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DETERMINATION OF THE CONCENTRATIONS OF SOME TRACE ELEMENTS (URANIUM, ARSENIC, BERYLLIUM, AND VANADIUM) IN WATER AND SEDIMENTS OF SHATT AL-ARAB RIVER- SOUTHERN IRAQ

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ABSTRACT

The current study included two sites in the middle part of Shatt Al-Arab- Southern Iraq (Al-Ashar and Al-Deir sites), the concentrations of trace elements which represented by Uranium, Arsenic, Beryllium and Vanadium were measured in water and sediments of four seasons from autumn 2018 to summer 2019 . The concentrations of trace elements showed variations at the level of significance in the water and sediments, Uranium recorded its highest concentration in the study water (6.1 µg/l) at the spring of Al-Deir site. While its highest concentrations in sediments reached (2.4 µg/g) at Al-Ashar site, moreover   the highest concentration of Arsenic in water was (4.2 µg/l) at autumn of Al-Deir site and (6.1 µg/g) for sediments at Al-Ashar site ,as well as the concentration of Beryllium was below the detection limit (BDL) in water , while its highest concentration in sediments was recorded (1.1µg/g) as well as the highest concentration of Vanadium was (8.4 µg / l) in water and (87µg/g) in sediments.
Keywords: Shatt Al-Arab River, trace elements, water, sediments.

Introduction

Heavy metals is a term that generally refers to metallic elements with an atomic weight greater than 20, also called trace elements due to their presence in low concentrations in nature at a rate not exceeding 0.1%, and they were defined by (Lenntech, 2004; Al-Hejuje, 2014) as mineral elements with high density and toxic to organisms at low concentration. Trace elements are considered among the most important pollutants that most researchers agree on their danger and severity of toxicity (Bradney *et al*., 2019; Gupta *et al*., 2019) in addition to petroleum hydrocarbons such as poly cyclic aromatic hydrocarbons, which are among the most prevalent pollutants and affecting the water environment (Guerra-Gracia *et al*., 2003). Where petroleum pollution and trace elements are the most important causes in the destruction of the aquatic ecosystem and the aquatic animals in it (Lenntech, 2004; Pourang *et al*., 2005). Industrial processes, wastewater and agricultural fertilizers are among the main sources of contamination with minerals, as well as the presence of heavy elements in pigments, plastic and paper components. Furthermore, disinfection materials and many different household materials contain varying proportions of heavy metals (Abel, 2002; Ulmanu *et al*., 2003). Therefore, the preservation of the quality of human nutrition is sought by the human being through the detection of pollution levels due to their toxic effects on the health of consumers and appear of various disease symptoms (Viarengo, 1989; Benoff *et al*., 2000).

Materials and Methods

Sample collection

Samples of water and sediments were collected from the Shatt al-Arab River - southern Iraq from the two sites (Al-Ashar and Al-Deir) from November (2018) to June (2019).The water for measuring heavy elements was collected by 2 liter polyethylene bottles at a depth of about 25 cm below the water surface from the middle of the River as well as sediment samples, they were collected using a grab sampler, then they were placed in sealed plastic bags and transferred to the laboratory.

Concentration of trace elements in water

Water samples were digested according to the Apha method (1995) as follows: Take (100) ml of the sample and put it in a 200 ml volumetric flask and add (5) ml of HNO_3 to it, then the sample was placed on a hot plate without boiling, then another (5) ml of HNO_3 was added to it until the white salt was formed. The white salt was dissolved with drops of HCL then, water was added to complete the volume at 100 ml, after which it was kept in sealed plastic containers until measurement with an ICP-MS device.

Concentration of trace elements in sediment

The sediment samples were dried in an electric oven at (50) ℃ for a period of (24) hours, after the samples were ground by mortar and passed through a sieve, and the digestion process was carried out according to (Binning and Baird, 2001) .The heavy metals concentration of water and sediments in ICP-MS device was analyzed by Zarazma Company for Mineral Studies, Tehran- Iran.

Determination of the concentrations of some trace elements (uranium, arsenic, beryllium, and vanadium) in water and sediments of shatt Al-arab river- southern Iraq

601

Statistical analysis

Data were statistically analyzed using the analysis of variance (ANOVA test one way). Data were collected statistically using the software SPSS, at the probability level of $P \leq 0.05$.

Results

The results of the current study showed that there were clear significant differences at the level of significance P< 0.05 for the concentrations of Uranium, Arsenic, Beryllium and Vanadium in the water of the two selected study sites and for the four seasons. In the water of the two sites, it was found that there were significant differences in the values of Uranium concentrations, where Uranium did not record any concentrations in the autumn and winter seasons of the two sites. While, significant concentrations were recorded for the spring and summer seasons, as it reached the highest (16.1 µg / l) in the spring of Al-Deirsite table (1), Figure (1).

Moreover, the results of the rates of Arsenic concentrations in the study water showed significant differences between the two sites at the significance level P< 0.05, where the concentrations of the Arsenic reached to (4.2 µg / l) in Al-Deirsite, table (1), Figure (2). On the contrary, the results of the Beryllium concentrations rates showed that there were not recorded any concentrations in all four seasons and for two sites which targeted in the current study, table (1).While the rates of Vanadium concentrations in the water of the two sites showed not a clear variation at the level of P> 0.05.Whereas, no concentrations were recorded for the autumn and winter seasons, while the concentrations in the spring and summer seasons reached to (8.4 µg / l) in the summer of Al-Deir site. Where the arrangement of the rates of Vanadium concentrations in the study water was given the following arrangement: Autumn= winter >spring> summer, table (1).

The results of the accumulation of heavy metals in sediments showed the presence of significant differences at the level of significance P< 0.05 between the two study sites in Shatt Al-Arab and the four seasons, while there were no significant differences for some metals in some seasons. For Uranium, Al-Asharsite recorded the highest accumulated value of sediments in the summer by concentration reached to (2. µg / g) dry weight, while the rates of Al-Deirsite ranged between (1.5- 2.2 µg /g) dry weight. The results of the accumulation of Arsenic in the sediments showed clear differences between the seasons. Where, the highest concentration were recorded in the winter of Al-Ashar and Al-Deirsites by (6.1 and 4.4 µg /g) respectively. On the other hand, the lowest concentrations were (1.8 and 2.2 µg /g) in the summer of the Al-Deirand Al-Ashar sites, respectively. The results of Beryllium concentrations in the sediments showed a significant difference and variation between the four seasons, where the concentrations of the cumulative rates of Beryllium in the sediments ranged between (0.7 - 1.1µg /g) dry weight. On the contrary, the values of the cumulative rates of Vanadium in the sediments of the two sites showed very high values compared to the Uranium, Arsenic and Beryllium. Where, it reached the highest concentration in the sediments of the Al-Ashar site by (87 µg /g) dry weight in the winter season as the highest cumulative value recorded in the sediments of the two sites of different seasons. While the summer season recorded the lowest concentrations compared to the other seasons, where it was (61 and 74.3 µg /g) for the sites of Al-Deirand Al-Ashar respectively table (2).

Table 1 : The concentration mean of trace elements (µg /l) in the water of the Shatt Al-Arab River.

Sites	Seasons	Uranium	Arsenic	Beryllium	Vanadium
Al-Ashar	autumn	BDL	BDL	BDL	BDL
	winter	BDL	1.4	BDL	BDL
	spring	5.31	BDL	BDL	4.41
	summer	3.96	2	BDL	8
Al-Deir	autumn	BDL	4.2	BDL	BDL
	winter	BDL	0.32	BDL	BDL
	spring	6.1	BDL	BDL	4.7
	summer	3.3	0.52	BDL	8.4

(BDL):Below the Detection Limit

Table 2 : The concentration mean of trace elements (µg /g) in the sediments of the Shatt Al-Arab River.

Sites	Seasons	Uranium	Arsenic	Beryllium	Vanadium
Al-Ashar	autumn	1.64	3.7	1.1	83
	winter	1.7	6.1	1.1	87
	spring	2	2.6	1.1	85
	summer	2.4	2.2	0.9	74.3
Al-Deir	autumn	1.5	3.9	1.1	78
	winter	1.6	4.4	1	82
	spring	2	3.8	1	74
	summer	2.2	1.8	0.7	61
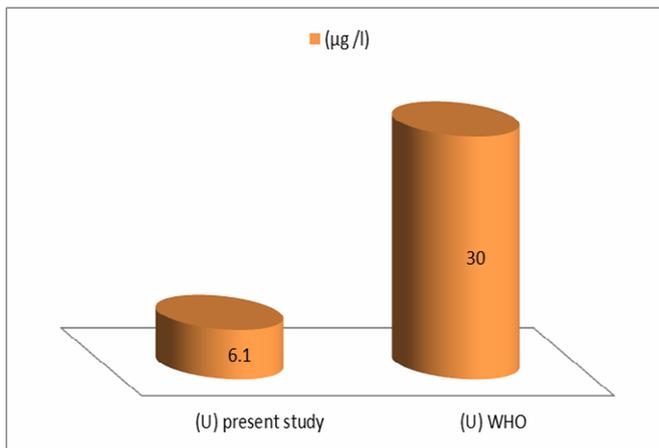
Fig. 1 : Comparison of the highest concentration of Uranium (µg /l) with permitted levels according to WHO in drinking water.
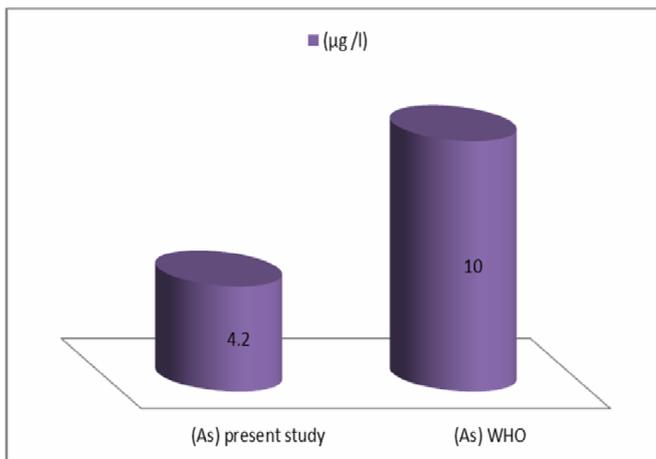
Fig. 2 : Comparison of the highest concentration of Arsenic (µg /l) with permitted levels according to WHO in drinking water.

Discussion

The human resources that represent all the sources related to human activities, such as the various industrial wastes, the excessive use of agricultural pesticides and the residues of oil refining processes are among the most important sources that increase pollutants with heavy metals to the water environment (Fialkowski *et al.*, 2003; Song *et al*., 2010). AS well as many of the heavy metals are present within the sediment composition in the form of major components, where the heavy metals and pollutants can be accumulated in sediments. Sediments can expulsion those pollutants to the water environment, especially when the water is of low concentration of these elements due to the exchange reactions, and those reactions increase with the increase in temperature, in addition to the effect of water flow speed and the small size of sediments, in general, the increase in the concentrations of heavy metals causes severe physiological damage to the organisms, which often leads to their death (Morel *et al*., 1991; Fernandes *et al*., 2008; Li *et al*., 2020; Nour, 2020). In the current study, the recording of Uranium concentrations in the Shatt al-Arab water during the spring and summer seasons in comparison to the absence of any concentration during the winter and autumn seasons,it may be due to the large bodies of water that entered from Iranian lands in the spring of 2019 that entered the Shatt al-Arab via the Sweib River passing through the Hawizehmarsh, which may contain part of the contaminated war remnants. Where the Shatt al-Arab received large water

bodies due to the torrents from Iran which extended from spring 2019 until the summer of the same year ,in addition, the Shatt al-Arab is a center for large quantities of various sediments, which may reach more than 200,000 tons annually (Albadran *et al*., 2002).Furthermore in the current study, the high concentrations of Uranium in the spring and summer seasons in the water compared with the winter and autumn seasons are not considered a threat to human life compared to the reports of the World Health Organization(WHO) (Frisbie *et al*., 2013), as well as in the present study, the values of Arsenic levels in water gave safe determinants compared to the World Health Organization standard (10 µg /l) for drinking water (Driehaus *et al*., 1998; Ahmad and Bhattacharya, 2019). In addition, the current study the values of Beryllium concentrations was below the detection limit in water for all seasons and this may be due to nature of pH in Shatt Al-Arab River where it are alkaline . The concentrations of Vanadium in the study water for the autumn and winter seasons were below the detection limit (BDL) and this may be due to its tendency to accumulate in sediments, since sediments are a source of accumulation of pollutants (de Díaz *et al*., 2001). In the current study, it was generally observed that the concentrations of trace elements in sediments increased in the winter season compared with their concentration in other seasons, where the high values of trace elements of sediments in winter season, generally may be due to several roles, including the role of rain and the dredging of pollutants into the water environment and the role of the pH ,where it is high during the winter season and the role of low temperatures, and this increase of adsorption and precipitation (Gaur *et al*., 2005; Fernandes *et al*., 2008).

Conclusion

In the present study, the values of Uranium and Arsenic levels in Shatt Al-Arab River water gave safe determinants compared to the World Health Organization standard for drinking water. Furthermore, the concentrations of trace elements in sediments were higher than in the water, and this indicates that the sediments are a source of pollutants, and that the high flow of water reduces their values in sediments and increases them in the water.

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Determination of the concentrations of some trace elements (uranium, arsenic, beryllium, and vanadium) in water and sediments of shatt Al-arab river- southern Iraq

603

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