# Assessment of Some Heavy Metals in the Shadegan and Hawr Al Hawizea Wetland Waters from Iran

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#### Abstract

**Background:** Heavy metal contamination of wetland waters can adversely affects human health. **Methods:** The Arsenic (As), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Mercury (Hg), Manganese (Mn), Lead (Pb), and Zinc (Zn) of Shadegan and Hawr Al Azim wetland waters in the Khuzistan Province, South Western Iran were assessed from October 2011 to September 2012. **Results:** Shadegan and Hawr Al Azim wetland waters were contaminated with Cr, Fe, Mn, Hg and Zn as they were more than the Environmental Protection Agency (EPA) normal levels. One-sample t-test showed a significant difference between these wetland waters contaminated heavy metals and the EPA normal levels. **Application:** Although these wetland waters were contaminated by the mentioned heavy metals, they will likely accumulate in the fauna and flora tissues. Afterwards they were biomagnified there after their entering in the marine food chains. Finally they were fed by predators such as birds and fish and threatened human health through food chains.

Keywords: Assessment, Contamination, Heavy metal, Water, Wetland

### 1. Introduction

In recent years, the nation's water resources are threatened by the various pollutions such as industrial effluents, fertilizers, chemical pesticides, and wastewaters<sup>1,2</sup>. Protecting the wetlands such as Shadegan and Hawr Al Azim (Hawr Al Hawizea) can protect our safety and welfare<sup>3</sup> because they take on characteristics that make them distinct<sup>4;</sup> moreover, they are the most productive ecosystem among ecosystems of the world<sup>5</sup>. Some wetlands benefits in the world are: water quality improving, water pollutant removing, flood protecting, erosion controlling, groundwater recharging, wildlife habitat providing, recreational and cultural function serving, aesthetic appreciation, creatures' biodiversity reservoirs, natural research center, tourism destination potential and local resident socioeconomic advantages<sup>6,7</sup>. Also they have eco-environmental conditions to prevent the dust phenomena that are extremely important and are a regional and interregional complex problem in the recent decades<sup>7</sup>. So wetlands need to be monitored and managed over the time to assess their ecologically functioning<sup>3</sup>. To manage wetlands effectively it is necessary to have adequate knowledge of their any pollution to ensure that there are no any contaminations<sup>4</sup>.

The various aquatic ecosystems such as wetlands are encountered to wide range of heavy metal pollution. Really it has been drawn the attention of the researchers

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to theirs8. Heavy metals have persistent nature. As a result they are one of the major and the most widespread groups of contaminants. They eliminate slowly from environment<sup>9-11</sup>. In this respect contaminating the wetland waters with the metals can adversely affect on human health for their water supply and support agricultural activities. Various harmful effects including abnormal development of the fetus, procreation failure, and immunodeficiency have exhibited due to aquatic metal exposure<sup>12</sup>. So, having a strategy and plan for the water conservation and pollution control is as an issue in the country's infrastructure<sup>1</sup> such as wetlands. Also the aquatic organisms and wildlife are dependent to their water quality habitats. They encountered to the serious threats especially the endangered or the threatened species such as insects or other organisms. However, as mentioned protecting the wetlands in turn can protect our safety and welfare. Also the protection of threatened and endangered species is important in normal developments<sup>13</sup>.

Shadegan and Hawr Al Azim wetlands in Khuzistan Province, South West of Iran, are considered to be the most special ecosystems in the world, as mentioned the above with some various benefits. They have excellent natural attraction and create annually an appropriate habitat for a large number of migratory birds arriving from Northern Europe, Canada and Siberia. Their wildlife and natures are threatened by different kinds of pollutants such as industrial and urban wastes. Also the peoples may be suffering from Mosquito-borne diseases and their nuisance by high density of mosquito emerging<sup>14</sup> preventing tourist activities. It is necessary to be measured the water heavy metals to inform human for preventing or reducing their water pollution which they can be searched by regular environmental surveys. In this regard annually various studies must be taken. However, few studies were done on our country wetland waters. Farrokhian et al.<sup>15</sup> measured the Cadmium, Lead, Nickel and Copper of Shadegan wetland in a relatively old study<sup>15</sup>. In a very small and short time scales, Nasirian et al.<sup>7,16</sup> stated that Shadegan wetland waters were contaminated by some heavy metals<sup>16</sup>. Whereas the trend of the wetland water heavy metal contamination would not be evaluated by this study. But it seems it would be better the study is taken in a large and long time scales to evaluate the trend of the wetland water heavy metal contamination. Thus in this regard the present study was done to assess the water heavy metals of Shadegan and Hawr Al Azim wetlands in Khuzistan Province, South Western Iran from October 2011 to September 2012.

## 2. Materials and Methods

#### 2.1 Geographical Information

This study was carried out in Shadegan and Hawr Al Hawizea or Hawr Al Azim wetlands with a hot and humid climate in Khuzistan Province, South Western Iran. Shadegan wetland is known as the largest wetland in Iran and contains an area of 537,700 hectares, placed 52 km far from Abadan and 40 km far from Ahvaz and closed from North to Shadegan city and Khor Doraq, from South to Bahmanshir river, from West to Darkhovien and Abadan road and from East to Khure-Musa. It is mainly supplied by Karoun river waters. The coordinates of Shadegan wetland area are:  $48^{\circ} 17^{'} - 48^{\circ} 50^{'} E 30^{\circ} 17^{'} - 30^{\circ} 58^{'} N^{7,16}$ .

Hawr Al Azim and Hawr Al Hawizeh are parts of a single hydrologic system forming the largest permanent freshwater wetlands in Lower Mesopotamia and situating in the North Azadegan Plain, 80 km Southwest of Ahvaz County, near the border between Iran and Iraq. They covers an area of about 56654 hectares, most (37266 hectares) of which locates within the Hawr Al Azim wetland. Their coordinates are: 47° 20′ - 47° 55′ E - 30° 58′ - 31° 50′ N <sup>17</sup>.

#### 2.2 Site Selection

The water samplings were conducted from six different sites including: 1. Water canal entrance to Shadegan Wetland (SW<sub>1</sub>) located at the West of the wetland between Darkhovien city and wetland at 15 km of Shadegan-Darkhovien road where waste output of sugarcane expansion plan released into the wetland. 2. The middle of Shadegan Wetland area (SW<sub>2</sub>) located at 10 km in its middling of this wetland. 3. Ragbeh and Sarakhieh villages surrounding and tourism station of Shadegan Wetland areas (SW<sub>3</sub>) located at the West of the wetland at 5 km of Shadegan-Darkhovien road. 4. Waste output from sugarcane expansion plan (SW<sub>4</sub>) located at the North Western of the wetland at 40 km of Ahvaz-Abadan road where waste output of sugarcane expansion plan comes out. 5. The entry of Shadegan city wastewater to Shadegan Wetland (SW<sub>2</sub>) located between Shadegan city and wetland at the East of the wetland where urban waste released into the wetland. 6. The wide middle area of Hawr Al Hawizeh or Hawr Al Azim wetland (HH) located at 10 km in its middling of this wetland<sup>18</sup>.

#### 2.3 Water Sampling

Water samples were collected using one liter acid-washed (10% Nitric acid) poly-ethylene containers. Then 1 ml

concentrated Nitric acid (HNO<sub>3</sub>) was added to each sample and transported to the laboratory after labeling and packaging.

#### 2.4 ICP-OES Metal Analysis

The water samples for metals testing including Arsenic (As), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Mercury (Hg), Manganese (Mn), Lead (Pb), and Zinc (Zn) were subjected to ICP-OES (Germany SPECTRO Company, Spectro ARCOS Model) instrument to quantify the composition of the given samples<sup>19</sup>.

#### 2.5 Statistical Analysis

Data concerning the investigated water metal pollutants between the different selected sites and dates and between the selected sites and months were analyzed by One-way analysis of variance (ANOVA) followed by Post Hoc tests (Tukey HSD), respectively using PASW Statistics 18. Onesample t-test was used for comparing the water metal pollutants with the Environmental Protection Agency (EPA) normal levels<sup>20</sup>.

#### 2.6 Results and Discussion

Tables 1 and 2 shows the water heavy metals which were measured in the different selected sites of Shadegan and Hawr Al Azim wetlands by µg/L and µg/g from October 2011 to September 2012. Generally, the levels of As, Cd, Co, Cu and Pb in the water which were sampled monthly from different sites of both wetlands during October 2011 to September 2012, were observed lower than the EPA water standards. This fact indicates that the water has not been contaminated by these metals; whereas the values of Cr, Fe, Mn, Hg, and Zn in some month samplings were higher than the EPA water normal levels (shown in bold in the Tables 1 and 2). This fact indicates that the waters of these wetlands have been contaminated by these heavy metals (Tables 1 and 2). Also Figure 1 show trends of the investigated water heavy metals (µg/g) in the different selected sites of Shadegan and Hawr Al Azim wetlands, from October 2011 to September 2012.

The water Cr values in the  $SW_1$  and  $SW_5$  in the October, December and September; the  $SW_2$ ,  $SW_3$  and  $SW_4$  in the October, December, March, April and September; and the HH in the October observed higher than the EPA normal levels<sup>20</sup> indicating water contamination to Cr (shown in bold in the Tables 1 and 2). The lowest and the



**Figure 1.** Trends of the water heavy metals investigated  $(\mu g/g)$  in the different selected sites of Shadegan and Hawr Al Azim Wetlands, from October 2011 to September 2012.

highest water contamination Cr values observed in the SW<sub>3</sub> and SW<sub>4</sub>, and in the SW<sub>2</sub> and SW<sub>5</sub> in the March and October, respectively (Tables 1 and 2, and Figure 1). The results of one-sample t-test revealed a significant differences between the water Cr values and EPA normal levels (P<0.0001) Table 3<sup>20</sup>. The results of one-way analysis of variance (ANOVA) did not show any significant differences between the Cr values of the sites (P=0.056), whereas it showed a significant differences between the Cr values of the months (P<0.0001) (Table 4). Also Post Hoc tests (Tukey HSD) showed a significant differences between the Cr values of the HH with the  $SW_1$ ,  $SW_2$ ,  $SW_3$ ,  $SW_4$ and SW<sub>z</sub>; and October with the other months; December with the March, April, June and July; and September with the March, June and July (P<0.05), whereas they did not show any significant differences between the other sites and months (P>0.05) (Tables 5 and 6).

The water Fe values of the SW<sub>1</sub> and SW<sub>4</sub> in the March, April, June, July, September; the SW<sub>2</sub> and SW<sub>3</sub> (except July) in the March, April, June and July; the SW<sub>5</sub> in the all months (except the July); and the HH in the March, June and September observed higher than the EPA normal levels<sup>20</sup> indicating water contamination to Fe (shown in bold in the Tables 1 and 2). The lowest and the highest water Fe contamination values observed both in the SW<sub>5</sub> in the October and March (Tables 1 and 2, and Figure 1). The results of one-sample t-test revealed a significant differences between the Fe values of the sites and months with the EPA normal levels (P<0.0001) Table 3. Also the results

| te | Saacon       | Month      |        |       |       |        | Heav   | y metal |       |        |        |       |
|----|--------------|------------|--------|-------|-------|--------|--------|---------|-------|--------|--------|-------|
| Si | Season       | Month      | As     | Cd    | Со    | Cr     | Cu     | Fe      | Hg    | Mn     | Pb     | Zn    |
|    | Autumn       | October    | <15.32 | <1.11 | <4.98 | 38.86  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | December   | <15.32 | <1.11 | <4.98 | 28.02  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    | Winter       | March      | <15.32 | <1.11 | <4.98 | 26.42  | <24.59 | 305.29  | <5.63 | 47.09  | <22.33 | <2.17 |
| M  | Spring       | April      | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 111     | <5.63 | 11     | <22.33 | <2.17 |
|    |              | June       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 235     | 319   | 18     | <22.33 | <2.17 |
|    | Summer       | July       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 31.15   | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | September  | <15.32 | <1.11 | <4.98 | 30.89  | <24.59 | 42.24   | <5.63 | <10.39 | <22.33 | <2.17 |
|    | Autumn       | October    | <15.32 | <1.11 | <4.98 | 39.11  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | December   | <15.32 | <1.11 | <4.98 | 28.70  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    | Winter       | March      | <15.32 | <1.11 | <4.98 | 26     | <24.59 | 67.58   | <5.63 | <10.39 | <22.33 | <2.17 |
| M  | Spring       | April      | <15.32 | <1.11 | <4.98 | 28     | <24.59 | 51      | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | June       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 190     | 157   | <10.39 | <22.33 | <2.17 |
|    | Summer       | July       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 26.89   | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | September  | <15.32 | <1.11 | <4.98 | 30.51  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    | Autumn       | October    | <15.32 | <1.11 | <4.98 | 38.06  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | December   | <15.32 | <1.11 | <4.98 | 29.18  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
| ~  | Winter       | March      | <15.32 | <1.11 | <4.98 | 24.97  | <24.59 | 102.33  | <5.63 | <10.39 | <22.33 | <2.17 |
| MS | Spring       | April      | <15.32 | <1.11 | <4.98 | 27     | <24.59 | 48      | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | June       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 88      | 96    | <10.39 | <22.33 | <2.17 |
|    | Summer       | July       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | September  | <15.32 | <1.11 | <4.98 | 27.39  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    | Autumn       | October    | <15.32 | <1.11 | <4.98 | 38.19  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | December   | <15.32 | <1.11 | <4.98 | 29.24  | <24.59 | <15.77  | <5.63 | 15.8   | <22.33 | <2.17 |
| -  | Winter       | March      | <15.32 | <1.11 | <4.98 | 24.94  | <24.59 | 333.04  | <5.63 | 78.45  | <22.33 | <2.17 |
| M  | Spring       | April      | <15.32 | <1.11 | <4.98 | 27     | <24.59 | 88      | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | June       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 113     | 69    | 18     | <22.33 | <2.17 |
|    | Summer       | July       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 44.14   | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | September  | <15.32 | <1.11 | <4.98 | 25.71  | <24.59 | 220.21  | <5.63 | 39.12  | <22.33 | <2.17 |
|    | Autumn       | October    | <15.32 | <1.11 | <4.98 | 39.15  | <24.59 | 17.44   | <5.63 | 32.13  | <22.33 | 7.4   |
|    | December     |            | <15.32 | <1.11 | <4.98 | 26.73  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
| 10 | Winter March |            | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 1581.57 | <5.63 | 148.06 | <22.33 | <2.17 |
| SW | Spring       | April      | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 121     | <5.63 | 76     | <22.33 | <2.17 |
|    |              | June       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 391     | 60    | 596    | <22.33 | <2.17 |
|    | Summer       | July       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 64.73   | <5.63 | 28.83  | <22.33 | <2.17 |
|    |              | September  | <15.32 | <1.11 | <4.98 | 27.62  | <24.59 | 395.13  | <5.63 | 245.36 | <22.33 | 6.87  |
|    | Autumn       | December   | <15.32 | <1.11 | <4.98 | 27.45  | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    | Winter       | March      | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 25.71   | <5.63 | <10.39 | <22.33 | 7.68  |
| H  | Spring       | April      | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
| H  |              | June       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 24      | 52    | <10.39 | <22.33 | <2.17 |
|    | Summer       | July       | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | <15.77  | <5.63 | <10.39 | <22.33 | <2.17 |
|    |              | September  | <15.32 | <1.11 | <4.98 | <24.49 | <24.59 | 44.23   | <5.63 | 21.43  | <22.33 | <2.17 |
| Γ  | Device detec | tion limit | 15.32  | 1.11  | 4.98  | 24.49  | 24.59  | 15.77   | 5.63  | 10.39  | 22.33  | 2.17  |
|    | EPA norm     | al level   | 10     | 5     | 500   | 100    | 1300   | 300     | 2     | 50     | 15     | 5000  |

Table 1. Water heavy metals investigated ( $\mu$ g/L) in the different selected sites of Shadegan and Hawr Al Azim Wetlands, from October 2011 to September 2012

| ite | Season                   | Month      |        |        |        |       | Heavy  | metal  |        | 1      |        |        |
|-----|--------------------------|------------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|
| ŝ   | 0000011                  | montii     | As     | Cd     | Со     | Cr    | Cu     | Fe     | Hg     | Mn     | Pb     | Zn     |
|     | Autumn                   | October    | < 0.38 | < 0.03 | <0.12  | 1.08  | < 0.62 | <0.39  | < 0.14 | <0.26  | < 0.56 | < 0.05 |
|     |                          | December   | < 0.38 | < 0.03 | <0.12  | 0.78  | < 0.62 | < 0.39 | <0.14  | <0.26  | < 0.56 | < 0.05 |
|     | Winter                   | March      | < 0.38 | < 0.03 | <0.12  | 0.73  | < 0.62 | 7.55   | <0.14  | 1.18   | < 0.56 | < 0.05 |
| SW  | Spring                   | April      | < 0.38 | < 0.03 | < 0.12 | <0.68 | < 0.62 | 2.74   | < 0.14 | 0.28   | < 0.56 | < 0.05 |
|     |                          | June       | <0.38  | < 0.03 | <0.12  | <0.68 | < 0.62 | 5.81   | 7.93   | 0.45   | <0.56  | < 0.05 |
|     | Summer                   | July       | <0.38  | < 0.03 | <0.12  | <0.68 | < 0.62 | 0.77   | < 0.14 | <0.26  | <0.56  | < 0.05 |
|     |                          | September  | < 0.38 | < 0.03 | <0.12  | 0.86  | < 0.62 | 1.04   | <0.14  | < 0.26 | < 0.56 | < 0.05 |
|     | Autumn                   | October    | <0.38  | < 0.03 | <0.12  | 1.09  | < 0.62 | <0.39  | < 0.14 | <0.26  | <0.56  | < 0.05 |
|     |                          | December   | <0.38  | < 0.03 | <0.12  | 0.81  | < 0.62 | <0.39  | < 0.14 | <0.26  | < 0.56 | < 0.05 |
| 2   | Winter                   | March      | < 0.38 | < 0.03 | <0.12  | 0.72  | < 0.62 | 1.67   | < 0.14 | <0.26  | < 0.56 | < 0.05 |
| SWS | Spring                   | April      | <0.38  | < 0.03 | <0.12  | 0.78  | <0.62  | 1.26   | < 0.14 | <0.26  | <0.56  | < 0.05 |
|     |                          | June       | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 4.71   | 3.9    | <0.26  | < 0.56 | < 0.05 |
|     | Summer                   | July       | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 0.66   | < 0.14 | <0.26  | < 0.56 | < 0.05 |
|     |                          | September  | <0.38  | < 0.03 | <0.12  | 0.85  | <0.62  | <0.39  | <0.14  | <0.26  | <0.56  | < 0.05 |
|     | Autumn                   | October    | <0.38  | < 0.03 | <0.12  | 1.06  | <0.62  | <0.39  | <0.14  | <0.26  | <0.56  | < 0.05 |
|     |                          | December   | < 0.38 | < 0.03 | <0.12  | 0.81  | <0.62  | <0.39  | <0.14  | <0.26  | <0.56  | < 0.05 |
| 33  | Winter                   | March      | <0.38  | < 0.03 | <0.12  | 0.69  | <0.62  | 2.53   | <0.14  | <0.26  | <0.56  | <0.05  |
| SW  | Spring                   | April      | <0.38  | < 0.03 | <0.12  | 0.75  | <0.62  | 1.19   | <0.14  | <0.26  | <0.56  | < 0.05 |
|     |                          | June       | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 2.18   | 2.39   | <0.26  | < 0.56 | < 0.05 |
|     | Summer                   | July       | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | < 0.39 | < 0.14 | <0.26  | < 0.56 | < 0.05 |
|     |                          | September  | < 0.38 | < 0.03 | <0.12  | 0.76  | < 0.62 | < 0.39 | < 0.14 | < 0.26 | < 0.56 | < 0.05 |
|     | Autumn                   | October    | < 0.38 | < 0.03 | <0.12  | 1.06  | < 0.62 | < 0.39 | < 0.14 | <0.26  | < 0.56 | < 0.05 |
|     |                          | December   | < 0.38 | < 0.03 | < 0.12 | 0.81  | < 0.62 | < 0.39 | < 0.14 | 0.40   | < 0.56 | < 0.05 |
| 4   | ₩inter<br>Spring         | March      | < 0.38 | < 0.03 | <0.12  | 0.69  | < 0.62 | 8.24   | < 0.14 | 1.96   | < 0.56 | < 0.05 |
| SW  | Spring                   | April      | < 0.38 | < 0.03 | < 0.12 | 0.75  | < 0.62 | 2.18   | < 0.14 | < 0.26 | < 0.56 | < 0.05 |
|     |                          | June       | < 0.38 | < 0.03 | < 0.12 | <0.68 | < 0.62 | 2.8    | 1.72   | 0.45   | < 0.56 | < 0.05 |
|     | Summer                   | July       | < 0.38 | < 0.03 | <0.12  | <0.68 | <0.62  | 1.09   | <0.14  | <0.26  | < 0.56 | < 0.05 |
|     |                          | September  | < 0.38 | < 0.03 | <0.12  | 0.71  | < 0.62 | 5.45   | <0.14  | 0.98   | < 0.56 | < 0.05 |
|     | Autumn Octo              |            | < 0.38 | < 0.03 | <0.12  | 1.09  | < 0.62 | 0.43   | <0.14  | 0.8    | < 0.56 | 0.17   |
|     | December<br>Winter March |            | < 0.38 | < 0.03 | <0.12  | 0.74  | < 0.62 | < 0.39 | <0.14  | <0.26  | <0.56  | < 0.05 |
| 5   | Winter March             |            | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 39.11  | <0.14  | 3.7    | <0.56  | < 0.05 |
| SW  | Spring                   | April      | <0.38  | < 0.03 | <0.12  | <0.68 | <0.62  | 3.09   | <0.14  | 1.9    | <0.56  | < 0.05 |
|     |                          | June       | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 9.67   | 1.49   | 14.91  | <0.56  | < 0.05 |
|     | Summer                   | July       | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 1.6    | <0.14  | <0.26  | <0.56  | < 0.05 |
|     |                          | September  | < 0.38 | < 0.03 | <0.12  | 0.77  | < 0.62 | 9.77   | <0.14  | 6.15   | <0.56  | 0.16   |
|     | Autumn                   | December   | < 0.38 | < 0.03 | <0.12  | 0.76  | < 0.62 | <0.39  | <0.14  | <0.26  | < 0.56 | < 0.05 |
|     | Winter                   | March      | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 0.64   | <0.14  | <0.26  | <0.56  | 0.18   |
| HI  | Spring                   | April      | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | < 0.39 | <0.14  | <0.26  | < 0.56 | < 0.05 |
|     |                          | June       | < 0.38 | < 0.03 | <0.12  | <0.68 | < 0.62 | 0.59   | 1.29   | <0.26  | < 0.56 | < 0.05 |
|     | Summer                   | July       | < 0.38 | < 0.03 | <0.12  | <0.68 | <0.62  | <0.39  | <0.14  | <0.26  | < 0.56 | < 0.05 |
|     |                          | September  | < 0.38 | < 0.03 | <0.12  | <0.68 | <0.62  | 1.09   | <0.14  | 0.54   | <0.56  | < 0.05 |
| D   | evice detec              | tion limit | 0.38   | 0.03   | 0.12   | 0.68  | 0.62   | 0.39   | 0.14   | 0.26   | 0.56   | 0.05   |
|     | EPA norm                 | al level   | 0.01   | 0.005  | 0.5    | 0.1   | 1.3    | 0.3    | 0.002  | 0.05   | 0.015  | 5      |

Table 2. Water heavy metals investigated ( $\mu g/g$ ) in the selected sites of Shadegan and Hawr Al Azim Wetlands, from October 2011 to September 2012

|       |        |     |          |       |       |          | 1     | U   |          |
|-------|--------|-----|----------|-------|-------|----------|-------|-----|----------|
| M.4.1 |        | Wat | er       | Se    | lecte | d site   |       | Mor | nth      |
| Metal | t      | df  | Р        | t     | df    | Р        | t     | df  | Р        |
| Cr    | 0.72   | 40  | 0.476    | 10.21 | 41    | < 0.0001 | 10.31 | 41  | < 0.0001 |
| Fe    | 2.35   | 40  | 0.024    | 10.54 | 41    | < 0.0001 | 10.61 | 41  | < 0.0001 |
| Hg    | 1.99   | 40  | 0.053    | 12.59 | 41    | < 0.0001 | 12.35 | 41  | < 0.0001 |
| Mn    | 1.81   | 40  | 0.078    | 11.96 | 41    | < 0.0001 | 11.81 | 41  | < 0.0001 |
| Zn    | 1007.6 | 40  | < 0.0001 | 5.81  | 41    | < 0.0001 | 3.36  | 41  | 0.002    |

Table 3.One-sample t-test analysis between the EPAnormal levels and observed water heavy metal rates ofthe different selected site and month samplings

Table 4.One-way ANOVA analysis between thedifferent selected site and month samplings of theobserved water heavy metal rates

| Matal | Se   | lected | site  |       | Month | ı        |
|-------|------|--------|-------|-------|-------|----------|
| Metal | F    | df     | Р     | F     | df    | Р        |
| Cr    | 2.46 | 5      | 0.056 | 90.42 | 6     | < 0.0001 |
| Fe    | 2.49 | 5      | 0.054 | 2.46  | 6     | 0.048    |
| Hg    | 0.99 | 5      | 0.441 | 8.03  | 6     | < 0.0001 |
| Mn    | 3.42 | 5      | 0.015 | 1.07  | 6     | 0.402    |
| Zn    | 1.59 | 5      | 0.195 | 0.86  | 6     | 0.533    |

of One-way analysis of variance (ANOVA) did not show any significant differences between the Fe values of the sites and months (P=0.054 and P=0.048) Table 4.

The water Hg values observed higher than the EPA normal levels in the June indicating water contamination to Hg in the June of the all site samplings (shown in bold in the Tables 1 and 2) whereas observed lower than the EPA normal levels<sup>20</sup> in the other sites and months. The lowest and the highest water Hg contamination values observed in the HH and SW<sub>1</sub>, respectively both in the June (Tables 1 and 2, and Figure 1). The results of one-sample t-test revealed a significant differences between the Hg values of the sites and months with the EPA normal levels (P<0.0001) Table 3. Also The results of one-way analysis of variance (ANOVA) did not show any significant differences between the Hg values of the sites (P=0.441) Table 4, whereas showed a significant differences between the Hg values of the months (P<0.0001) Table 4 which is observed a significant differences between the Hg values of the June with the other months (P<0.05) followed by Post Hoc tests (Tukey HSD) and did not show any significant differences between the other months (P>0.05) Table 6.

The water Mn of the SW<sub>1</sub> in the March, April and June; the SW<sub>4</sub> in the December, March, June and September; the SW<sub>5</sub> in the October, March, April, June and September; and the HH in the September observed higher than the

EPA normal levels indicating water contamination to Mn (shown in bold in the Tables 1 and 2) whereas observed lower than the EPA normal levels in the other months. The lowest and the highest water Mn contamination values observed in the SW<sub>1</sub> and SW<sub>5</sub> in the April and June, respectively (Tables 1 and 2, and Figure 1). The results of one-sample t-test showed a significant differences between the Mn values of the sites and months with the EPA normal levels<sup>20</sup> (P<0.0001) Table 3. Also the results of One-way analysis of variance (ANOVA) showed a significant differences between the Mn values of the sites (P=0.015) Table 4, whereas did not show any significant differences between the Mn values of the months (P<0.0001) Table 4.

The Zn values of the  $SW_5$  in the October and September; and the HH in the March observed slightly lower than the EPA normal levels indicating water suspected to Zn contamination (shown in bold in the Tables 1 and 2) whereas observed lower than the EPA normal levels in the other sites and months.

The Pearson correlation analysis revealed a significant negative relationship between the water Cr values with the months (P<0.0001), whereas revealed a significant positive relationship between the water Fe and Mn values (P=0.004), and Zn values with sites (P=0.041) Table 7.

In overall, as revealed in the Tables 1 and 2, and Figure 1, the water of Shadegan and Hawr Al Azim wetlands have been contaminated by Cr, Fe, Mn, Hg and Zn. In this respect contaminating the wetland waters by these heavy metals can adversely affect on human health of their water supply; also, it supports agricultural activities by providing a source of water for irrigation and livestock and for domestic consumption, sustainable forestry, nursery areas for juveniles of commercially valuable fish species and fisheries, forage resources, craft materials and medicinal plants; it also provides habitat for birds, which can play an important role in helping to control pests on nearby farms means that there is less need for costly and polluting chemical spraying to control insect pests. Also many bird, fish, mammal, reptile, and amphibian species are dependent to the wetlands for their breeding, foraging, and covering. Some species that they cannot survive elsewhere are providing by unique habitat of the special wetland conditions. Migratory birds depend on the wetlands. The life cycle of the many endangered and threatened species occur in the wetlands. Protection of threatened and endangered species is important in standards development <sup>13</sup>. However, this study showed that the water of these wetlands have been contaminated by heavy metals threatening their lives.

| Tab  | · · · · ·       | -net laws          | `             |            | 2                  |                 |               |                    |               |                |                    | •             |                    |                   |               |                    |               |       |  |
|------|-----------------|--------------------|---------------|------------|--------------------|-----------------|---------------|--------------------|---------------|----------------|--------------------|---------------|--------------------|-------------------|---------------|--------------------|---------------|-------|--|
|      |                 |                    | $SW_1$        |            |                    |                 | $SW_2$        |                    |               |                | $SW_3$             |               |                    | $SW_4$            |               |                    | $SW_5$        |       |  |
| 4    | fetal           | Mean<br>difference | Std.<br>error | Р          | difi               | Mean<br>Ference | Std.<br>error | Р                  | N<br>diff     | fean<br>erence | Std.<br>error      | Р             | Mean<br>difference | Std.<br>error     | Р             | Mean<br>difference | Std.<br>error | Р     |  |
|      | $SW_2$          | 0.0171             | 0.01745       | .0.6       | 21                 |                 | ı             | 1                  |               |                | 1                  | ı             | ı                  | 1                 | ı             | 1                  |               | ı     |  |
|      | $SW_3$          | 0.0086             | 0.01745       | .0 ¢       | 96 0               | 0.0257          | 0.01749       | 0.685              |               |                |                    | 1             | 1                  | 1                 |               | 1                  |               | ı     |  |
| C    | $\mathrm{SW}_4$ | 0.0157             | 0.01745       | 6.0 6      | 44 0               | 0.0329          | 0.01749       | 0.435              | 0.0           | 0071           | 0.01749            | 0.998         | ı                  | 1                 | '             | 1                  | 1             | ı     |  |
|      | $SW_5$          | 0.0243             | 0.01745       | 0.73       | 34 0               | .0414           | 0.01749       | 0.201              | 0.0           | 0157           | 0.01749            | 0.944         | 0.0086             | 0.01749           | 0.996         | ı                  | ı             | ı     |  |
|      | НН              | 0.0910*            | 0.01821       | i <0.0(    | 001 0.             | 1081*           | 0.01821       | <0.000.0>          | 1 0.0         | )824*          | 0.01821            | 0.001         | 0.0752*            | 0.01821           | 0.003         | 0.0667*            | 0.01821       | 0.012 |  |
|      | $SW_2$          | 0.1614             | 1.1579        | >0.9       | 66                 | 1               | ı             | 1                  |               |                | 1                  | 1             | ı                  | 1                 |               | 1                  | 1             | ı     |  |
|      | $SW_3$          | 0.1614             | 1.1579        | >0.9       | )> 66(             | 0.0001          | 1.1579        | >0.999             |               |                | ı                  |               | ı                  | ı                 | '             | ı                  | 1             | ı     |  |
| Mn   | $\mathrm{SW}_4$ | 0.2314             | 1.1579        | >0.9       | 0 660              | .3929           | 1.1579        | >0.999             | 0             | 3929           | 1.1579             | >0.999        | ı                  | ı                 | '             | 1                  | 1             | ı     |  |
|      | $SW_5$          | 3.6414*            | 1.1579        | 0.0        | 40 3.              | 8029*           | 1.1579        | 0.029              | 3.6           | 3029*          | 1.1579             | 0.029         | 3.41               | 1.1579            | 0.063         | 1                  | 1             | ı     |  |
|      | НН              | 0.1148             | 1.2052        | >0.9       | 0 66               | .0467           | 1.2052        | >0.999             | 0.0           | 0467           | 1.2052             | >0.999        | 0.3462             | 1.2052            | >0.999        | 3.7562*            | 1.2052        | 0.043 |  |
| *The | mean difi       | ference is sig     | nificant at   | t the 0.05 | level              |                 |               |                    |               |                |                    |               |                    |                   |               |                    |               |       |  |
| Tabj | le 6. ]         | ľukey HSL          | ) analys      | sis amo    | ng the o           | bservec         | l water       | heavy m            | ietal ra      | tes of th      | ie month           | sampli        | ngs after (        | One-way           | ANOV          | A significa        | nnce          |       |  |
|      |                 |                    | October       |            | Ď                  | ecember         |               | V                  | March         |                |                    | April         |                    | Ϊ                 | une           |                    | July          |       |  |
|      | Metal           | Mean<br>difference | Std.<br>error | P d        | Mean<br>difference | Std.<br>error   | P             | Mean<br>lifference | Std.<br>error | Р              | Mean<br>difference | Std.<br>error | P d                | Mean<br>ifference | Std.<br>error | P differe          | un Std.       | Ъ     |  |
|      | Decembe         | <b>r</b> 0.291*    | 0.0198 <      | <0.0001    | ,                  | ,               |               |                    |               |                |                    | ,             |                    |                   |               | 1                  | ·             | 1     |  |

| 5        | T 001 |                    |         | 11111 OTO | י אוווא נוויר י    |               | כח אמור |                    | Mauch 16      |         |                    | - 1      | ı sanıpıı | ı sampungs and |              |                |                                | 1 sampungs arter One-way ANOVA significanc |                                       |
|----------|-------|--------------------|---------|-----------|--------------------|---------------|---------|--------------------|---------------|---------|--------------------|----------|-----------|----------------|--------------|----------------|--------------------------------|--|---------------------------------------|
|          |       | -                  | October |           | Ω                  | ecember       |         |                    | March         |         |                    | <b>A</b> | pril      | pril           | pril         | pril June      | pril June                      | pril June                                  | pril June June                        |
| Metal    |       | Mean<br>difference | Std.    | Р         | Mean<br>difference | Std.<br>error | Р       | Mean<br>difference | Std.<br>error | Ρ       | Mean<br>difference | Std.     |           | Ъ              | P difference | P Mean Std.    | P Mean Std. P difference error | r P Mean Std. P Mean                       | P Mean Std. P Mean Std.               |
| December |       | 0.291*             | 0.0198  | <0.0001   | 1                  | I             | 1       | I                  | 1             |         | I                  | 1        |           | 1              |              | 1              |                                |  |                                       |
| March    |       | 0.378*             | 0.0198  | <0.0001   | 0.0867*            | 0.0189        | 0.0189  | 0.001              |               | 1       | 1                  | ,        |           |                | •            |                | •                              | - 1  | - 1                                   |
| April    |       | 0.356*             | 0.0198  | <0.0001   | 0.065*             | 0.0189        | 0.026   | 0.0217             | 0.0189        | 0.908   |                    |          | 1         |                | •            | 1              | •                              | 1  | 1                                     |
| June     | 1     | 0.396*             | 0.0198  | <0.0001   | 0.105*             | 0.0189        | <0.0001 | 0.0183             | 0.0189        | 0.957   | 0.040              | 0.0189   | 0.370     |                |              | 1              | •                              | 1  | 1                                     |
| July     |       | 0.396*             | 0.0198  | <0.0001   | 0.105*             | 0.0189        | <0.0001 | 0.0183             | 0.0189        | 0.957   | 0.040              | 0.0189   | 0.370     |                | 0.00001      | 0.00001 0.0189 | 0.00001 0.0189 >0.999          | 0.00001 0.0189 >0.999 -                    | 0.00001 0.0189 >0.999 -               |
| Septembe |       | . 0.3043*          | 0.0198  | <0.0001   | 0.0133             | 0.0189        | 0.991   | 0.0733*            | 0.0189        | 0.009   | 0.0517             | 0.0189   | 0.125     |                | 0.0917*      | 0.0917* 0.0189 | 0.0917* 0.0189 0.001           | 0.0917* 0.0189 0.001 0.0917*               | 0.0917* 0.0189 0.001 0.0917* 0.0189   |
| Decembe  |       | 0.00001            | 0.5901  | >0.999    | ,                  | ı             |         |                    |               |         |                    |          |           |                | '            |                | •                              | 1  | 1                                     |
| March    |       | 0.00001            | 0.5901  | >0.999    | <0.0001            | 0.5626        | >0.999  | 1                  |               | 1       | 1                  |          |           |                | ,            | 1              | •                              | 1  | 1                                     |
| April    |       | 0.00001            | 0.5901  | >0.999    | <0.0001            | 0.5626        | >0.999  | 0.00001            | 0.5626        | >0.999  | ı                  |          | ·         |                |              | 1              |                                |  | 1                                     |
| June     |       | 2.98*              | 0.5901  | <0.0001   | 2.98*              | 0.5626        | <0.0001 | 2.98*              | 0.5626        | <0.0001 | 2.98*              | 0.5626   | <0.0001   |                | ,            | 1              |                                | · · · · · · · · · · · · · · · · · · ·      |                                       |
| July     |       | 0.00001            | 0.5901  | >0.999    | <0.0001            | 0.5626        | >0.999  | 0.00001            | 0.5626        | >0.999  | 0.00001            | 0.5626   | >0.999    |                | 2.98*        | 2.98* 0.5626   | 2.98* 0.5626 <0.0001           | 2.98* 0.5626 <0.0001 -                     | 2.98* 0.5626 <0.0001 -                |
| Septemb  | er    | 0.00001            | 0.5901  | >0.999    | <0.0001            | 0.5626        | >0.999  | 0.00001            | 0.5626        | >0.999  | 0.00001            | 0.5626   | >0.999    | •              | 2.98*        | 0.5626         | 0.5626 <0.0001                 | 0 2.98* 0.5626 <0.0001 0.00001             | 0 2.98* 0.5626 <0.0001 0.00001 0.5626 |

\*The mean difference is significant at the 0.05 level

|      | Metal       | Fe     | Hg     | Mn      | Zn     | Site   | Month    |
|------|-------------|--------|--------|---------|--------|--------|----------|
|      | Correlation | -0.225 | -0.214 | -0.140  | 0.174  | -0.214 | -0.580** |
| Cr   | Sig.        | 0.157  | 0.178  | 0.382   | 0.276  | 0.178  | < 0.0001 |
|      | Ν           | 41     | 41     | 41      | 41     | 41     | 41       |
|      | Correlation |        | 0.091  | 0.435** | 0.015  | 0.134  | 0.021    |
| Fe   | Sig.        | -      | 0.573  | 0.004   | 0.924  | 0.404  | 0.897    |
|      | Ν           |        | 41     | 41      | 41     | 41     | 41       |
|      | Correlation |        |        | 0.059   | -0.089 | -0.205 | 0.149    |
| Hg   | Sig.        | -      | -      | 0.715   | 0.581  | 0.199  | 0.352    |
|      | Ν           |        |        | 41      | 41     | 41     | 41       |
|      | Correlation |        |        |         | 0.141  | 0.243  | 0.134    |
| Mn   | Sig.        | -      | -      | -       | 0.380  | 0.126  | 0.405    |
|      | Ν           |        |        |         | 41     | 41     | 41       |
|      | Correlation |        |        |         |        | 0.320* | -0.074   |
| Zn   | Sig.        | -      | -      | -       | -      | 0.041  | 0.647    |
|      | Ν           |        |        |         |        | 41     | 41       |
|      | Correlation |        |        |         |        |        | 0.000    |
| Site | Sig.        | -      | -      | -       | _      | -      | 1.000    |
|      | N           |        |        |         |        |        | 42       |

| Table 7.  | Pearson correlation analysis amo | ong the |
|-----------|----------------------------------|---------|
| water hea | vy metal, site and month samplin | gs      |

\*\*Correlation is significant at the 0.01 level (2-tailed).

\*Correlation is significant at the 0.05 level (2-tailed).

Heavy metals in Shadegan and Hawr Al Hawizeh wetlands may come from natural as well as artificial sources. Heavy metals that are naturally introduced into these wetlands may come generally from weathering of rocks, erosion of soils and water-soluble salt dissolution. Naturally heavy metals introducing into aquatic environments independently of human activities usually have not detrimental effects. However, as Shadegan and Hawr Al Hawizeh wetlands are industrializing, the heavy metals introducing by human activities affect their water quality. Although some heavy metals may be vital for proper living organism metabolism but it is toxic at their high levels, others currently may be as non-essential but it is toxic even at relatively low levels. Heavy metals are released to Shadegan and Hawr Al Hawizeh wetlands are from numerous sources. Typical sources are municipal wastewater, manufacturing industries, mining, and agricultural cultivation and fertilization. They have increased their pollution leading to the deaths of its marine animals contaminated by heavy metals.

Although, these wetland waters have been contaminated by Cr, Fe, Mn, Hg and Zn, in this study, it can be considered that to be accumulated in the waterbed sediment and bioconcentrated in the wildlife and animal tissues. These facts established by assessing some fish muscles and insect tissues that they had lived in the wetlands<sup>7,16,21,22</sup> causing their high heavy metal pollution. Afterwards, their entering in the marine food chains they biomagnified there in the long periods. Then they fed by predator such as birds and fish and threatened human health through food chains by their human consuming. The heavy metals which are dissolved in the water have the greatest potential of causing the most deleterious toxic effects on organisms by their taken up. Various harmful effects including abnormal development of the fetus, procreation failure, and immunodeficiency have exhibited due to aquatic metal exposure<sup>12</sup>.

In the current study, the values of the Cr, Fe, Mn, Hg and Zn were observed higher than the EPA water normal levels (shown as bold font style in Table 2), however Farrokhian et al.<sup>15</sup> reported the water cadmium, lead, nickel and copper metal pollutants of the Shadegan wetland higher than the aquatic limits<sup>15</sup>. Also the values of the cadmium and lead metals in the fish muscle tissues in Hawr Al Azim wetland were determined. Results showed that some fish species were contaminated by high values of lead and cadmium<sup>21</sup>.

## 3. Conclusion

Shadegan and Hawr Al Azim wetlands have been contaminated by Cr, Fe, Mn, Hg and Zn and they can be accumulated in the fauna and flora tissues. These facts established by assessing some fish muscles and insect tissues that they had lived in the wetlands bioaccumulated with high heavy metals. Such contamination might threatened human health through food chains.

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