Assessment of Some Heavy Metals in Water and Sediments Using Bio-Concentration Method of Al-Ma’ail River in Al-Kahla’a District, Maysan, Southern Iraq

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Abstract

Al-Ma'ail river is one of the small Iraqi rivers, as it extends over a distance of approximately 47 km. Al-Ma'ail river is located next to Halfaya oil field, which is the main source of pollution to Al-Ma'ail river, consequently, the environmental quality of Al-Ma'ail river is under great pressure from a variety of human activities. Although water is commonly used as an indicator of contamination by heavy metals, sediments are considered as water important in assessing the environmental situation. In this study, water and sediment samples were analyzed to assess the pollution status of heavy metals in Al-Ma'ail river, with the aim of determining its ability to sustain aquatic life. Samples were taken from five sites along Al-Ma'ail river between the branch area of Al-Ma'ail river from the Al-Kahla river (which also branches from Tigris River upon its exit from Amara City), until Al-Ma'ail river reaches pond of Umm Al-Na'aj (marshland). Ten Water and five sediment samples were collected in August 2020. Samples were analyzed for eight heavy metals: As, Cd, Cr, Cu, Pb, V, Ni and Zn, using AAS techniques. As for the water samples, all the concentrations were over the standards (except Zn which was within the limits in all samples), While Cu concentration in (samples SW1 to SW7) are within the standards (except SW8 and SW9 are close U.S.EPA and within WHO). Concentrations of heavy metals in sediments were over the limits in all samples. The bio-concentration values of heavy metals were calculated and all metal rates were found within the acceptable range for the U.S. EPA, except for vanadium, which was higher than the permissible limit and was a bio-accumulative and considered as an indicator of oil pollution. The results indicate the presence of long-term contamination of the eight selected heavy metals in the river sediments which may be of concern to the health of the aquatic ecosystem.

Keywords: Maysan; River sediments; Al-Ma’ail river; Heavy metal; Bio-concentration

1. Introduction

Al-Ma'ail river is one of the branches of the Al-Kahla river from the rivers that flow into the Umm Al-Na'aj pond and the Hawizeh Marshland. On the left side of Al-Ma'ail river (Al- Zubayr) lies next to the Halfaya oil field extending along its length from its branching area from the Al-Kahla river to its outlet in the pond of Umm Al-Na'aj and Al-Hawizeh Marshland. On the right side of the river, there are agricultural lands, cement and bricks factories that provide raw materials to the company operating in the Halfaya oil field (Petro-China). Therefore, the environmental quality of Al-Ma'ail river has subjected to great pressure from a variety of human activities. Although water is commonly used as an indicator of heavy metals contamination, sediments are also important in the assessment of anthropogenic impacts.
The lower part of Al-Ma‘ail river, represented by the Umm Al-Na‘aj Pond and Al-Hawizeh Marsh, is a significant habitat for many plant and animal species. The presence of heavy metals in aquatic ecosystems is becoming an increasing problem of concern about their influence on plant and animal life, due to their tendency to remain as an environmental pollutant for a long time and also to magnified through the food chain (Ogunfowokan et al. 2013). The goal of this study is to investigate and assess the spatial variation in the concentration of heavy metals in Al-Ma‘ail river waters and sediments, the influence and effects of the industrial processes within Halfaya oil field on the environmental situation, even assess its suitability for different purposes by local people, besides determining its ability to sustain aquatic life. Many studies that dealt with the study of the effects of heavy metals due to their importance in determining environmental pollution and the risks of increasing or decreasing these metals on the environment and humans (Al-Obeidi and Al-Jumaily, 2020; Al-Jumaily and Al-Berzanje, 2020; Fatah et al. 2020; Jumaah and Al-Shammaa, 2020).

2. Location of The Study Area

The study area is located in the southern part of Iraq within the Mesopotamian Plain. The study area including Maysan Governorate represented by the villages of Abu Khasaf and Al-Ma‘ail in which Al-Ma‘ail (Al-Zubair) river passes through them. The study area is restricted to latitudes (31° 40’–31°38’ N) and longitudes (47° 18’–47°30’ E) (Fig.1).

3. Materials and Methods

3.1. Sampling and Pre-Treatments

Samples were taken from five sites along Al-Ma‘ail river divided along distance of 47 km during August 2020 (Fig.1). The site characteristics are presented in Table 1. Ten samples of water and five samples of river sediments were collected from the right bank of the Ma‘ail river. Samples were analyzed for eight heavy metals: As, Cd, Cr, Cu, Pb, V, Ni and Zn. The pH and temperature were measured in the field. Water samples were collected 50 cm below the surface using 500 mL polyethylene bottles with screw caps. Samples of the depth 5-10 cm River sediments were collected in polythene bags using a rust-proof scoop. All samples were kept in cool boxes, at 4 °C, during transportation, and analyzes were performed upon receipt of samples to the laboratory belongs to the Ministry of Science and Technology. The collected sediment samples were dried in air, the larger particles were handpicked and the remainder were grounded into a powder form. Fraction <63 μm was used for mineral analysis.

| Site | Coordinates  | pH   | Temperature | Land use                        | Location                                      |
|------|--------------|------|-------------|---------------------------------|-----------------------------------------------|
| S1   | N 31°40’00” E 47°18’34” | 8.3  | 27.21 C˚   | Agricultural, rural and industrial with the Halfaya oil field | Branching/Basrah-Kaha Road                     |
| S2   | N 31°40’59” E 47°22’25” | 8.1  | 26.9 C˚    | Agricultural and industrial with the Halfaya oil field | The beginning of the Halfaya oil field         |
| S3   | N 31°39’59” E 47°25’35” | 8.02 | 30.7 C˚    | Agricultural, and industrial with the Halfaya oil field | Hafaya oil field gas isolation station, Iraq   |
| S4   | N 31°39’39” E 47°28’07” | 7.96 | 29 C˚      | Agricultural, and industrial with the Halfaya oil field | Drilling tower closest to the bank of the river |
| S5   | N 31°38’42” E 47°30’47” | 7.89 | 30.4 C˚    | Agricultural, and industrial with the Halfaya oil field | The last two towers drilled for the Halfaya oil field |
3.2. Laboratory Work Analysis of Heavy Metals

3.2.1. Water samples

The concentrations of heavy metals for the water samples were obtained after passing several steps. Starting by mixing the water sample with hydrochloric acid at a concentration of 37% and nitric acid at a concentration of 65% and heating the mixture on a thermostatic plate. The resulting solution was placed in a 100 ml volumetric flask, after which the solution was diluted with distilled water and mixed well (Mihaela et al. 2014). The atomic absorption spectrophotometer was used to measure the concentrations of heavy metals.

3.2.2. Sediment Samples

Sediment samples were analyzed after preparing solutions for the given samples by drying the sediments and then digesting them using aqua-regia (1:3 HNO₃: HCl). The mixture consisting of the sediment solution and aqua-regia was heated to its boiling point and then cooled to room temperature. No. 42 filter paper is used and distilled water is added to the filtrate in a volumetric flask until the mixture reaches 50 ml (Mihaela et al. 2014). Atomic absorption spectrometer was used as well to obtain the concentrations of heavy elements for such sediment samples.

3.2.3. Quality Control and Assurance

The quality of the analysis process was controlled by following the scientific and practical procedures by using the blanks. Preparations / reagents for each metal were prepared by 5 reagents for each metal. All concentrations were higher than the detection limits shown in Table 2. However, collection of the stock solutions used was under of controlled and approved quality.

Table 2. The detection limits of the heavy metals

| Metals | Water | Sediments |
|--------|-------|-----------|
|        | DL.1  | DL.2  | DL.3 | DL.4 | DL.5 | DL.6 | DL.1 | DL.2 | DL.3 | DL.4 | DL.5 | DL.6 |
| As     | 0     | 0.1   | 0.2  | 0.4  | 0.8  | 1.6  | 0    | 1.5  | 3    | 6    | 12   | 24   |
| Cd     | 0     | 0.1   | 0.2  | 0.4  | 0.8  | 1.6  | 0    | 1.25 | 2.5  | 5    | 10   | 20   |
| Cr     | 0     | 0.1   | 0.2  | 0.4  | 0.8  | 1.6  | 0    | 7.5  | 15   | 30   | 60   | 120  |
| Cu     | 0     | 0.1   | 0.2  | 0.4  | 0.8  | 1.6  | 0    | 10   | 20   | 40   | 80   | 160  |
| Pb     | 0     | 0.25  | 0.5  | 1    | 2    | 4    | 0    | 15   | 30   | 60   | 120  | 240  |
| Ni     | 0     | 0.25  | 0.5  | 1    | 2    | 4    | 0    | 10   | 20   | 40   | 80   | 160  |
| V      | 0     | 0.1   | 0.2  | 0.4  | 0.8  | 1.6  | 0    | 10   | 20   | 40   | 80   | 160  |
| Zn     | 0     | 0.5   | 1    | 2    | 4    | 8    | 0    | 25   | 50   | 100  | 200  | 400  |

4. Results and Discussion

The values of heavy metal concentrations in water and sediment samples are presented in Table 3. The evaluation of the results was made based on international and regional standards.
Fig.1. Locations of the sample’s sites, Al-Ma’ail river
concentration of metals in the part of the region close to Halfaya oil field, because of the presence of oil.

The results of sediment analyzes of As, Cd, Cr, Cu, Pb, Ni, V, Zn showed an increase in the concentration of metals in the part of the region close to Halfaya oil field, because of the presence of oil.
wells in the eastern bank of Al-Ma’ail River and all the waste of the extraction and drilling operations caused contamination of environmental elements, including sediments.

![Fig. 2. Heavy metals concentrations in water samples](image)

The mean concentrations of heavy metals in sediment showed variation between sampling sites, with trends along Al-Ma’ail river, were the increase in trend toward downstream. The variation in the concentration of heavy metals along the course of Al-Ma’ail river revealed a contamination of sediments especially at SS4-SS5 as those sites are located close to Halfaya oil field this reflects that oil contamination in the sediments of river by sorption processes, as the oil field releasing their waste into the river without any treatments Fig.3. The order of heavy metal concentration in sediments in Al-Ma’ail river was: Zn > Pb > V > Cr > Ni > Cu > As > Cd.

4.1. Bio-Concentration Factor

A bio-concentration is the accumulation of a chemical in or on an object when the source of the chemical is only water (Landis et al. 2011). Bio-concentration is a term that originated for use in the field of aquatic toxicology (Morrison, 2000). Bio-concentration can also be defined as the process by which the chemical concentration in an aquatic organism or anybody exposed to water increases as a
result of its exposure to the chemical that the water carries (Jon and Frank, 2004). In this case, ratio of metals in the sediment phase to that in the water phase (bio-concentration) was estimated according to the following formula (Utete et al. 2013):

\[ BC = \frac{C_1}{C_2} \]  

(1)

where C1 is the concentration of heavy metal in sediments; C2 is the concentration of heavy metal in water.

4.2. Effect of pH on BC

Bioconcentration factors calculated for Al-Ma’ail river showed that heavy metals concentration in sediments were higher than the corresponding level in water. Heavy metals are considered to be highly ionized substances. Their ability to be ionized increases or decreases depending on the pH of the medium (Arif et al. 2015). The bioconcentration factor increases with basic solutions than in acidic solutions, i.e. directly proportional to the pH (Cecilie et al. 2001) and as shown in Fig. 4 and 5, it seems not all heavy metals behaves similarly according to their relationship between each other but it differs from the other group of As, Cd, Ni, and Zn. This could be interpreted as there is another factor may be affected on.

| Metals | Para (ppm) | S1 | S2 | S3 | S4 | S5 |
|--------|------------|----|----|----|----|----|
| As     | W          | 0.098 | 0.102 | 0.109 | 0.216 | 0.193 |
|        | S          | 8.3 | 10.1 | 13.4 | 17.5 | 19.2 |
|        | BC         | 84.7 | 99 | 122.9 | 81 | 99.5 |
|        | W          | 0.098 | 0.095 | 0.106 | 0.209 | 0.188 |
|        | S          | 3.9 | 5.2 | 7.8 | 10.7 | 12 |
| Cd     | BC         | 39.8 | 54.7 | 73.6 | 51.2 | 63.8 |
|        | W          | 0.17 | 0.289 | 0.31 | 0.729 | 0.68 |
| Cr     | S          | 69 | 76 | 90 | 101 | 105 |
|        | BC         | 405.9 | 262.1 | 290.3 | 138.4 | 154.4 |
|        | W          | 0.14 | 0.31 | 0.28 | 1.399 | 1.25 |
| Ca     | BC         | 100.0 | 54.8 | 82.1 | 24.3 | 32 |
| Pb     | W          | 0.19 | 0.43 | 0.74 | 1.68 | 1.66 |
| V      | S          | 59 | 85 | 117 | 153 | 178 |
| Ni     | BC         | 310.5 | 197.7 | 158.1 | 91.1 | 107.2 |
|        | W          | 0.051 | 0.08 | 0.07 | 0.1 | 0.09 |
|        | S          | 46 | 58 | 91 | 123 | 131 |
| Zn     | BC         | 902 | 763.2 | 1263.9 | 1255.1 | 1488.2 |
|        | W          | 0.47 | 0.56 | 0.67 | 1.73 | 1.56 |
|        | S          | 43 | 60 | 80 | 102 | 112 |
|        | BC         | 91.5 | 107.1 | 119.4 | 59 | 71.8 |
|        | W          | 0.68 | 0.76 | 0.95 | 2.18 | 1.89 |
|        | S          | 106 | 178 | 269 | 301 | 382 |
|        | BC         | 155.9 | 234.2 | 283.2 | 138.1 | 202.1 |

| BCF Limits (USEPA, 1999) | Considered Bioaccumulative (> 1,000) | Considered Very Bioaccumulative (> 5,000) |
|--------------------------|--------------------------------------|------------------------------------------|

*W: Water Samples, **S: Sediment Samples, ***BC: Bioconcentration
When an adsorbate (the ion or molecule adsorbed to a surface) forms a stable bond with an adsorbent, a surface complex is formed (the solid phase whose surface provides the site for contaminant adsorption). Ion adsorption mechanisms include the creation of surface complexes of the inner-sphere and outer-sphere that are similar to those that form in aqueous solution. The surface complexes of the outer-sphere are primarily the product of electrostatic interaction. Inner-sphere complex formation requires some degree of covalent bonding between the adsorbate and adsorbent and thus, chemical specificity. For this purpose, outer-sphere complex formation is sometimes referred to as physisorption, while chemisorption is called inner-sphere complex formation. In inner-sphere coordination, ions adsorbed are more tightly bound and are less likely to desorb from the surface due to displacement by other solution ions. (Ian et al. 2006). BC values fluctuate for As, Cd, Ni and Zn their behavior very similar to each other within BC values increase toward pH≈8 then decreases as pH getting greater than 8. When pH value approach ≈ 8 there was sudden change in the shape of the curve for all metals. This can be interpreted in terms of many factors as physisorption and chemisorption. Depending on acid-base reactions at surface sites, pH-dependent ionization reactions in surface hydroxyl groups of minerals and organic matter give rise to a variable charge that may be positive or negative. Many Fe and Al oxides, for instance, are positively charged at pH<8 and negatively charged at pH>8, Ian et al. (2006), this can be lead to the behavior of BC and pH curves for most of heavy metals which shows decrease in BC with pH increase when pH becomes >8 as the case in (As, Cd, Ni and Zn). Because when pH>8 at some sites,
it will be negatively charge and that attract cations to being adsorb at their surface, that mean increase in bioconcentration. Then when pH value becomes pH<8, the surface site become positively charge and that attract anions to being adsorbed on the sediment surface, the case (sites 3, 4, 5), caused drop in BC and decrease in pH. In case of Pb there is almost direct relationship between pH and BC whereas, Cr and Cu curves showed little different than Pb, but all of them (Cr, Cu, and Pb) their curves similar to each other (Fig. 4).

![Graph showing the relationship between bioconcentration of vanadium and pH](image)

**Fig. 5.** Relationship between bioconcentration of vanadium and pH

Regarding the BC curve of vanadium (Fig. 5), its behavior was opposite to that of the rest of the metals, as the BC values were high when the pH values decreased, with a sudden decrease in BC when the pH≈8, and then the curve show little rise towards pH increase. This indicates that there is no relationship between the BC curve for vanadium and pH, in addition to the possibility that other factors are governed by the BC curve. Vanadium ions can be absorbed more intensely in inner-sphere coordination and are less likely or difficult to absorb from the surface of sediments. Being the most common indicator of oil pollution (Montgomery, 2013), high values in the BC curve of vanadium reflect its high percentages in the sediments of Al-Ma'ail river, despite its low levels in the river waters, which confirms that the source of pollution in the study area is the Halfaya oil field. Vanadium concentrations, followed by Cr concentrations were significantly higher in sediments compared to those in water, as presented in Table 4. Metallic bioconcentration order in Al-Ma'ail river was: V > Cr > Zn > Pb > As > Ni > Cu > Cd. Generally, packing metals in a sediment setting relies on physico-chemical interactions at the interface between the sediment and the water in the water. As hydroxides, carbonates and insoluble oxides form, heavy metals are precipitated, due to alkaline pH. In addition, in the aqueous process, heavy metals may interact with suspended particles and settle down, resulting in a high concentration of these elements in the sediments (Goher, 2002; Mititelu et al., 2012).

**5. Conclusions**

The obtained results showed that the heavy metal concentrations in surface water of Al-Ma'ail river were higher than the international and regional water quality standards except Cu at SW8 and SW9 are more than IQS but within WHO and little more than US EPA. About SW10 was more than IQS standards and within the rest WHO and US EPA. Whereas with regard to the concentrations of heavy metals in sediments, they showed a variation in their behavior between water and sediments and their
The results indicate a long-term pollution by heavy metals especially vanadium in the river sediments which could be of concern for the health of the aquatic ecosystem. By measuring the bioconcentration BC of heavy metals in general and vanadium in particular, it was concluded that the source of pollution of Al-Ma’ail river water and sediments is point source of oil contamination represented by the Halfaya oil field which is located on the left bank of Al-Ma’ail river. Special attention should be highlight on the issue of metals remobilization from sediments desorption because their effects may become significant during the seasons and the years of high-water level washing of the soil which is surrounding the river bank by rainwater.

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References

Arif, T. J., Mudsser, A., Kehkashan, S., Arif, A., Inho, C., Qazi, A. R. H., 2015. Heavy metals and human health: Mechanistic insight into toxicity and counter defense system of antioxidants. International Journal of Molecular Science, 16(12), 29592-29630.

Al-Bassam, K. S., Yousif, M. A., 2014. Geochemical distribution and background values of some minor and trace elements in Iraqi soils and recent sediments. Iraqi Bulletin of Geology and Mining, 10 (2), 109-156.

Al-Jumaily, H. and Al-Berzanie, E., 2020. Health risk of zinc pollution in agricultural soil in some leaves of selected leafy vegetables in Kirkuk, Iraq. Environmental Toxicology Journal, 53 (2D), 64-79.

Al-Obeidi, A. and Al-Jumaily, H., 2020. Geochemistry and environmental assessment of heavy metals in surface soil in Al-Hawija, southwest Kirkuk, Iraqi Geological Journal, 53, (2E),36-61.

Buday, T., 1980. The Regional Geology of Iraq (Stratigraphy and Paleontology). Dar Al-Kutb Publishing House, Mosul, Iraq, 443p.

Cecilie, R., Kresten, O. K., Stevan, T., 2011. Optima choice of pH for toxicity and bioaccumulation studies of ionizing organic chemicals. Environmental Toxicology and Chemistry, 30 (11), 2395-2406.

Enache, I., 2008. The Second Joint Danube Survey Expedition – Hazardous Metals and Metals Concentration from Danube River Sediment. Analele Universitatii din Bucuresti – Chimie.

FAO/WHO, 2006. Final Report, food safety risk analysis a guide for national food safety authorities. ISSN 0254-4725.

Goher, M. A., 2002. Chemical studies on the precipitation and dissolution of some chemical elements in lake qarun. Ph.D. Thesis, Faculty of Science, Azhar University, Cairo, Egypt, 153.

Iraqi Quality Standards IQS, 2009. Iraqi Standards of Drinking Water No. 417 Modification No.1.

Ian, L. P., Charles P. G., Mark L. B., 2006. Environmental and Pollution Science. Academic Press is an imprint of Elsevier 30 Corporate Drive, Suite 400, Burlington, MA 01803, USA 525 B Street, Suite 1900, San Diego, California 92101-4495, USA 84 Theobald’s Road, London WC1X 8RR, UK.

Jon, A., Frank, A. P. C., 2004. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. Environmental Toxicology and Chemistry, 23 (10), 2343-2355.

Kabata-pendas, A., Pendas, H., 2001. Trace elements in soils and plants, 3rd ed., CRC Press, Boca Raton, FL.

Fatah, K., Hamed, M., Saeed, M.H., Dar, R., 2020. Evaluations groundwater quality by using GIS and water quality index techniques for wells in Bardarash area, Northern Iraq. Iraqi Geological Journal, 53 (2C), 87-104.

Landis, W. G., Sofield, R. M., Yu, M. H., 2011. Introduction to environmental toxicology: Molecular Structures to ecological landscapes, (Fourth ed.). Boca Raton, FL: CRC Press, 117-162.

Mihaela, I., Florica, M., Gina, G., and Gyorgy, D., 2014. Assessment of heavy metal in water and sediments of Danube River, Journal of environmental protection and ecology, 15 (3), 825-833.

Mititelu, M., Nicolescu, F., Ionita, C.A., Nicolescu, T.O., 2012. Study of heavy metals and organic pollutants in some fishes of the Danube River. Journal Environment Protection Ecology, 13 (2), 869.

Montgomery, C., W., 2013. Environmental Geology. McGraw-Hill, Higher Education, Boston, 10th ed., 357P.
Morrison, H. A., 2000. Biococentration and biomagnification in the aquatic environment. In Boethling RS; Mackay D (eds.). Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences. Boca Raton, FL, USA: Lewis, 189-231.

Jummah, M. S., Alshammaa, A. M., 2020. Hydrochemical assessment of groundwater of Euphrates aquifer in Anah, western Iraq for irrigation purposes. Iraqi Geological Journal, 53, (2C), 121-133.

Ogunfowokan, A. O., Oyekunle, J. A. O., Olutona, G. O., Atoyebi, A. O., Lawal, A., 2013. Speciation study of heavy metals in water and sediments from Asumle River of the Obafemi Awolowo University, Ile-Ife, Nigeria. International Journal Environment Protection, 3 (3), 6-16.

Utete, B., Nhiwatiwa, T., Barson, M., Mabika, N., 2013. Metal correlations and mobility in sediment and water from the gwebi river in the Upper Manyame Catchment, Zimbabwe. International Journal Water Science, 2 (4), 1-8.

U.S. EPA., 1999. U.S. Environmental Protection Agency Guidance Manual Turbidity Provision.

USEPA (US Environmental Protection Agency), 2018. Integrated Risk Information System (IRIS). http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.sho Substance List.

Vinogradov, A. P., 1959. The Geochemistry of rare and Dispersed Chemical Elements in Soil, 2nd ed., Revised and Enlarged: New York, Consultants Bureau Enterprises, 209 p.

Vodyanitskii, Y. N., 2016. Standards for the contents of heavy metals in soils of some states, Annals of Agrarian Science, 14 (3), 257-263.

WHO., 2011. Guidelines for Drinking Water Quality. 4th edition. World Health Organization. 564p.