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A Study on the Fate of Some Heavy Metals in Water and Sediments in Lotic Ecosystems

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Abstract

Five heavy metals (Cd, Cu, Pb, Fe and Zn) were selected to determine the degree of contamination of Al - Husseinya river. Their distributions, concentrations in the waters (dissolved and particulate phases) and sediments (Exchangeable and residual phases) were included. Physicochemical properties of the river (water temperature, pH, electrical conductivity, total alkalinity, total hardness, calcium and magnesium) were studied. The average of the studied heavy metals in the dissolved phase of the water were 1.4 , 1.15 , 3.74 , 5.46 and 7.66 µg / l for Cd, Cu, Pb, Fe and Zn, respectively. Heavy metals concentrations in the particulate form were 3.67, 110.23, 63.97, 732.98 and 167.2 µg/g for Cd, Cu, Pb, Fe and Zn, respectively. In the sediments, the concentrations of these heavy metals in the exchangeable phase were 2.53, 38.00, 43.45, 169.00 and 42.16µg/g for Cd, Cu, Pb, Fe and Zn, respectively. While in the residual phase were 2.54, 32.82, 50.33, 1452.75 and 53µg/g for Cd, Cu, Pb, Fe and Zn, respectively. The results revealed that the concentrations of heavy metals in water for the particulate phase were higher than in the dissolved phase. While in sediment, their concentrations in the residual phase were higher than their concentrations in the exchangeable phase except for Cu which was in the exchangeable phase higher than in the residual phase.

Key words: Heavy metals, Water, Sediments, Al-Hussainya river.

Introduction

Heavy metals (HM) are elements which having a density more than 5g/cm^3. HM are divided into groups. The first one is necessary elements which play important role in the metabolic processes of organisms, cells at low concentrations such as Nickel, Copper and Zinc, at high levels of these elements became toxic. Other types of elements are those which cause adverse effects on organisms even at low concentrations such as Cadmium, Lead and Mercury [1].

HMs are present naturally in water, sediments, plants, animals, and can be released into the environment by many processes such as weathering of rocks, leaching of soil, forest fires and other natural factors. In addition to anthropogenic activity, which plays a major role in polluting the environment with heavy metals [2]. Geochemical composition, agrochemical and industrial wastes are the main sources of aquatic environment pollution with heavy metals [3].

Pollution of waters with heavy metals have many adverse effects on aquatic organisms, in addition to this, the bioaccumulation and bioconcentration of these metals in the aquatic food chain put the consumers such as humans in risk [4]. HMs are persistent and stable pollutants, so their toxicity causes many health and ecological problems [1]. When the heavy metals enter the aquatic ecosystem they exist in two phases in the water: dissolved phase and particulate phase [5]. Their concentrations affect many factors in the water, such as pH, salinity, total suspended solids, phytoplankton and organic chemical materials [6]. HM concentrations are affect by temperature [3] and electrical conductivity [7], and other factors.

In sediments, the HMs are presented in several forms which include exchangeable, bounded (to carbonates, bounded to iron and manganese oxides, bounded to organic matter) and residual [8]. Their solubility and release from the sediments to water column depends on several factors such as temperature, pH, water velocity and dissolved oxygen [9].

Many studies were conducted to estimate the pollution with heavy metals in a number of aquatic ecosystems in the Iraq, such as on the Euphrates River in the Middle of Iraq [10 , 11] and on Al - Gharraf River [12] and on the Shatt Al-Arab in the South of Iraq [13]. Wongu and Okaka [14] referred to impact the discharge of Agriculture, Industrial and residential. They revealed that the six HMs (Cd, Cr, Fe, Mn, Ni and Zn) were found in high concentration in the Warri River in Nigeria. Many studies were conducted on many global waterbodies to determinate the heavy metals in waters, sediments and aquatic organisms [7,15,16]. The study aimed to study the fate of five heavy metals (Cd, Cr, Fe, Mn, Ni and Zn) in the Al - Hussainya river. This study is a contribution for the main water sources of Karabala province, Iraq.

Eexperimentals

Description of study area

Al - Hussinya River is the lone source of drinking and irrigation water in Karbala province. Six sites were chosen along the river for sampling all of the sites that have been padded except in site 1 . Water and sediment samples were collected from sites for the period from October 2012 to September 2013..

Physicohemical parameter analysis

Water temperature was measured by using a thermometer. pH and electrical conductivity (EC) measured by using HANNA instrument. Total alkalinity, total hardness, Calcium ion and Magnesium ions were measured according to methods that were described by [17].

Heavy metals analysis

Heavy metals were measured in water samples in two phases, dissolved and particulate. The dissolved phase was measured according to [5], while the particulate phase was measured according to [18]. In sediments, the exchangeable and residual phases were extracted according to [19] and [18], respectively. Heavy metals were measured by using Flame Atomic Absorption Spectrophotometer (Model Pye Unicam SP9).

Results and Discussion

The physicochemical properties of the river are shown in (Table 1). The water temperature ranged between 12.7 – 31.3 C°, it increased during hot months and decreased during cold months these results corresponded with other Iraqi studies [20 , 21]. The river ranged between slightly alkaline to alkaline waters; pH values ranged 9.42 – 7.5 in December 2012 and August 2013, respectively. The pH values are affected by many factors such as temperature [10]. Other factors affect pH values such as the biological activity and CO_2 concentration [22], the nature of climate [23], discharge of municipal and industrial wastewaters [24 , 25] and the drift of catchment area [26]. The present results agreed with other Iraqi studies [27 , 28].

Table 1: Rang (Mean± SD) of some physicochemical and biological properties in the Al - Hussainya river during the study period

Sites / Parameters	ST1	ST2	ST3	ST4	ST5	ST6
Water temperature (C °)	12.7 – 29.4 21.9 ± 5.9	13.7 – 29.6 22.2 ± 5.6	14 – 30.1 22.5 ± 5.7	13.8 – 30.4 22.7 ± 5.8	13.4 – 30.4 23 ± 5.7	14.2 – 31.1 23.7 ± 5.6
PH	7.5 – 8.7 8.06 ± 0.32	8.8 – 7.5 8.1 ± 0.38	9.3 – 7.6 8.2 ± 0.42	9.2 – 7.7 8.2 ± 0.37	9.4 – 7.5 8.3 ± 0.45	9.3 – 7.6 8.2 ± 0.43
EC (µs / cm)	896.67 - 416.67 1206.61 ± 37.84	840 – 1386.67 1191.03 ± 49.6	856.67 – 1406.67 1194.22 ± 156.2	850 – 1380 1195.19 ± 154	980 – 1413.33 1194.25 ± 126.8	1046. – 1386.67 1235.47 ± 91.8
Total alkalinity mg $CaCO_3$/l	111.67 – 161.33 130.31 ± 19.68	108 – 157.67 128.86 ± 15.34	106.67 – 152.67 125.67 ± 14.47	108 – 151.33 127.53 ± 13.96	106.67 - 155 128.56 ± 13.38	106.33 – 162 126.89 ± 14.56
Total Hardness mg $CaCO_3$/l	300 – 503.33 415.72 ± 66.08	320 – 493.33 403.83 ± 63.22	320 – 500 408.33 ± 62.63	280 – 516.67 404.11 ± 65.83	240 – 460 400.33 ± 63.45	240 – 476.67 412.22 ± 66.08
Calcium (mg / l)	72.37 – 160.32 102.34 ± 25.2	45.42 – 149.63 100.49 ± 27.02	56.65 – 146.96 100.54 ± 27.75	– 70 160.32 ± 105.21 25.55	40.08 – 129.63 94.71 ± 23	40.61 – 129.6 101.91 ± 23.84
Magnesium (mg / l)	18.7 – 63.11 38.86 ± 13.09	21.77 – 53.39 37.03 ± 11	24.4 – 55.81 38.23 ± 9.75	17.1 – 64.73 34.61 ± 12.93	- 30.7 52.7 ± 39.82 9.24	60.83 – 13.67 13.21 ± 38.2

Electrical conductivity (EC) values ranged (840-1416.67 µs/cm) in February and May, respectively. The present study results were close to other studies [29, 30]. Total alkalinity values ranged (162 – 106.33 mg / l) in March 2013 and July 2013. The concentrations of total alkalinity were affected by many factors such as organic pollution [25, 26], rainfall which causes drifting the catchment area [31], and water levels [32]. The results also showed that the alkalinity of river was attributed to bicarbonate ions. Many Iraqi rivers are characterized by their alkalinity that an attributed to bicarbonate ions [11, 33, 34]. The river was very hard according to Lind [17]. The values of total hardness ranged (240 – 516.67 mg/l) in October 2012 and January 2013, respectively. The high values of the hardness in the river were related to the different factors: the geological nature of the lands that the river passes through it [35] and the effect of agriculture and anthropogenic activities [36]. The increasing of hardness during winter months due to rainfall, which cause drifting of the catchment area with their pollutants to the river [37]. Total hardness records had positive correlation with calcium ions ($r = 0.718$, $P < 0.01$), many rivers in Iraq are characterized by being very hard [33 , 38 , 39].

The concentrations of Calcium ion recorded were higher than Magnesium ion concentrations; this may be due to the presence of calcium ion in a percentage higher than magnesium ion in the earth crust and soil [5]. The values of calcium ions ranged (40.08 – 160.32 mg / l) in October 2012 and December 2012, respectively. It also recorded a positive correlation with EC ($r = 0.569$, $P < 0.01$). The results of calcium ions showed seasonal variation where lower values of calcium ions were recorded in autumn. That may be due to its consumption by the phytoplankton [17], or to increase the pH in the water that leads to precipitate calcium ion as calcium carbonate [40] .While rainfall caused increasing its concentration in the water in winter due to the drifting of the catchment area [10].

Magnesium concentrations showed fluctuation in this study, which ranged (13.67 – 64.73 mg/l) in April 2013 and January 2013. High values of Magnesium ion in the water during January due to rainfall, while decreasing levels may be due to consumption of this ion by phytoplankton [41].

Heavy Metals in Water

The concentration of the dissolved phase ranged between 1.15 μg / l for Cu and 7.66 μg / l for Zn (Table 2). Heavy metal concentrations in the dissolved phase were as follows; Zn > Fe > Pb > Cd > Cu. A significant variation was noticed among most of the months and sites.

HMs recorded higher concentrations in summer (May, June, July, August) while they recorded lower concentrations in winter (December, 2012 and January, 2013) . The increase of their concentrations during summer may be due to high temperature, which increases the solubility of them. This conclusion is confirmed by a positive correlation between them and temperature. Also, might be due to decreasing the pH during summer that also increases their concentrations as confirmed by a negative correlation between them and pH [9]. While the decreasing of their concentration may be due to many factors such as water levels [16, 42], and alkalinity [43]. And also, formation complexes with organic matters [8], the amount of particulates [6], and the density of phytoplankton [44]. Anthropogenic activities and throwing of wastes directly to the river may also affect their concentrations [14, 45, 46]. Despite this, the dissolved heavy metals concentrations did not exceed the permissible concentration according to national and WHO guidelines (Table 3).

The concentration of heavy metals in the particulate phase ranged (3.67 – 732.98 μg / g) for each of Cd and Fe, respectively (Table 2). Their concentrations were as follows: Fe > Zn > Cu > Pb > Cd. The concentration of heavy metals in the particulate phase was higher than their concentration in the dissolved phase. This result might be due to the increased particulate matter in the river, which include living and non - living components. The living components. The living components consist of planktons and other microorganisms, while the non – living organisms consist of silts and clay particles, in addition to organic and inorganic particles [47]. The main sources of particulate matter in the rivers are drifting of catchment area, effluent of industrial and sewage waste waters and agricultural drainage waters, in addition to air depositions and re-suspended particles[4].

Table 2: The concentrations of heavy metals in the waters (Dissolved and Particulate phase) [first line: range and second line: mean ± SD].

Sites / Elements	St 1	St 2	St 3	St 4	St 5	St 6
Cd (Dissolved µ/l	0.72 – 2.69 1.44 ± 0.81	0.76–2.91 1.43 ± 0.91	0.86 – 2.73 1.73 ± 0.85	0.81 – 2.45 1.32 ± 0.74	0.61 – 1.89 1.09 ±0.54	0.7 – 2.62 1.4 ± 0.79
Cd (Particulate) µ/gm	2.45 – 6.83 4 ± 1.82	2.68 – 7.77 4.25 ± 2.17	2.89 – 5.28 5.11 ± 2.77	1.67 – 4.26 2.65 ± 1.1	2.29 – 3.71 2.75 ± 0.62	2.35 – 5.03 3.26 ± 1.15
Cu (Dissolved µ/l	0.54 – 2.07 1.17 ± 0.62	0.56 - 2.28 1.21 ± 0.7	0.64 – 2.11 1.37 ± 0.55	0.49 – 1.88 1.1 ± 0.55	0.46 – 1.46 0.9 ± 0.4	0.52 – 2.03 1.14 ± 0.59
Cu (Particulate) µ/gm	50.8 – 197.5 110.59 ± 56.77	55.21 – 215.8 116.73 ± 65.34	64.8 – 203.5 132.8 ± 51.63	47.12 – 180.4 106.41 ± 52.1	44.07 – 139.5 86.35 ± 36.65	50.14 – 191.9 108.53 ± 55.24
Pb (Dissolved µ/l	2.36 – 6.45 3.88 ± 1.61	2.54 – 6.82 3.89 ± 1.8	2.77 – 6.57 4.32 ± 1.47	2.07 – 5.6 3.49 ± 1.36	2.05 – 4.67 3.05 ± 1.03	2.34 – 6.25 3.8 ± 1.55
Pb (Particulate) µ/gm	40.85 – 106.7 65.46 ± 26.03	44.15 – 115 66.79 ± 29.82	48.1 – 111.7 74.24 ± 24.71	35.92 – 97.43 60.53 ± 23.9	35.63 – 81.23 52.97 ± 18.07	40.5 – 103.6 63.84 ± 25.07
Fe (Dissolved µ/l	3.75 – 8.5 5.57 ± 1.89	3.97 – 9.02 5.62 ± 2.21	4.51 – 8.79 6.77 ± 1.65	3.42 – 7.69 5.11 ± 1.69	3.2 – 5.97 4.28 ± 1.11	3.66 – 8.31 5.43 ± 1.85
Fe (Particulate) µ/gm	503.29 – 1140.8 746.89 ± 251.15	505.98–1210.62 754.29 ± 295 .2	605.33–1179.42 908.24 ± 219.55	459.07–1032.15 685.21 ± 224.28	429.52 – 801.31 574.48 ±146.65	491.23 – 1115.29 728.79 ± 245.98
Zn (Dissolved µ/l	3.39 – 14.21 7.85 ± 4.45	3.59 – 15.3 8.09 ± 5.11	4.11 – 15.92 9.23 ± 4.79	2.98 – 12.97 7.16 ± 4.12	2.89 – 9.95 5.99 ± 3.06	3.31 – 13.74 7.63 ± 4.31
Zn (Particulate) µ/gm	135 – 207.5 170.2 ± 30.77	141.8 – 223.3 177.73 ± 37.24	165.2 – 236.7 199.13 ± 29.41	120.5 – 190.1 154.68 ± 28.77	109.3 – 152.7 137.38 ± 21.59	130.4 – 199.3 164.13 ± 29.61

Many factors affect on the concentrations of particulate heavy metals in waters such as pH, temperature, organic matters [42] and water velocity [48]. The results of particulate heavy metals showed significant variation between among months and sites. In summer recorded were higher concentrations, while in winter recoded were lower concentrations during this study. Their elevation during summer might be due to increasing temperature. Which increases their solubility and re-adsorption on particles , or because of increasing wind velocity that gives rise to water turbulence and release of these metals from sediments to water column [42].

Table 3: Compared the concentration of heavy Metals (µg/l) with Iraqi and WHO Guidelines.

Heavy metals	Present study		Iraqi determinants for maintenance the waters and rivers from pollution of 1967	Iraqi guidelines for drinking water quality and domestic uses of 1984 , and the first update for 2001	WHO drinking water guidelines of 1993
	Dissolved	Particulate			
Cd	1.4	3.67	5	3	3
Cu	1.15	110.23	50	1000	2000
Pb	3.74	63.97	50	10	10
Fe	5.46	732.98	300	300	-
Zn	7.66	167.2	500	3000	3000

Heavy Metals in Sediments

Sediments represent the final recipient of pollutants from natural and anthropogenic sources. Thus, they are considered as a good bioindicator for water pollution. They also, release the pollutants that contaminate them in the water column as a result of the effect of the physicochemical factors. Which then have been taken by the aquatic organisms and thus transmitted through the food chain. Their accumulation in the organisms causes toxic effects to them [16, 49].

HMs in the sediments during this study were measured in the exchangeable and residual phases. Their concentrations in the exchangeable phase ranged from 53 µg/g for Cd and to 169 µg/g for Fe. Their concentration's sequences were as follows: Fe > Pb > Zn > Cu > Cd. While their concentrations in the residual phase ranged from 2.54 µg/g for Cd and 1452.75 µg/g for Fe, and their concentration's sequences appeared as follows: Fe > Zn < Pb > Cu > Cd (Table 4).

Their concentrations in the residual phase were higher than their concentrations in the exchangeable phase except Cu was in the exchangeable phase higher than in the residual phase. These results might be due to the drainage of wastes directly into the river or spraying pesticides. Frthermore, as a result of decomposition and plant residues, in addition to discharge from drinking water treatment plants [50].

The results of heavy metals in sediments showed significant differences among some sites and months. In summer season they recorded higher concentrations, while winter season recorded lower concentrations during the study period. Increasing of HMs in summer might be due to elevation of temperature. The highest temperature recorded in the summer increased the rate of organic decomposition [51].

These results confirmed the positive correlation between them and temperature. While concentration decreased in winter, which might be due to rainfall and dilution effects [45]. The elevation of dissolved oxygen concentrations in water enhances the rates of organic matters oxidation under aerobic conditions and release heavy metals to water column [9].

Table 4 : The concentrations of heavy metals in the sediments (Exchangeable and Residual phase) [first line : range and second line : mean ± SD]

Sites Elements	St 1	St 2	St 3	St 4	St 5	St 6
Cd (exchangeable μ/gm	2.24 - 2.74 2.51 ± 0.21	2.35 – 2.91 2.64 ± 0.33	2.7 – 4.14 3.09 ± 0.66	2.13 - 2.53 2.35 ± 0.23	1.94 – 2.16 2.06 ± 0.27	2.21 – 2.75 2.49 ± 0.28
Cd (residual) μ/gm	2.12 - 2.83 2.51 ± 0.34	2.18 – 3.11 2.67 ± 0.4	2.44 – 4.45 3.19 ± 0.8	2.05 – 2.61 2.26 ± 0.25	1.75 – 2.33 2.11 ± 0.27	2.08 – 2.8 2.47 ± 0.33
Cu (exchangeable) μ/gm	17.2 - 65.83 38.7 ± 18.9	19.1 – 72.67 40.91 ± 21.92	22.6 – 68.13 45.85 ± 17.12	16.57 – 61.54 36.81 ± 17.5	15.23 – 47.25 28.85 ± 12.55	17.25 – 64.81 36.9 ± 18.84
Cu (residual) μ/gm	15.5 – 56.78 32.73 ± 16	16.96 – 63.45 34.81 ± 19.16	18.4 – 60.4 40.11 ± 15.67	14.24 – 52.68 31.49 ± 14.92	13.72 – 41.26 25.54 ± 10.81	15.09 – 56.78 32.28 ± 16.16
Pb (exchangeable μ/gm	27.52 – 73.22 44.68 ± 18.16	29.81 – 79.41 45.36 ± 21.15	32.4 – 76.45 50.64 ± 17.16	24.06 – 65.48 40.61 ± 16.4	24.57 – 54.36 35.76 ± 11.94	26.9 – 72.53 43.69 ± 18.37
Pb(residual) μ/gm	31.74 – 85.71 51.94 ± 21.87	33.9 – 92.15 52.61 ± 24.73	37.2 – 89.16 58.3 ± 20.23	28.3 – 75.26 47.08 ± 18.3	27.69 – 63.45 41.41 ± 14.1	30.8 - 83.91 50.67 ± 21.06
Fe(exchangeab) μ/gm	118.57 – 268.31 175.71 ± 59.33	119.01 – 284.73 177.41 ± 69.9	142.37 – 277.47 213.63 ± 52.28	107.96 – 242.75 161.15 ± 53.16	101.02 – 134.16 117.62 ± 14.1	115.54 – 262.32 171.41 ± 58.15
Fe (residual) μ/gm	997.51 – 2261.15 1480.34 ± 497.53	1002.85–2399.39 1495.06 ± 584.86	1199.71–2338.23 1800.23 ± 435.31	909.75 – 2045.62 1357.99 ± 444.33	851.28 – 1588.11 1138.55 ± 290.26	973.63 – 2210.53 1444.44 ± 487.26
Zn (exchangeable μ/gm	33.25 – 50.88 42.14 ± 7.7	36.2 – 56.8 44.98 ± 9.51	41.2 – 58.91 53.91 ± 7.94	28.79 – 47.8 38.37 ± 7.73	26.41 – 42.6 33.89 ± 6.81	31.4 – 47.83 39.71 ± 6.84
Zn (residual) μ/gm	42.05 – 63.94 52.8 ± 9.3	44.7 – 70.2 56.25 ± 11.8	51.4 – 76.1 68.08 ± 10.63	37.65 – 58.65 47.8 ± 8.52	35.92 – 49.7 43.31 ± 5.86	39.8 – 60.59 49.79 ± 8.88

Spatial variations in heavy metals concentrations in sediments may be due to differences of environments, anthropogenic activity and population density. In addition to nature of pollutants that arrive to the river [10, 15]. The differences of sediment texture among sites also lead to spatial concentration variability, the accumulation of these heavy metals was enhanced by decreasing the grain size of the sediments [45, 49, 52]. The results showed that Fe recorded higher concentrations as compared with other elements during this study.

Conclusion

- The results of physicochemical properties of the river showed temporal and spatial variations during the study period.
- Heavy metals concentrations showed seasonal and spatial variations. Whereas higher concentrations were recorded in summer, while in winter recorded lower concentrations.
- Heavy metal concentrations in particulate phase were higher than in dissolved phase.
- The concentration of heavy metals in residual phase was higher than in exchangeable phase except for copper.
- Iron concentration was higher in sediments and in particulate phase of water.
- The presence of high levels of studied heavy metals was a serious matter of concern and potential for human exposure to heavy metals through different means.

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