



A Study of Physicochemical Parameters and Nine Heavy Metals in the Euphrates River, Iraq

FIKRAT M. HASSAN*, MAYSOON M. SALEH and JASIM M. SALMAN

*College of Science for Women, University of Baghdad, Iraq.
College of Science, University of Babylon, Iraq.

fik.has@googlemail.com

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Abstract: This study was conducted to reveal possible environmental effects on the Euphrates River from the Al-Hindiya barrage to the downstream end of Al-Kufa city in the middle of Iraq. Seven sites were selected along the study area and sampled during March 2004 to February 2005. We measured physical and chemical properties (air and water temperature, pH, electrical conductivity, TDS, TSS and dissolved oxygen) as well as, concentration and distribution of some heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in both dissolved and particulate phases, in the water and sediments (exchangeable and residual phases). The studied area was slightly alkaline, with very hard water and high BOD₅. The nutrients showed clear seasonal fluctuations in their concentrations. It was shown that the concentrations of metals in the particulate phase were higher than those in dissolved phase in water. In sediments, the mean concentrations of heavy metals as exchangeable phase were less than in the residual phase.

Keywords: Physicochemical parameters, Heavy metals, Euphrates River, Pollution.

Introduction

As a result of military activities in Iraq since 1980, many military factories were built along the Euphrates and Tigris rivers. These led to an increase in environmental problems, including water contamination, air pollution and ecosystem degradation¹. Water is polluted artificially by human activities or naturally. In newly reclaimed lands, agricultural and industrial activities may create different sources of pollution². Pollutants that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage while also posing a risk to human health³.

The most toxic pollutants present in the aquatic system are PAHs, heavy metals and organo-chlorines that have detrimental effect on water quality and are harmful to aquatic life⁴. Aquatic organisms are highly sensitive to change in physical and chemical properties of water such as dissolved gases (O₂ and CO₂), pH, alkalinity, hardness and nutrients and to other limnological characteristics⁵⁻⁷. Pollutants that are introduced into the environment are distributed in water, sediment, and biota⁸. Heavy metals are naturally introduced into rivers from

such sources as rock weathering, soil erosion, and the dissolution of water-soluble salts⁹. In natural aquatic systems, sediments play a major role in the control of dissolved metals¹⁰. Microorganisms and plants can have a profound influence on the chemical reactions of heavy metals¹¹ and the heavy metal pollution of aquatic systems is often more obviously reflected in high metal levels in sediments, macrophytes and benthic animals, than in elevated concentrations in water¹².

Many previous studies showed the concentration and distribution of heavy metals in different aquatic systems. Hwrowitz¹³ studied the heavy metal concentrations in suspended matter of some rivers in the USA such as the Mississippi, Susquehanna and Skunk rivers. Many heavy metals, such as Cu and Pb, are related to the solid phase at Waihou River in Newzealand¹⁴. Yilmzer and Yaman¹⁵ studied water pollution by heavy metals in the Ceyhan River in Turkey and showed the greater values of these metals found in the particulate phase. In another study, Ezeronye and Ubalua¹⁶ showed there was no relationship between increase of heavy metals and total count of bacteria in a river.

Many studies in different regions of the world have used the sediment of rivers and estuaries as indicators for heavy metals¹⁷⁻¹⁹. The Euphrates River divides into two branches namely Hindiyah and Al-Hilla in its middle region in Iraq. Its total length is about 2800 km, with 35% of this river length found in Iraq where it is discharging 818 m/sec²¹. Many previous studies investigating physical and chemical characteristics of the Euphrates River, such as Hassan & Al-Saadi²², studied the phytoplankton distribution in the Hilla River and Hassan^{23,24} studied Limnological characters of the Hilla and Diwanya rivers.

In previous studies, different physical, chemical, biological parameters were used to evaluate the quality of the river and observe the water pollution by heavy metals²⁵⁻³⁰. The present study aims to:

1. Investigate the monthly changes in physical and chemical properties in Al-Hindiyah River (Euphrates River).
2. Determine the concentration and distribution of nine heavy metals in water (dissolved and particulate phase), and sediment (exchangeable and residual phase), and to determine the main sources of heavy metals in the study area.

Experimental

Seven sites were selected along the Euphrates River (Hindiyah River) between Hindiyah barrage and Al-Kufa town. The study period was between March 2004 and February 2005. Air and water temperature, pH and electric conductivity were measured in the field using a thermometer, pH-meter (model HANNA) and E.C. meter (Model Bischof L17). Total dissolved solids (TDS), Total solid suspended (TSS), dissolved oxygen, BOD5, total alkalinity, total hardness, calcium, magnesium and sulphate were estimated³¹. Nitrite, nitrate and phosphate were estimated following Parsons³², silicate was executed according to Strickland and Parsons³³.

Heavy metals in water are measured using ion exchange technique procedure to determine the dissolved heavy metals³⁴. The particulate heavy metal was measured by digesting particulates collected on Millipore filter membranes of 0.45 μm with HCL: HNO₃: HClO₃: HF according to Sturgeon *et al*³⁵. In sediment, heavy metals in exchangeable and residual phases were extracted according to Chester & Voutsinou³⁶ and Sturgeon *et al*³⁵, respectively. These heavy metals determined by flame atomic absorption spectrophotometer (Model Pyeunicam SP9). Total organic carbon and texture of sediment values were determined according to methods of Gaudette *et al*³⁷ and Forth & Turk³⁸, respectively.

Results and Discussion

Air and water temperatures were in the range 6-40 °C to 10-34 °C, respectively (Table 1). Electrical conductivity was observed 110 $\mu\text{s}/\text{cm}$ at site 6 and 1100 $\mu\text{s}/\text{cm}$ at site 4 respectively .

Table 1. Physical and chemical characters of water in Euphrates River. (First line: (Mode) Second line: Mean (\pm S.D)).

Sits Parameters	Site.1	Site.2	Site.3	Site.4	Site.5	Site.6	Site.7
Water temperature	6-38	8-33	11-37	9-40	6-40	7-36	10-39
	25(\pm 9.54)	24(\pm 8.56)	24(\pm 8.41)	25(\pm 10.22)	28(\pm 10.92)	(12.02 \pm)21	(12.35 \pm)23
Air temperature	31-10	10-29	11-32	11-34	11-34	10-31	12-30
	22 (\pm 7.43)	21(\pm 7.22)	21(\pm 7.11)	22(\pm 8.06)	23(\pm 7.63)	19(\pm 9.46)	20(\pm 9.30)
pH	7.49-8.9	7.48-8.1	7.2-7.9	7.49-8.0	7.5-7.9	7.2-7.8	7.3-7.9
	7.8(\pm 0.37)	7.7(\pm 0.16)	7.6(\pm 0.22)	7.7(\pm 0.17)	7.7 \pm 0.14)	7.0(\pm 2.22)	7.0(\pm 2.22)
EC, μ s/cm	400-840	460-840	420-900	480-1100	460-900	110-800	470-980
	627.5(\pm 151.3)	640(\pm 134.2)	672.5(\pm 134.91)	697.3(\pm 164.4)	654.2(\pm 148.1)	555(\pm 257.6)	617.5(\pm 248.1)
TDS, mg/L	517-890	561-960	532-1057	566-1022	510-1050	650-1045	660-1165
	733.4(\pm 116.0)	744.9(\pm 115.0)	776.3(\pm 153.1)	783.9(\pm 150.4)	773.7(\pm 150.3)	771.7(\pm 271.2)	743.0(\pm 271.6)
TSS, mg/L	3.10-33.50	1.90-58.60	0.30-35.70	0.60-32.20	0.1-45.6	1.3-28.4	2.4-20.7
	14.9(\pm 9.2)	13.9(\pm 16.4)	10.8(\pm 9.1)	9.4(\pm 9.9)	11.7(\pm 12.7)	9.2(\pm 7.7)	9.5(\pm 6.7)
DO, mg/L	3.1-11.8	4.0-11.6	5.0-10.6	4.4-12.4	4.6-13.0	5.6-11.0	4.8-11.4
	7.7(\pm 2.8)	7.7(\pm 2.7)	7.6(\pm 1.8)	8.0(\pm 2.5)	8.8(\pm 2.4)	7.1(\pm 3.0)	6.9 \pm (3.0)
% Saturation of DO	46.0-148.0	42.5-149.0	45.4-135.0	42.7-158.0	46.7-172.0	49.6-135.6	44.5-145.6
	94.4(\pm 35.2)	89.3(\pm 36.7)	87.2(\pm 28.0)	93.9(\pm 34.2)	105.1(\pm 38.4)	79.8(\pm 36.0)	80.1(\pm 39.2)
BOD ₅ , mg/L	1.4-6.8	0.20-6.6	0.8-5.0	0.6-8.0	1.6-6.6	1.0-6.7	1.8-6.6
	3.7(\pm 2.0)	3.0(\pm 2.0)	2.9(\pm 1.2)	3.5(\pm 2.3)	3.7(\pm 1.8)	3.2(\pm 1.9)	3.6(\pm 1.9)
Total alkalinity mg(CaCO ₃)/L	103-153	102.0-150.0	101.0-152.0	103.0-152.0	91.0-153.0	106.0-167.0	100.0-154.0
	12.31(\pm 13.6)	119.5(\pm 12.5)	117.1(\pm 16.3)	118.7(\pm 16.1)	121.0(\pm 6.19)	117.0(\pm 40.1)	114.3(\pm 39.1)
Total hardness mg (CaCO ₃)/L	370.0-800.0	250.0-670.0	210.0-720.0	350.0-710.0	270.0-810.0	310.0-800.0	320.0-820.0
	588.3(\pm 144.2)	530.8(\pm 113.8)	544.1(\pm 135.0)	571.6(\pm 113.7)	553.3(\pm 125.5)	570.8(\pm 227.7)	566.6(\pm 221.8)
Ca mg (CaCO ₃)/L	108.2-192.3	96.6-232.4	112.2-208.4	56.1-208.4	116.2-260.5	96.1-240.0	208.4-112.2
	142.9(\pm 27.2)	143.6(\pm 33.4)	148.2(\pm 33.8)	136.2(\pm 39.4)	156.6(\pm 42.3)	135.2(\pm 58.1)	135.2(\pm 52.5)
Mg, mg (CaCO ₃)/L	4.7-120.0	13.2-82.7	12.1-108.2	2.3-106.8	9.6-104.6	1.3-113.0	72.3-116.7
	59.0(\pm 38.6)	52.1(\pm 25.2)	58.4(\pm 31.8)	56.4(\pm 40.4)	60.2(\pm 28.6)	72.9(\pm 36.2)	75.3(\pm 26.5)
Nitrate, μ g/L	0.06-1.3	0.06-0.8	0.07-0.5	0.01-1.1	0.06-0.6	0.06-0.08	0.06-0.4
	0.19(\pm 0.36)	0.1(\pm 0.2)	0.13(\pm 0.17)	0.1(\pm 0.3)	0.14(\pm 0.18)	0.6(\pm 0.2)	0.9(\pm 0.1)
Nitrite, μ g/L	3.8-278.0	6.8-265.0	6.2-360.9	4.3-249	3.6-267.0	4.5-173.0	1.0-100.0
	70.8(\pm 95.4)	99.1(\pm 95.4)	92.1(\pm 108.3)	74.7(\pm 73.3)	67.6(\pm 78.2)	39.1(\pm 47.8)	32.9(\pm 34.0)
Phosphate, μ g/L	0.0-0.7	0.0-0.7	0.0-0.7	0.0-0.7	0.0-0.7	0.0-0.6	0.0-0.6
	0.5(\pm 0.1)	0.5 (\pm 0.1)	0.5(\pm 0.1)	0.5 (\pm 0.1)	0.5 (\pm 0.1)	0.4(\pm 0.2)	0.4(\pm 0.2)
Sulphate, mg/L	27.7-1805.0	21.1-1114.0	28.5-1010	24.0-995.5 4	20.7-892.0	97.2-1130.0	93.2-1100.0
	626.6(\pm 538.8)	483.2(\pm 356.3)	466.6(\pm 330.2)	447.9(\pm 296.7)	471.1(\pm 284.4)	478.9(\pm 360.8)	485.0(\pm 369.7)
Silicate, μ g/L	140.3-830.0	123.4-1012	54.4-1038.0	55.1-1466.0	53.13-1542.0	39.8-1271.0	49.8-775.0
	36.5(\pm 265.2)	420.5(\pm 308.3)	449.0(\pm 287.0)	435.3(\pm 405.2)	467.1(\pm 436.2)	402.1(\pm 391.6)	349.2(\pm 291.3)

During the study period, pH was in the ranges from 7.2 to 9.9, TDS and TSS ranged from 510-1165 and 0.10-58.60 mg/L respectively, these values increased in winter months and decreased in summer months³⁹⁻⁴².

The solubility of oxygen in an aquatic system is influenced the temperature and dissolved salts⁴³. Highly variable concentrations of dissolved oxygen were recorded at the study sites between 3.1 mg/L at site 2 and 13 mg/L at site 5 (Table 1). The result showed no significant differences among the sites.

High values of BOD₅ were recorded in most study sites and these exceed limits recommended by WHO⁴⁴. This may be due to direct discharge of sewage into the river at the study sites^{45,46}. Total alkalinity ranged between 91 mg CaCO₃/L and 167 mg CaCO₃/L (Table 1). Positive correlations were recorded between total alkalinity and both dissolved oxygen and BOD₅ ($r=0.560$, $p<0.01$ and $r=0.572$, $p=0.01$, respectively). Many studies have found that Iraqi water was slightly alkalinity^{22,23,40,47}.

The present study found high concentrations of total hardness in all sites during different months. It ranged between 210 mg CaCO₃/L and 820 mg CaCO₃/L, with no significant difference among study sites while there were a negative correlation with temperature and dissolved oxygen ($r=0.531$, $P<0.01$ and $r=-0.517$, $P<0.01$, respectively).

Calcium value ranged from 56.10-260.50 mg CaCO₃/L, while magnesium concentration ranged from 1.3-120 CaCO₃/L. There were no significant differences between sites and months, and there was no correlation between calcium and magnesium.

High magnesium values may be a result of soil erosion²³ or to a high density of phytoplankton⁴⁹. The values of nitrite and nitrate ranged from 0.064-1.3 µg/L and 1-360.95 µg/L respectively and no significant differences between sites. There were significant differences between months. The results recorded positive correlations between nitrate with dissolved oxygen, BOD₅, total alkalinity and nitrite ($r=0.800$, $P<0.01$; $r=0.642$, $p<0.01$; $r=0.591$, $P<0.01$; $r=0.820$, $P<0.01$) respectively.

The variation in nitrate concentration may be due to the input from groundwater, plant fertilizers, pesticides and other pollutants to the river⁵⁰.

Soluble reactive phosphate in most sites was low or ND, but values to 0.77 µg/L were recorded. Low concentrations may be due to precipitation on sediment⁵¹ or accumulation in aquatic plant and phytoplankton⁵².

The sulfate values ranged from 20.76-1805 mg/l (Table 1), while silicate ranged from 39.8-1542 µg/L. A significant difference was recorded among months and also there was a negative correlation with pH and EC, ($r=-0.614$, $P<0.01$; $r=-0.586$, $P<0.01$, respectively) and positive correlations with air and water temperature and BOD₅ ($r=0.849$, $P<0.01$; $r=0.902$, $P<0.01$; $r=0.502$, $P<0.01$, respectively).

The present study showed high values of silicate through the summer and autumn that may be because of the decay of diatoms by high temperature⁴³ or by increase in the solubility of metal salts in water⁵³, this result agrees with many studies in Iraqi aquatic systems^{23,24,27}.

Table 2 show the concentration of heavy metals in water and sediments in Euphrates River. The dissolved heavy metals ranged between the lowest limit for Ni & Pb (0.06 µg/L) and the highest limit for Fe (103.9 µg/L). While, the particulate heavy metals ranged between 0.1 µg/g for Cr and 617 µg/g for Fe.

Table 2. Means of heavy metals concentration in water and sediments in the study area.

Element	Water		sediment		
	Dissolved µg/L	Particulate µg/g	Residual µg/g	Exchangeable µg/g	Total µg/g
Cd	2.14	10.20	5.50	5.72	11.22
Co	1.16	8.09	4.34	3.90	8.24
Cr	0.07	0.24	0.24	0.15	0.47
Cu	2.48	13.60	7.10	7.34	14.14
Fe	105.60	660.00	351.90	309.80	661.70
Mn	6.12	33.70	18.84	18.86	37.70
Ni	0.07	0.19	0.10	0.27	0.37
Pb	0.10	0.50	0.32	0.27	0.59
Zn	10.50	59.90	38.72	28.94	67.66

The concentrations of some heavy metals in water of Euphrates River were low according to WHO and USEPA guidelines, but there were high compared to other Iraqi aquatic systems⁵⁴⁻⁵⁶. This difference with other Iraqi studies may be related to the difficulty of investigating heavy metals in toxic aquatic system, where heavy metal concentrations will be low. Moreover the many factors affect the concentrations, such as: the flow of the dredged materials from upper regions of the river, dilution and increase of water flow, direct drainage from farmlands, factories, sewage disposal plants, dissolution of sediments, increases in the numbers of phytoplankton in water, bioaccumulation, chemical adsorption on sediments and complexes with organic matter⁵⁷⁻⁶⁰.

The results of this study showed positive correlation between heavy metals in dissolved and particulate phases and positive correlation with air and water temperature, dissolved oxygen, BOD_5 and with sulphate and silicate.

The concentration of heavy metals in the particulate phase were Ni < Cr < Pb < Co < Cd < Cu < Mn < Zn < Fe.

High concentrations of heavy metals were recorded in exchangeable and residual sediment. This concentration ranged between 0.1 µg/g for Cr and 308.46 µg/g for Fe (exchangeable phase) and 0.09 µg/g for Ni and 351.9 µg/g for Fe. The dissolved elements are transformed into particulate matter through uptake by phytoplankton, oxidation and adsorption in the basins⁵⁸.

Positive correlations were found between some heavy metals and dissolved oxygen, BOD_5 , nitrite, nitrate, reactive phosphate and silicate. The increase of heavy metal concentration may be due to multiple source of pollution such as sewage, pesticides, industrial waste, *etc.*¹⁸, or by decomposition of plankton, diatoms and benthic organism⁵⁸. Many other factors affect heavy metal concentration in sediments, such as grain size and percentage of total organic carbon (% TOC)⁶¹. The results showed that sediment texture in Euphrates River was sand-silt-clay in most sites (Figure 1) and that there was high in TOC% (Figure 2), but there was no significant difference between TOC and heavy metals in sediment. The behavior and distribution of heavy metals in sediments may be affected by water hydrology, domestic discharge and many biological, chemical and geological operations in aquatic system⁶².

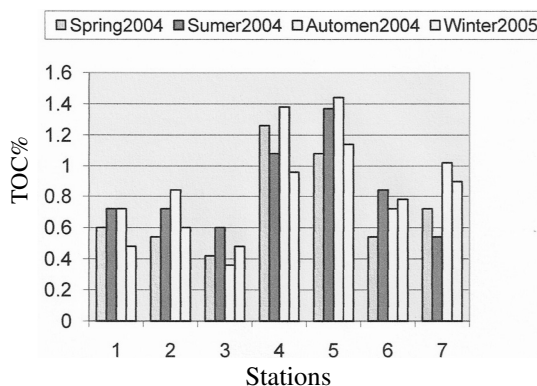


Figure 1. Seasonal variations for percentage of total organic carbon (TOC) in sediment at the study area.

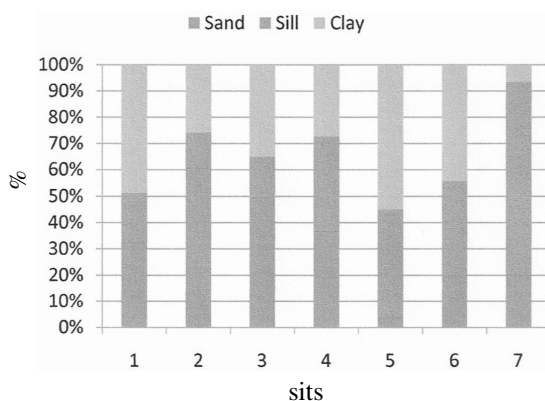


Figure 2. Percentage of sediment texture at the study area.

Conclusions

The waste of military factories, urban run-off, city sewage and the agricultural activities were affecting the physicochemical characteristics of Euphrates River. The heavy metals were accumulated in the sediment of river and it was shown in this study. The mean concentrations of studied metals in particulate phase were higher than those in dissolved phase in water.

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