

## Risk Assessment and Environmental Geochemistry of Pb, Cu and Fe in Surface Sediments (Case Study: Hashilan Wetland, Kermanshah, Iran)

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**ABSTRACT** The total concentration and percentage of heavy metals content in the sediment of Hashilan wetland, Kermanshah province, was assessed in summer 2015. The total concentrations of Cu, Pb, and Fe were around 18.57, 6.95 and 379.24  $\mu\text{g g}^{-1}$ , respectively. Successive extractions of the samples showed a decreasing trend as follows: residual>organic matter>iron and manganese oxides>exchangeable parts. The comparison of the total metal concentrations and SQGs and NOAA standards proposed high concentrations of Pb and Fe contents, while RAC suggested that Cu, Pb, and Fe had posed a low-moderate risk, low risk and no risk to the system, respectively. Furthermore, the results showed that the most common sources of Pb and Fe were natural while sources of Cu was anthropogenic. Continuous monitoring of the wetlands, particularly water inputs are recommended.

**Key words:** Hashilan wetland, Surface sediments, Heavy metals, Fractionation

### 1 INTRODUCTION

The value of wetlands to human society consists of several physical, chemical and biological functions. The basic components of aquatic systems, including water, soil, plants, animals, and nutrients constitute the uniform system of wetlands (Mansoori, 2007). Being potentially toxic to creatures, nowadays heavy metals are the most important life threatening contaminants in aquatic environments (Pasyna and Nriago, 1998; MdSaifullet *et al.*, 2014), especially through food chains (SabzAlizade

and Naseri, 2011). Sediments, which are usually subject to pollution threats from natural and human activities (Gorkem and Duyuse, 2008), are accounted as the biggest sink for contaminants and play important roles in accumulating some heavy metals in the benthic invertebrates and transferring them to higher levels of food chains (Sayadi *et al.*, 2015; Shirneshan *et al.*, 2013; Yap *et al.*, 2002; Long, 1996; Fichet *et al.*, 1999). Therefore, monitoring sediment could be considered as an appropriate way to assess contamination in

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aquatic environments (Gagnou and Fisher, 1997), and often used to identify the contamination source in both spatial and temporal scales to involve long-term geochemical processes (Birch *et al.*, 2001; Shirneshan *et al.*, 2013).

Translocation of heavy metals from sediments to the upper water resources could occur as a result of biological activities and physiochemical parameters (Hughes and Chester, 1967; Helling *et al.*, 1990; Chen and Gupta, 1990; Karbassi, 1998; Karbassi and Volvi, 2010; Karbassi *et al.*, 2010; Shirneshan *et al.*, 2013). Since several factors are involved in heavy metal contamination, the assessment of the total concentration of heavy metal is not sufficient to get all the required information in assessing the environmental impact of the contaminated sediments (Obbard and Cuong, 2006). As a result, chemical separation studies have become necessary tools to assess the sources of heavy metals (Bagheri *et al.*, 2011; MdSaiful *et al.*, 2014), and studies in this regard have become crucial to proper management of aquatic environment (Hakanson, 1980; Salamons and Forstner, 1984; Calmano *et al.*, 1993; Dickinson *et al.*, 1996; Sharma *et al.*, 1999; Saeedi *et al.*, 2004; Caeiro *et al.*, 2005; Saeedi *et al.*, 2012). Such studies have been extended to various parts of the world, including Iran, that show the extent of heavy metal contaminations and their sources (Duyusen and Gorkem, 2008; Bagheri *et al.*, 2013; Shirneshan *et al.*, 2013; Silinet *et al.*, 2013).

It seems that agricultural practices such as irrigation, the application of fertilizers and pesticides considerably affect the distribution of heavy metals (Silin *et al.*, 2013). Agricultural practices in Hashilan region is common, accelerating heavy metal inputs to the system (Mohammadi *et al.*, 2013). High heavy metals concentration in Hashilan provides a constant

ecological and health risk to the wetland. In order to determine the contributions of natural and anthropogenic sources in transferring heavy metals in the Hashilan wetland, the concentrations of heavy metals in surface sediments were fractionated and evaluated based on the international sediment quality standards of ISQG (Interim Sediment Quality Guidelines -Canada) and NOAA (National Oceanic and Atmospheric Administration).

## 2 MATERIALS AND METHODS

### 2.1 Site Description

Hashilan Wetland (46° 15' 54" E and 34° 34' - 34° 35' N) is situated 36 km northwest of Kermanshah Province, west of Iran (Mohammadzade *et al.*, 2013). Sediment samples were randomly collected (in three replications) from 0-10 cm layer at five stations (north, south, east, west and center) in 2015 (Figure 1). The samples were kept cool and transferred to the Environmental Science Lab, Malayer University, in the polyethylene bags for further analysis. The location of the sediment samples was recorded using a GPS (Table 1).

### 2.2 Preparation of sediment samples

The samples were first oven-dried at 80-95°C for at least 16 hours to reach a constant weight, then crushed in a stone mortar and sieved through a 63µm sieve. Finally, the powdered samples were kept in polyethylene containers at in a refrigerator.

**Table 1** Geographical coordinations and descriptions of Hashilan sampling stations

| Stations | Geographical coordinates             | Sea level (m) | Landuse description |
|----------|--------------------------------------|---------------|---------------------|
| North    | 34° 35' 1.31" N<br>46° 53' 26.32" E  | 1310          | Water inlet lagoon  |
| East     | 34° 34' 32.25" N<br>46° 53' 28.28" E | 1310          | Pear tree           |
| Center   | 34° 34' 33.66" N<br>46° 52' 56.16" E | 1309          | Big kool            |
| South    | 34° 34' 54.39" N<br>46° 52' 40.12" E | 1309          | Willow trees        |
| West     | 34° 34' 39.14" N<br>46° 52' 19.37" E | 1310          | Rabkholudarijh      |



**Figure 1** General location of the study area and spatial pattern of sampling stations

### 2.3 Analysis of total concentration of Cu, Pb and Fe in sediment samples

First, about 1 g of dried sub-samples were digested in a hot block digester by a 4:1 v/v ratio of nitric acid (69%) and perchloric acid (60%) for 1 and 3h at the temperatures of 40 and 140 °C, respectively. The digested samples were then diluted with double-distilled water to 25 ml and filtered with Whatman filter paper 0.45µm and kept in polyethylene containers in the fridge (Yap et al., 2002; Li et al., 2001).

### 2.4 Analysis of Cu, Pb and Fe concentrations in various geochemical parts of sediments

Geochemical fractionation of Cu, Pb and Fe in the sediments was done by the use of successive extraction procedure as follows (Yap et al., 2002; Li et al., 2001): 10 g sub-samples was shaken on a shaker with 50 ml of 1M ammonium acetate and pH 7 at room temperature to obtain the exchangeable form. The form bound to oxides and hydroxides of iron and manganese, remaining material from

the previous step was acidized with 50 ml hydroxyl ammonium chloride to pH 2, then placed on the shaker in room temperature for three hours with hydrochloric acid. To investigate the form bounded to organic matter, the remaining of previous stage was first oxidized with 30% H<sub>2</sub>O<sub>2</sub> in a water bath at 90-95°C, then cooled down and placed on the shaker for three hours with 0.1 M ammonium acetate pH 2 in room temperature. Finally, to obtain a residual form, the remaining of the third stage was put in a hot block digester with a 4:1 compound of nitric acid (69%) and perchloric acid (60%) at the temperatures of 40 and 140°C for 1 and 3 hours, respectively. The final solution was filtered through Whatman filter paper 41 and diluted with 70 ml distilled water. Concentration of desired elements in geochemical fractionation was measured by the means of Analytic Jena ContraAA 700 atomic absorption spectrometry.

The data were reported in  $\mu\text{g g}^{-1}$  of sample dry weight. The instrumental Limit of Detection (LOD) of Fe, Cu and Pb were 0.02, 0.03 and 0.001  $\mu\text{g g}^{-1}$  dry, respectively. Recovery of the AAS method for heavy metals was measured 80- 95%.

The statistical software package version 9.1 (SAS Institute Inc, NC, USA) was used for all statistical analyses. The assumptions of normality and homogeneity of variances were investigated using Shapiro-Wilk and Levene tests, respectively. Then, any significant differences between the average concentrations of heavy metals in different stations were assessed using one-way analysis of variance (ANOVA) procedure and Duncan multiple range test. In addition, any correlation between Cu, Pb, and Fe concentrations was explored using a Pearson correlation test.

### 2.5 Enrichment factor (EF)

Enrichment factor is computed to estimate the sediment chemistry in relation to anthropogenic and natural contamination sources using the equation (1) (Zonta *et al.*, 1994; Loska *et al.*, 2003; Suthar *et al.*, 2009; Shirneshan *et al.*, 2013).

$$EF (\%) = (C - C_{\text{Min}})/(C_{\text{Max}} - C_{\text{Min}}) \times 100 \quad (1)$$

C: Mean metal concentration in sediments ( $\text{mg kg}^{-1}$ )

$C_{\text{Max}}$  and  $C_{\text{Min}}$ : Maximum and minimum estimated concentrations

### 2.6 Environmental risk assessment code

Risk assessment code (RAC), first introduced by Perin (1985), and was applied to assess the mobility and bioavailability of heavy metals in surface sediments (Wang *et al.*, 2010).

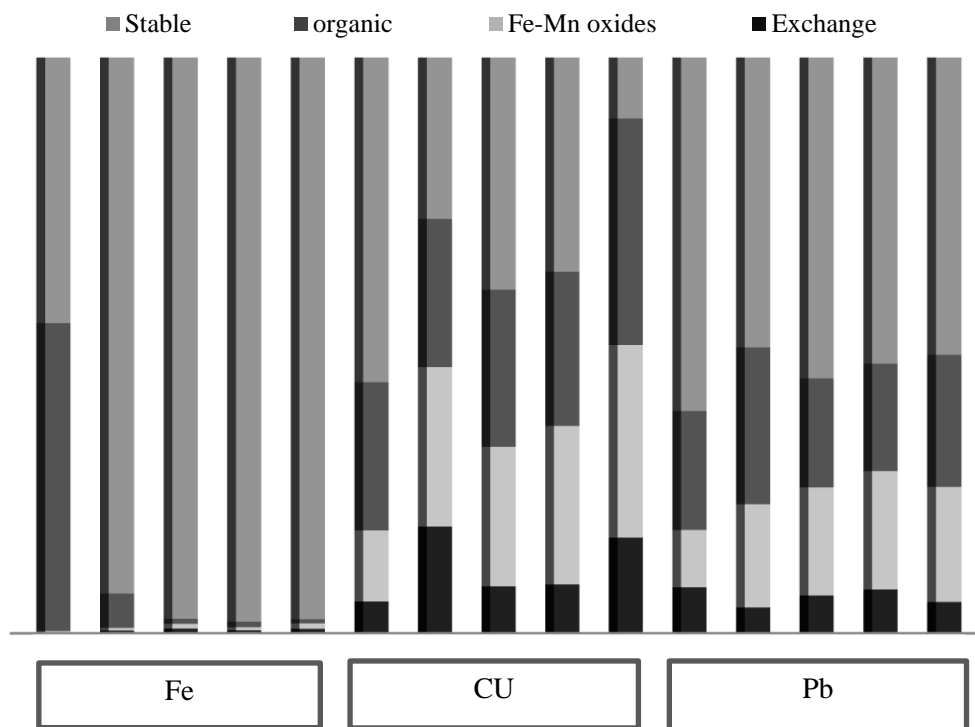
## 3 RESULTS

### 3.1 Heavy metal concentration and percentage in geochemical forms

The mobility, access, and potential toxicity of heavy metals in the sediment were assessed using the concentration and percentage of metals, including Cu, Pb, and Fe (Figure 2). Natural and anthropological sources of Pb, Cu and Fe in Hashian wetland sediment are shown in Figure 3.

### 3.2 Comparison of metal concentrations and international standards

The heavy metal contents were compared with the global standard values suggested by SOGs (Standard Operating Guidelines) (TEC and PEC indices) and NOAA (ERL and ERM indices) (Table 5). The calculated amounts related to EF and the summary of comparisons are presented in Table 2 and Table 3, respectively.



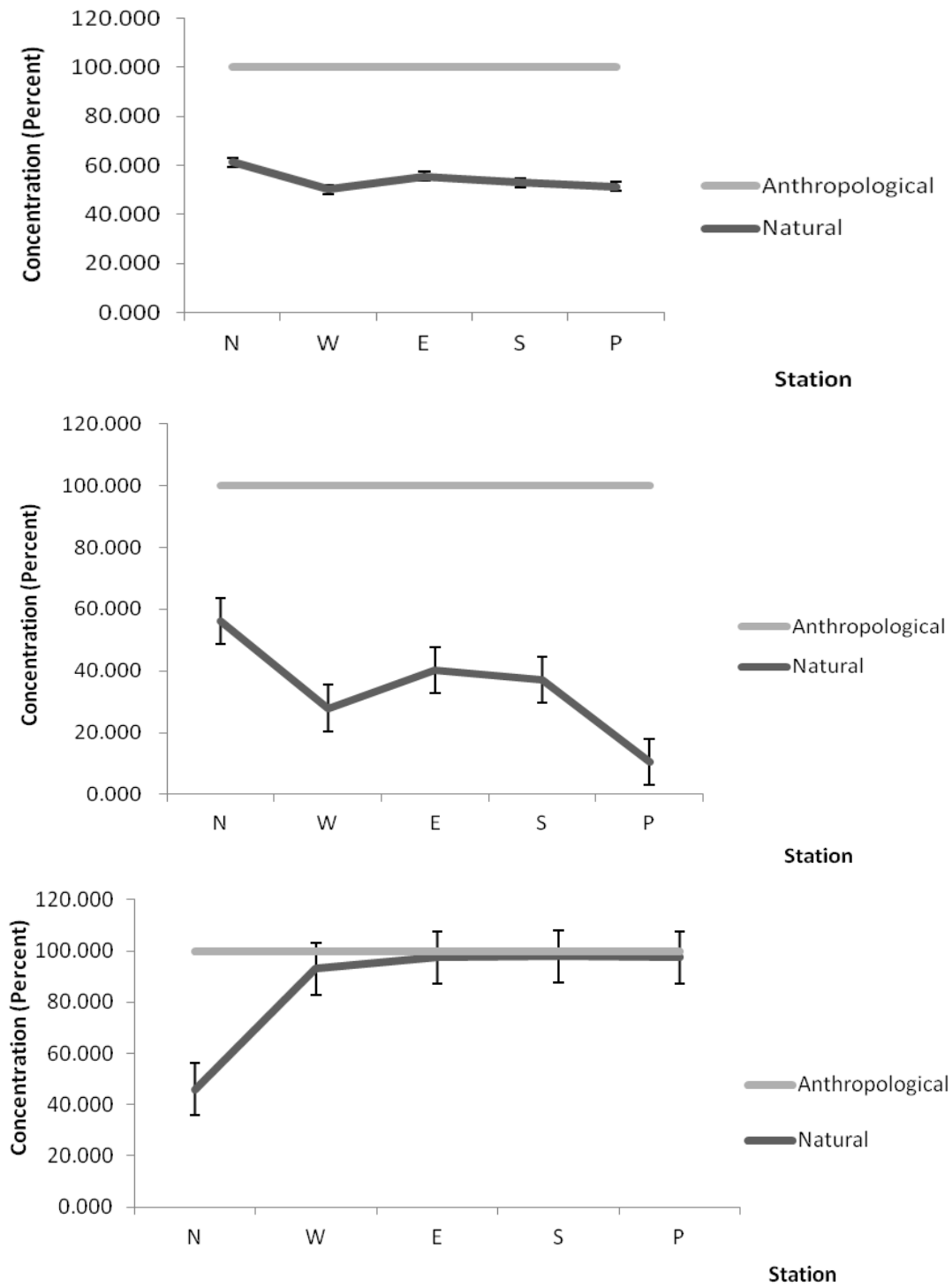
**Figure 2** Distribution of Cu, Pb, and Fe percentage in geochemical forms of sediment

**Table 2** A summary of enrichment index of different heavy metals in surface sediment

| Stations | Replication | EF (Cu) | EF (Pb) | EF (Fe) |
|----------|-------------|---------|---------|---------|
| N        | 3           | 60.21   | 54.24   | 73.51   |
| W        | 3           | 25.52   | 19.13   | 28.71   |
| E        | 3           | 30.21   | 21.71   | 6.67    |
| S        | 3           | 18.67   | 17.57   | 11.11   |
| P        | 3           | 4.29    | 9.71    | 10.05   |

**Table 3.** Comparison of heavy metal concentrations with environmental risk assessment code

| RAC            | Index | Cu          | Pb        | Fe        |
|----------------|-------|-------------|-----------|-----------|
| No risk        | < 1   |             |           | 0.21-0.82 |
| Low risk       | 1-10  | 5.55-8.55   | 4.51-8.04 |           |
| Medium risk    | 11-30 | 16.78-18.73 |           |           |
| High risk      | 31-50 |             |           |           |
| Very high risk | >75   |             |           |           |



**Figure 3** Natural and Anthropological sources of Pb (up), Cu (middle) and Fe (down) in Hashian wetland sediment

## 4 DISCUSSION

### 4.1 Concentration and metal percentage in geochemical parts

Considering the average concentrations and percentages of Cu, Pb, and Fe in geochemical forms of the surface sediment and their enrichment index, the maximum ( $1609 \mu\text{g g}^{-1}$ ) and minimum ( $1.11 \mu\text{g g}^{-1}$ ) Cu concentrations at the sampling stations were attributed to the residual part. However, the highest ( $5.97 \mu\text{g g}^{-1}$ ) and lowest ( $0.29 \mu\text{g g}^{-1}$ ) Pb concentrations were related to the residual and exchangeable parts, respectively. The highest ( $450.47 \mu\text{g g}^{-1}$ ) and lowest ( $1.23 \mu\text{g g}^{-1}$ ) Fe concentrations consisted of organic matter and exchangeable part, respectively. The results of successive extractions indicated a decreasing trend of different geochemical parts in the following order: residual > organic matter > iron-manganese oxides > exchangeable. Further, the results also showed a natural source of Cu, Pb, and Fe metals in the sediment samples in different geochemical parts. The main source of Cu included anthropogenic activities (Figs. 3). In order to determine any significant differences in Cu, Fe and Pb concentrations among the stations, analysis of variance and Duncan test were applied. Results of Levene test for their concentrations indicated homogeneity of variances across groups ( $p > 0.05$ ). The results of Duncan revealed that there were significant differences between concentration of Cu in station 1 and 2 and concentration of Fe in station 1 with other stations. No significant differences were observed in Pb concentrations among the sites.

### 4.2 Enrichment factor

The enrichment factor (EF) values for Cu, Pb and Fe ranged from 4.29-60.21, 9.71-54.24, and 6.67-73.51, respectively. The maximum EFs were observed in the north station of Hashilan wetland, while the minimum EF of Cu and Pb were evident in the central station and for Fe in

the eastern station. The low index in the central station seemed to be due to the existence of reed colonies with high refining ability. The land uses that more severely caused contamination included rangelands, mountains, forests, recreational area of Sabzali Sarab, environment monitoring station, roads, and water transmission channel.

### 4.3 Comparison of sediment data and other studies

The average concentrations of Cu, Pb and Fe in the surface sediments of Hashilan wetland have been compared with the other studies around the world as follows:

### 4.4 Comparison of sediment data and international standards

The comparison of the heavy metal contents in this study with the international standards showed no toxicity risk of the Cu as its content was low in all the stations of Hashilan wetland (Table 5). The results of Pb and Fe were different. The average Pb content was low except for ERL (Effect Range Low) standard. It seemed that Fe content was more than the other metals in the wetland and its level was higher than PEL (Probable Effects Levels), ERM (Effects Range Median), PEC (Probable Effects Concentration) and ERL international standards.

**Table 4.** Comparison of heavy metal concentrations between the sediment samples of the study area and around the world

| Local  | Cu ( $\mu\text{g g}^{-1}$ ) | Pb( $\mu\text{g g}^{-1}$ ) | Fe( $\mu\text{g g}^{-1}$ ) | Reference                             |
|--|-----------------------------|----------------------------|----------------------------|---------------------------------------|
| Wetland Anzali, Iran   | 57.13                       | 27.61                      | 45424                      | Jamshidy Zanjani and Saedi, 2013      |
| Mangrove forest, Bushehr, Iran                               | 46.04                       | 94.8                       | 30736.72                   | Davari <i>et al.</i> , 2012           |
| Vigo Ria (NW Iberian Peninsula)                              | 18-82                       | 24-112                     | 18-34                      | Maria <i>et al.</i> , 2008            |
| Taranto Gulf<br>(Ionian Sea, Southern Italy)                 | 47                          | 59                         | 26313                      | Alessandro <i>et al.</i> , 2006       |
|  | 105                         | 219                        | 3.9                        | Acevedo-Figueroa <i>et al.</i> , 2006 |
|  | 22                          | 7.6                        | 4.9                        |                                       |
| Punta Mala, Bay Panama                                       | 56.3                        | 76.2                       | 9825                       | Defew <i>et al.</i> , 2005            |
| wetlands of Sydney, Australia                                | 9.6                         | 27.61                      | 9422                       | Connor and Thomas, 2003               |
| Queensland, Australia  | 3.08                        | 6.25                       | 13583.96                   | Preda and Cox, 2002                   |
| Morgan County, America                                       | 2.1                         | 2.5                        | 556                        | Mays and Edwards, 2001                |
| Goreckie Lake, Wielkopolski<br>National Park, western Poland | 12                          | 47.5                       | 9150                       | Zerbe <i>et al.</i> , 1999            |
| Milos bay, Greece  | 51                          | 151                        | 34000                      | Karageorgis <i>et al.</i> , 1998      |
| Bothnian Bay   | 52                          | 79                         | 52                         | Leivuori, 1998                        |
| Bothnian Sea   | 36                          | 42                         | 36                         |                                       |
| Gulf of Finland  | 43                          | 50                         | 43                         |                                       |
| Caribbean coast Costa Rica                                   | 8.4                         | 34.5                       | 8.4                        | Guzman and Jimenez, 1992              |
| UK estuaries (range)   | 7-2398                      | 20-2753                    | 7-2398                     | Bryan and Langston, 1992              |
| Gulf of Venice, Italy  | 17                          | 38                         | 17                         | Donazzolo <i>et al.</i> , 1981        |
| Hashilan Wetland   | 18.57                       | 6.95                       | 18.57                      | Current study                         |

**Table 5.** Comparison of heavy metal concentrations with international standards

| Refs | Fe    | Pb   | Cu     | Standards  |
|------|-------|------|--------|--|
| TEC  | 31.6  | 35.8 | -      | Hongyi, 2009; Mooraki et al, 2009  |
| PEC  | 149   | 459  | 459    | Galindo-Riano et al, 2009  |
| PEL  | 108   | 112  | 271    | CCME, 1999; Mooraki et al., 2009; Galindo-Riano et al., 2009                 |
| ERM  | 270   | 218  | 410    | Long, 1995; Mooraki et al., 2009; Galindo-Riano et al., 2009                 |
| ERL  | 34    | 7.46 | 150    | Long, 1995; Mooraki <i>et al.</i> , 2009; Galindo-Riano <i>et al.</i> , 2009 |
| -    | 18.57 | 6.95 | 379.24 | Current Study  |

## 5 CONCLUSION

The total contents of heavy metals Cu, Pb, and Fe were separately assessed in different geochemical parts of the sediment samples in the Hashilan wetland. Cu concentration decreased in the following order: north>east>west>south>center; the maximum content of Cu in the north station was mainly due to the different types of land uses in the station, while its minimum content was observed in the central station where human

interference was relatively low. The maximum and minimum Pb content was also observed in the north and central stations, respectively, as follows: north>east>west>south>center. However, the maximum and minimum Fe contents were measured in the north and east stations, respectively, with the order of north>west>south>center>east. Results indicated the natural origins for Pb and Fe, while anthropogenic origin for Cu.



The comparison of exchangeable part with RAC index showed no risk, low risk, and low-moderate risk for Fe, Pb, and Cu, respectively.

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## ارزیابی خطر و تفکیک ژئوشیمیایی فلزات سنگین (مس، سرب و آهن) در رسوبات سطحی (مطالعه موردی): تالاب هشیلان، کرمانشاه، ایران)

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**چکیده** بررسی میزان فلزات سنگین تالاب هشیلان (استان کرمانشاه) در تابستان ۱۳۹۴ با نمونه برداری از رسوبات سطحی آن در ۵ ایستگاه با ۳ تکرار انجام گرفت. غلظت کلسیم، آهن و منگنز در رسوبات، میانگین غلظت فلزات سنگین در بخش های ژئوشیمیایی رسوبات باروش استخراجی پیماندازه گیری گردید. میانگین غلظت کل مس، سرب و آهن به ترتیب ۱۸/۵۷، ۶/۹۵ و ۳۷۹/۲۴ میکروگرم بر گرم تعیین گردید. نتایج استخراج پی در پی در کلیه ایستگاه ها بیانگر روند نزولی بخش های پایدار، آلی، اکسیدهای آهن- منگنز و تبادل می باشد. مقایسه غلظت کلی فلزات با استانداردهای جهانی SQGs و NOAA، بالا بودن غلظت فلزات سرب و آهن را نشان می دهد. در همین راستا نتایج حاصل از کد ارزیابی ریسک، فلز مس را در محدوده ریسک کم تا متوسط، فلز سرب را در محدوده ریسک کم و فلز آهن را در وضعیت بدون ریسک نشان داد. نتایج به دست آمده از سهم فلزات در بخش های مختلف ژئوشیمیایی رسوبات، بیانگر غالب بودن منشأ طبیعی برای دو فلز سرب و آهن، و منشأ انسانی برای فلز مس می باشد. پایش مداوم محیط زیست تالاب بخصوص در بخش آب های ورودی پیشنهاد می گردد

**کلمات کلیدی:** تالاب هشیلان، رسوبات سطحی، فلزات سنگین، منشأیابی.