; Esmaeilzadeh et al. 2016b). One of the major problems that heavy metals cause with respect to their effects on aquatic organisms is their long biological half-life. Therefore, they are among the most frequently monitored micro-pollutants and reliable techniques have been established for their extraction and quantification, since sediment contamination by heavy metals in rivers and estuaries has become an issue of increasing environmental concern (Bolawa & Gbenle 2012; Vesali Naseh et al. 2012; Mohammadizadeh et al. 2016). These contaminants are stored in the water and sediments and enter the human food chain through aquatic creatures’ food and cause many health problems (Brix 1994; Sakar et al. 2011; Neyestani et al. 2016). These contaminants can be natural – i.e. caused by the geology of the region – and a region without any type of anthropogenic pollution can contain high amounts of heavy metals due to its own geology (Lacerda et al. 1998). Natural and anthropogenic contamination can enter wetlands by the drainage basin system and contaminate the water and sediments of the wetland (Abdallah & Mohamed 2013). Given the importance of aquatic ecosystems and their contamination, determining the origin of the elements and examining the pollution level of sediments in Amir-Kalayeh wetland was the main goal of this research, and in order to achieve this, statistical and geochemical analyses were employed.

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MATERIALS AND METHODS

Study area

Amir-Kalayeh wetland, due to its unique ecosystem for migratory birds, was listed in the Ramsar international wetlands in 1975. This wetland, with an area of 1,132 acres, is located near the Caspian Sea, between 50° 09’ 57.6″ to 50° 12’ 22.5″ north and 37° 18’ 07.9″ to 37° 22’ 16.8″ east. Its mean depth in the eastern part varies from 1.5 to 3.5 m and the eastern part is covered with everglades.

Water inputs are located in the southern part of the wetland, and consist of agricultural wastewater discharged to the wetland and groundwater resources. There are two discharging waterways in the north and north–west of the wetland, one of them transfers water from the wetland to the Kohneh Sepidrood River which is 1.5 m lower than the sea level. The other waterway transfers water from the wetland to the sea. In summer, the Kohneh Sepidrood is blocked to maintain the water level of the wetland. The total water that enters the wetland is about $1.5 \times 10^7$ m$^3$. Another feature of this wetland is that unlike other wetlands of the province no river enters it and the entry flow is insignificant; hence, no sediment will enter the wetland (Nezami Balouchi Shaaban et al. 2007; Sedigh Chaafjiri et al. 2013).

Methodology

To investigate the pollution, samples were taken from the wetland’s sediments in different parts, and after analysis and determining the concentrations of different elements, the results were analyzed in two steps. First, using statistical methods such as Pearson correlation coefficient, cluster analysis and factor analysis, the anthropogenic or natural origin of the elements was determined. In the next step, in order to find the geochemical characteristic of the sediments and identify the pollutants in the wetland, specific indicators such as contamination factor, pollution load index (PLI), enrichment factor and geoaccumulation index of the region were employed (Figure 1).

![Figure 1](https://iwaponline.com/wst/article-pdf/78/6/1276/504583/wst078061276.pdf)

**Figure 1** | Methodology to determine sediment contamination in Amir-Kalayeh.
Sampling and chemical analysis

During March 2014, surface sediment samples were collected from 12 stations in two parts (northern and southern) of the Amir-Kalayeh wetland (Figure 2). Sampling was done from parts of the wetland that are next to agricultural canals, water bodies far from the canals, near the environmental monitoring station, close to the old protection station and the inland areas of the wetland, so that samples represent the entire wetland. Sediment samples were collected at the depth of 30 cm using a Peterson grab sampler. The amount of sediment samples from each station was about 3 kg. A sample was taken from the environment around the wetland that has no special usage, and represents the baseline sediment of the wetland to determine some geochemical parameters of the wetland. Samples were packed in polyethylene bags and carried to the laboratory in an ice-box and stored at 4 °C until analysis. The samples were air dried and then were placed in an oven at 105 °C to achieve constant weight; afterwards sediment samples were passed through a mesh size less than 63 μm and subsequently powdered by an agate mortar and pestle. For analysis of metal content, the sediments were digested using a mixed solution of HF-HCL-HNO₃-CLO₄ according to the ASTM standard practice D4698-92 (ASTM 2015). Then the concentration of the elements were determined by the inductively coupled plasma optical emission spectroscopy (Varian VISTA-MPX). Blank samples were also

![Figure 2](https://iwaponline.com/wst/article-pdf/78/6/1276/504583/wst078061276.pdf)
prepared and used in steps to minimize the laboratory errors. A standard sediment sample (MESS-3) was analyzed to check the accuracy of the data obtained.

To determine the geochemical baseline value (concentration in uncontaminated sediment), soil from land with no particular use was sampled from around the wetland and analyzed.

Assessment of sediment contamination

Contamination factor

The sediments in their path from the parent rock in the highlands to the wetland encounter various events (Rubio et al. 2000). The contamination factor is calculated using the following equation, in which metal concentration in each sample is divided by the concentration in the baseline, which is determined from soils around the wetland with no land use:

$$CF = \frac{C_{\text{sample}}}{C_{\text{baseline}}}$$

where CF is contamination factor, $C_{\text{sample}}$ is the element concentration in the sample and $C_{\text{baseline}}$ is the element concentration in the baseline sample. If CF > 1, there is contamination in the sediments and if CF < 1, there is no elemental contamination (Hakanson 1980; Seshan et al. 2010; Varol 2011).

Pollution load index

PLI is calculated using the following equation:

$$\text{PLI} = \sqrt[2]{\text{CF}1 \times \text{CF}2 \times \text{CF}3 \times \ldots \times \text{CF}n}$$

If PLI is more than 1, then it indicates that there is sediment pollution (Adomako et al. 2008; Chakravarty & Patgiri 2009).

Enrichment factor

Spatial examination of the heavy metals in the sediments and comparing these concentrations with the uncontaminated baseline value is the first key to explore the transmission and deposit of pollutant heavy metals in coastal aquatic systems (Rai 2008; Bai et al. 2011b). The term geochemical baseline refers to the normal abundance of an element in a barren and empty soil or with no human interference (Cheng 2003). The capacity of the sediments to sustain heavy metals depends on their physical properties such as grain size and their mineralogical composition. The concentration of some heavy metals depends on the types of basin rocks, and therefore, maybe in some areas the high concentration of heavy metals is not unusual. For such interpretations, we need the enrichment factor (EF) of the elements (Çevik et al. 2009; Kaushik et al. 2009). One of the methods for determining the EF is the normalization method (Zhang et al. 2007; Sakan et al. 2014). Usually, elements such as Fe, Al, Mn, Sc, and Ti are used for normalization. In this research, iron (due to its geochemical characteristic and very insignificant changes in the environment) was also used as the reference (Zhang et al. 2007). The baseline mixture of the area under study was employed as the reference sample. The EF was calculated by the following equation (Sakan et al. 2009) (i.e. the method of normalization by the concentration of iron sample):

$$\text{EF} = \frac{X_{\text{sample}}}{X_{\text{crust}}}$$

where $X$ is the element under study. EF values are categorized as the following (Çevik et al. 2009): if EF < 1 there is no enrichment, if EF = 1–5 enrichment is low, if EF = 3–5 enrichment is medium, if EF = 5–10 enrichment is medium to high and if EF = 10–25 enrichment is high.

Geoaccumulation index

The geoaccumulation index ($I_{\text{geo}}$) for various elements in sediments is calculated by the following equation (Suthar et al. 2009; Bhuiyan et al. 2010):

$$I_{\text{geo}} = \log_2\left(\frac{c_n}{b_n}\right)$$

where $c_n$ is the concentration of the element in the sediment and $b_n$ is the concentration of the baseline limit. There are six degrees of contamination categories based on $I_{\text{geo}}$ calculation (Table 1).

Statistical analysis

After measuring the concentrations of the elements, Pearson correlation was calculated for them by SPSS software ($P < 0.05$). The Pearson correlation coefficient shows the
relationship between the distribution of different elements. Then in order to understand the statistical relationships and determine the anthropogenic and natural origins of the elements, cluster analysis was employed. Multivariate statistical clustering method in SPSS software was used for cluster analysis. The mean of intragroup data was used for the cluster analysis method and for identifying the outputs. The Pearson correlation coefficient was employed to evaluate the relationship between the concentrations of the elements. Factor analysis of the concentration data was used to determine the group of heavy metals with natural origin in the whole of the wetland’s sediments. These statistical analyses have been applied by various researchers to determine the relationship between metals and environmental indicators (Davis 1973; Jamshidi-Zanjani & Saeedi 2013; Zamani Hargalani et al. 2014; Karbassi et al. 2015).

RESULTS AND DISCUSSION

Results of analyzing the samples

Metal concentration in sediments of the Amir-Kalayeh wetland and mean metal concentrations in the earth’s crust and world sediments are presented in Table 2. The highest mean values of As, Pb, Mo and Zn were found at site W9, and for other metals at site W1, and the lowest mean values of metals were calculated at site W4. Mean concentrations of all studied metals (except for As, Mn, Pb) are lower than those of earth’s crust and world sediments. Therefore these results showed that most of the samples from the Amir-Kalayeh wetland are polluted with As, Pb, and Mn (Figure 3), which may be caused by the high usage of fertilizers and pesticides in the associated agricultural lands. The mean metal concentrations existed in the following order: Fe > Al > Mg > Mn > P > Zn > V >

<table>
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<tr>
<th>Table 1</th>
<th>Igeo guide based on Muller classification</th>
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<tr>
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<td>2–3</td>
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<th>Table 2</th>
<th>Elemental concentration in surface sediments (mg/kg)</th>
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<td>W1</td>
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<td>W2</td>
<td>163</td>
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<td>W3</td>
<td>165</td>
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<td>W4</td>
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<td>W5</td>
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<tr>
<td>Min</td>
<td>80</td>
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<tr>
<td>Average</td>
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<tr>
<td>Mean crust</td>
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<td>Mean world sediment</td>
<td>72,000</td>
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Cu > Pb > Ni > As > Cr > Co > Mo > Cd in the Amir-Kalayeh wetland sediments. Comparing the concentrations of heavy metals in the Caspian Sea sediments with global standards, Anzali wetland sediments as a wetland with similar conditions, and river sediments shows that the concentrations of heavy metals in Amir-Kalayeh wetland are mostly lower than the other cases, except for the baseline limit of the wetland itself (Esmaeilzadeh et al. 2014; Darvish Bastami et al. 2015).

W3 is in the central part of the water body far from the agricultural canals, so it is the cleanest part of the wetland; W4 and W5, which are near to the old checkpoint abandoned for a long time, are clean too. W1, the monitoring station, is polluted by nickel and vanadium; it is likely that this part of the wetland is polluted due to leakage of fuel from patrol boats. In the south part of the wetland, pollution by Mn, As and Mo is resulting from fertilizer, while pollution in the north is due to fuel and surface paint from boats. In the south part of the wetland, which is the intersection of three agricultural canals, shows the most pollution. These contaminants may be as a result of agricultural fertilizer entering through drainage canals.

Pearson correlation results

Values of Pearson correlation coefficients are presented in Table 3. The high correlation of aluminum with the elements may indicate that cobalt, chromium, copper, iron, magnesium, nickel, vanadium and zinc have a natural origin, since rocks and sediments are a source of these elements; in other words, these elements do not have an anthropogenic origin (Karbassi & Amirnezhad 2004; Zamani Hargalani et al. 2014; Karbassi et al. 2015). High correlation of arsenic with sulfur (R = 0.904), cadmium (R = 0.829), molybdenum (R = 0.817) and lead (R = 0.704) indicate the transmission of these elements in the sulfide phase. The high correlation of iron with nickel (R = 0.824), vanadium (R = 0.822) and zinc (R = 0.856) may indicate the transmission of nickel, vanadium and zinc through absorption by hydrous iron oxide.

The results of cluster analysis in the sediments

The correlation coefficients of heavy metals in the sediments of Amir-Kalayeh wetland were employed for statistical interpretation of the relationship between the elements and finding their origin. The correlation coefficients were assembled in a cluster analysis dendrogram and renamed as similarity coefficients. Cluster analysis has been applied to ascertain the relationship between various metals and environmental indicators (Hosseini Alhashemi et al. 2011; Jamshidi-Zanjani & Saeedi 2015). Dendrogram results are shown in Figure 4.

Being in the same group with aluminum indicates the natural origin of these elements. Cluster analysis results showed that, except for P, Mo, Cd, S, As, Mn and Ag, the heavy metals have natural origins and only the mentioned elements have anthropogenic origins. Lead has both natural and anthropogenic origins as well. The close correlation of arsenic with sulfur indicates the transmission of sulfur in the sulfide phase (Charkhabi & Sakizadeh 2006). Elements
Table 3 | Pearson correlation matrix of metals in Amir-Kalayeh wetland

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<tr>
<th></th>
<th>Ag</th>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
<th>S</th>
<th>V</th>
<th>Zn</th>
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<td>0.085</td>
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<td>0.530</td>
<td>0.358</td>
<td>0.565*</td>
<td>0.789**</td>
<td>0.236</td>
<td>0.592*</td>
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<td>0.829**</td>
<td>0.177</td>
<td>0.778*</td>
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<td>0.824**</td>
<td>0.817**</td>
<td>0.151</td>
<td>0.899**</td>
<td>0.291</td>
<td>0.423</td>
<td>0.904**</td>
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*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).
such as arsenic, phosphorus, manganese, molybdenum, sulfur, silver and cadmium in the same category may be the result of the pollution in this part of the wetland by chemical fertilizers and herbicides used in agricultural lands, especially rice fields (Zare Khosheghbal et al. 2015).

The results of factor analysis for the whole wetland sediments

Factor analysis of a set of variables produces a particular relationship of a hypothetical model with a main goal to reduce the number of data. After factor analysis, the number of factors will be reduced with a main purpose in geochemical interpretations of determining the main controlling variables among geochemical data series. After the factor analysis we can determine the group of elements that cluster together, which can be the indicator of a single paragenesis or origin. The number of columns in the result table of factor analysis shows the number of factors. In order to find the set of elements that sort to a factor, to each column we must select the elements that have high factor rates (usually more than 0.6) to categorize them into
a single group. Rotation of the dendogram leads to the presentation of the data rotation results in the output, for the best selection of elements that change together (Figure 5). Factor analysis verifies the results of cluster analysis.

Factor analysis shows that elements are with Al, because they originate from the land, and enter the wetland through surface erosion or river flows, while the other elements are anthropogenic and enter the wetland through human activities.

Results of contamination factor and pollution load index

The results of calculating CF and PLI are presented in Table 4. Arsenic, cadmium, manganese, molybdenum, and lead have CFs higher than 1, which means they contaminate the area. In this research, PLI is 0.9, which indicates that the sediments of Amir-Kalayeh wetland are not polluted.

The results of calculating the enrichment factor

In this research, enrichment factor values of the heavy metals in the area sediments can be found in Table 5. The high enrichment of elements such as manganese and molybdenum can be the result of high fertilizer usage in the associated agricultural lands (Zare Khosheghbal et al. 2013). Moreover, in the case of arsenic, it is probably caused by agricultural pesticides (Pekey 2006).

Geoaccumulation index results

Comparing the values of \( I_{\text{geo}} \) for the element in the sediments of Amir-Kalayeh with Muller indices (Table 1) we conclude that contamination intensity of Amir-Kalayeh wetland for all the elements is within the 'not polluted' category \( (I_{\text{geo}} \leq 1) \) (Table 6). The order of the Muller index for the selected elements is as follows:

\[
\text{Co, Mo, As, Pb, Cr, Ni, Cu, V, Zn, Mn, Fe, Cd}
\]

CONCLUSION

Statistical analysis was applied to determine the anthropogenic origin of the elements in the wetland. Pearson
correlation coefficient analysis indicated that there are high correlations between aluminum (as lithogenic indicator) and elements of cobalt, chromium, copper, iron, magnesium, nickel, vanadium and zinc. Hence, the metals are natural (Karbassi & Amirnezhad 2004; Zamani Hargalani et al. 2014; Karbassi et al. 2015). Cluster analysis and factor analysis indicated that the origins of lead, nickel, copper, zinc, vanadium, chromium and cobalt are natural, the geological features of the study area, whereas cadmium, molybdenum, manganese, silver and arsenic are from anthropogenic origin due to activities such as agriculture. Selected indices were CL, PLI, EF and $I_{geo}$. Results indicated that arsenic, cadmium, manganese, molybdenum, and lead have CFs higher than 1, which means that the area is polluted by these elements. For the Amir-Kalayeh wetland, the PLI was equal to 0.9; hence, the sediments in this area were not polluted. Manganese and molybdenum showed the highest EFs, probably because fertilizers are used in agricultural lands. Also, the high enrichment of arsenic is probably a result of using agricultural pesticides (e.g. copper arsenate and lead hydrogen arsenate). The $I_{geo}$ showed that none of the heavy metals were found in Amir-Kalayeh wetland, except for those arising from agricultural fertilizers, so it means the wetland is quite clean and it is not polluted by domestic and industrial wastes and activities. However, the enrichment of elements, due to the high usage of agricultural fertilizers and pesticides, in the sediments of the wetland requires more attention and proper management and use of the materials containing these elements in the rice fields near the wetland.

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