Original Article

Short-term assessment of heavy metals in surface waters of the Shatt Al-Arab River

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Abstract: The Shatt Al-Arab River's water quality deteriorates naturally due to salinity intrusion, and freshwater sources decrease. Seven sampling locations along the Shatt Al-Arab River in southern Iraq were used to examine the level of six heavy metals, including Cu, Cd, Ni, Co, Mn, and Fe, during Januar-December 2021. Salinity levels in the study area ranged from 1.55 upstream to 35.15 g/L downstream of the study area. The pH of surface water ranged 7.545-8.325, indicating alkaline conditions. The concentrations of six heavy metals, viz Cu, Cd, Ni, Mn, Co, and Fe in the study area were 3.741 ± 4.219 , 3.654 ± 4.169 , 7.700 ± 6.251 , 2.551 ± 3.898 , 2.292 ± 3.996 , and $18.236\pm5.583 \mu g/L$, respectively, which decreased in the order of Fe > Ni > Cu > Cd > Mn > Co. There was a considerable change in the quantity of heavy metals throughout the year, with the summer months having the highest concentration. There is a correlation between seawater intrusion and the concentration of heavy metals in the surface waters. The mean levels of the heavy metals were below the allowed values of WHO drinking water guidelines.

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Introduction

Increasing heavy metals in river ecosystems is a significant global issue. Over the last decades, there has been a significant rise in the quantity of heavy metals in river water (Mishra et al., 2022). The Shatt Al-Arab River starts at the confluence of the Tigris and Euphrates Rivers in Qurna, North of Basrah, Iraq, and flows approximately 200 km northwest of the Iraqi marine waters, south of the Al-Fao city (Aldoghachi, 2022). The river width ranges from 250 to 300 m, close to the Euphrates and Tigris confluence to about 700 m in Basrah and over 800 m close to its estuary (Abduljaleel et al., 2020). Its salinity varies greatly depending on the season and quantity of freshwater discharge (Abdallah, 2016). Abduljaleel et al. (2020) reported that the salinity of the water in the Euphrates, Tigris, and Shatt Al-Arab rivers dramatically increased over time. They emphasize how the lack of efficient river basin management programs causes the water quality of

Studies on the effects of urban contamination from the city and industry on the Shatt Al-Arab surface water in the Basrah region have been studied (Douabul et al., 2013; Al-Aboodi, 2018). Moyel (2014) used a water quality index to assess the water quality of the northern Shatt Al-Arab region to determine its suitability for drinking, irrigation, and aquatic life. Lafta (2014) and Abdallah (2016) calculated the upstream flow to predict seawater intrusion into Shatt Al-Arab, and it was only suitable for irrigation purposes. Salt concentrations are higher than those permitted for a particular use of water should be categorized as pollutants (Karamouz et al., 2003). Under the influence of geochemical processes, heavy metal contamination will transfer

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the Euphrates, Tigris, and Shatt Al-Arab rivers to deteriorate. The Shatt Al-Arab estuary and its upstream encountered increasing saltwater intrusion from the Iraqi marine waters, which has a negative impact on ecosystem productivity.

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with surface water and contaminate soil and water directly or indirectly (Liu et al., 2018). However, most works focus primarily on the characteristics of heavy metal contamination in soil and pay little attention to heavy metal pollutants transfer in surface water.

It is difficult to identify the distribution characteristics of heavy metals in agricultural ecosystems because of the integrated and cohesive substrate in the surrounding ecosystems (Lermi et al., 2020). Excessive pollutant discharge into surface rivers has caused major decreases in aquatic environmental indicators in recent years (Liu et al., 2016). In this study, the Shatt Al-Arab River is assessed regarding the influence of seawater intrusion from the Iraqi marine water on the concentrations of heavy metals with the main objective of assessing the levels of heavy metals (Cu, Cd, Ni, Co, Mn and Fe) in the surface waters of the Shatt al-Arab based on temporal and spatial variability.

Materials and methods

The main source of freshwater in Basrah is Shatt Al-Arab, with about 200 km long and an estuary with a three km width. Shatt Al-Arab extends 63 km till reaching Al-Fao. In the Basrah region, it provides services for industry, agriculture, navigation, and ecosystem biodiversity. Numerous small waterways branch out of both banks of the river in Basrah City; most waterways are used for agriculture. Table 1 shows the locations of the monitoring sites in this study. Seven sampling sites in the Shatt Al-Arab River were set up, and each site was positioned with a Global Position System (GPS) to ensure the representativeness of the collected samples. The seven sampling sites were Fao (sea area) (ST1), Fao city (ST2), Abu Al-Khaseeb (ST3), Basrah city (ST4), Sidebad Island (ST5), Hartha (ST6), and Qurna (ST7).

Surface water samples were taken at a depth of 30 cm in the middle of the river using a plastic bottle with a one-liter capacity that was fully filled. Water samples were collected monthly (January-December

Table 1. Monitoring stations and their coordinates.

Station	Name	Е	Ν
ST1	Fao (sea)	48°48'20.74"	29°47'36.81"
ST2	Fao city	48°29'31.07"	29°58'43.92"
ST3	Abu Al-Khaseeb	47°54'12.59"	30°28'41.65"
ST4	Basrah city	47°48'49.03"	30°33'6.97"
ST5	Sidebad Island	47°46'43.38"	30°34'20.80"
ST6	Hartha	47°44'47.87"	30°41'41.25"
ST7	Qurna	47°27'8.93"	30°59'5.50"

2021), divided into 6 periods: January-February (P1), March-April (P2) May-June (P3), July-August (P4), September-October (P5), and November-December (P6). One-liter polypropylene sample containers were used to hold the water samples, which had been cleaned three times in distilled water. To prevent water evaporation, all the water samples were parafilm-sealed after being fixed with HNO₃ to a pH<2. (APHA, 2005). The water temperature, salinity, and pH at the study sites were measured using a portable multi-meter water quality instrument (YASI, USA). The sample waters were transferred to the laboratory, kept in a lowtemperature incubator, and then examined for the presence of heavy metals. All samples were filtered using a 0.45 m cellulose acetate membrane filter to remove contaminants. The concentrations of heavy metals viz. Co, Ni, Cu, Cd, Mn, and Fe were measured using an atomic flame absorption spectrum technique at wavelengths of 248.3, 228.8, 240.7, 279.5, 264.88, and 324.8 nanometers, respectively.

Results

The water quality of the Shatt Al-Arab River deteriorates naturally due to salinity intrusion, and freshwater sources decrease. Salinity levels in the study area ranged from 1.55 (ST7) to 35.15 gm/L (ST1). The pH of surface water samples ranged between 7.545 to 8.325, indicating alkaline conditions in all studied sites (Table 2). While the temperature ranged between 14.85°C in the winter and 29.55°C in the summer months. The concentration of heavy metals (μ g/L) in the study area is shown in Table 3.

Heavy metals were found in all the surface water

Sampling sites	Water quality	Periods					
Sampling sites	Water quality	P1	P2	P3	P4	P5	P6
ST1	Temperature(°C)	15.35	17.55	27.3	29.05	27.145	17.16
	Salinity (gm/L)	34.35	34.75	34.4	35.15	19.53	17.73
	pH	7.65	7.85	8.05	7.81	7.795	7.76
	Temperature(°C)	15.56	18.35	27.65	29.55	27.51	17.37
ST2	Salinity (gm/L)	21.85	22.75	23.4	31.55	18.25	17.53
	pН	7.80	8.06	8.05	7.80	7.59	7.88
ST3	Temperature(°C)	18.15	21.99	26.85	29.45	17.57	17.19
	Salinity (gm/L)	5.91	5.25	5.17	16.32	22.25	15.23
	pH	7.96	8.14	7.66	7.82	7.595	7.88
	Temperature(°C)	15.82	21.95	26.65	28.69	27.14	17.09
ST4	Salinity (gm/L)	3.82	4.105	5.15	14.08	16.53	16.32
	pH	7.54	8.27	7.89	7.83	7.795	7.88
	Temperature(°C)	15.82	21.86	25.97	29.52	27.90	17.465
ST5	Salinity (gm/L)	3.43	3.91	4.69	14.41	15.61	13.05
	pН	7.54	8.325	7.68	7.84	7.75	7.955
ST6	Temperature(°C)	14.85	20.65	26.25	28.21	27.55	17.15
	Salinity (gm/L)	1.99	2.865	3.85	27.26	14.28	12.35
	рН	7.62	8.26	7.65	7.86	7.78	7.97
ST7	Temperature(°C)	16.54	21.3	26.6	29.15	28	17.8
	Salinity (gm/L)	1.55	1.85	2.94	5.31	4.22	3.18
	рН	7.65	8.14	7.65	7.95	7.85	8.03

Table 2. Water quality in surface water of the Shatt Al-Arab River at different locations and times during study period.

Table 3. Monitoring stations and their coordinates.

0 1' T'	Sampling	Heavy metals concentration $\mu g L^{-1}$						
Sampling Time	Site	Cu	Cd	Ni	Mn	Co	Fe	
January-February (P1)	ST1	12.5	12.45	12.5	12.31	9.33	25.36	
	ST2	7.52	4.65	18.66	2.09	ND	17.968	
	ST3	3.54	1.23	20.52	1.42	1	24.169	
	ST4	1.77	0.615	10.26	0.71	0.5	18.282	
	ST5	1.18	1.23	0.41	0.4733	0.3333	12.686	
	ST6	0.885	0.3075	5.13	0.355	0.25	11.792	
	ST7	0.708	0.246	4.104	0.284	0.2	11.23	
	ST1	13.15	12.815	13.26	11.305	12.605	24.185	
	ST2	3.44	4.685	18.31	1.33	1.555	19.864	
	ST3	2.515	2.145	16.265	1.54	1.525	26.719	
March-April (P2)	ST4	1.2575	1.0725	8.1325	0.77	0.7625	20.212	
	ST5	0.8383	2.145	0.715	0.5133	0.5083	14.024	
	ST6	0.6288	0.5363	4.0663	0.385	0.3813	13.036	
	ST7	0.503	0.429	3.253	0.308	0.305	12.415	
May-June (P3)	ST1	12.1	12.63	15.32	12.11	12.41	29.08	
	ST2	3.24	9.21	21.12	2.32	1.52	19.728	
	ST3	1.78	4.25	9.23	2.04	1.01	26.536	
	ST4	0.89	2.125	4.615	1.02	0.505	20.073	
	ST5	0.5933	4.25	1.4167	0.68	0.3367	13.928	
	ST6	0.445	1.0625	2.3075	0.51	0.2525	12.947	
	ST7	0.356	0.85	1.846	0.408	0.202	12.33	
July-August (P4)	ST1	13.99	14.11	12.99	11.5	13.5	28.06	
	ST2	5.88	6.55	14.36	1.52	3.01	20.656	
	ST3	4.22	5.36	12.36	1.02	1.73	27.785	
	ST4	0.89	2.125	4.615	1.02	0.505	20.073	
	ST5	1.4067	5.36	1.7867	0.34	0.5767	14.583	
	ST6	1.055	1.34	3.09	0.255	0.4325	13.556	
	ST7	0.844	1.072	2.472	0.204	0.346	12.91	
September-October	ST1	13.44	12.55	11.55	13.01	12.98	24.99	
	ST2	3.69	2.34	11.25	3.66	0.55	18.448	
	ST3	3.65	3.11	15.65	2.98	0.72	24.815	
	ST4	1.825	1.555	7.825	1.49	0.36	18.771	
(P5)	ST5	1.2167	3.11	1.0367	0.9933	0.24	13.025	
	ST6	0.9125	0.7775	3.9125	0.745	0.18	12.107	
	ST7	0.73	0.622	3.13	0.596	0.144	11.53	

Table 3. Continued

Sampling Time	Sampling	Heavy metals concentration $\mu g L^{-1}$						
	Site	Cu	Cd	Ni	Mn	Co	Fe	
November-December (P6)	St1	13.22	11.5	13.33	11.22	9.56	22.55	
	ST2	8.11	1.16	6.22	1.23	1.33	17.856	
	ST3	5.36	0.65	3.17	1.09	1.03	24.018	
	ST4	2.68	0.325	1.585	0.545	0.515	18.168	
	ST5	1.7867	0.65	0.2167	0.3633	0.3433	12.607	
	ST6	1.34	0.1625	0.7925	0.2725	0.2575	11.718	
	ST7	1.072	0.13	0.634	0.218	0.206	11.16	
Mean		3.741	3.654	7.700	2.551	2.292	18.236	
±SD		4.219	4.169	6.251	3.898	3.996	5.583	

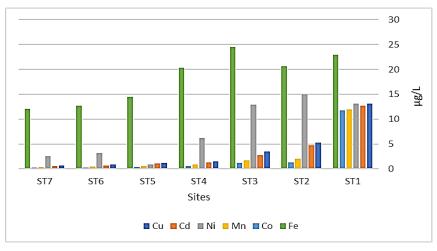


Figure 1. The distribution of heavy metals in the surface waters of the Shatt Al-Arab River at the study sites.

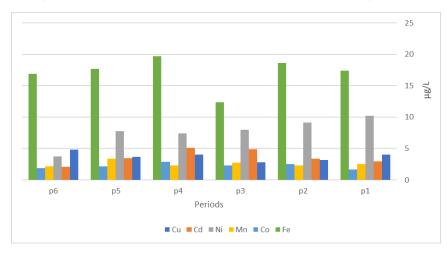


Figure 2. Distribution of heavy metals in the surface water of the Shatt Al-Arab River at different times.

samples with significant temporal and spatial variations. The average concentrations of six heavy metals, including Cu, Cd, Ni, Mn, Co, and Fe were 3.741 ± 4.219 , 3.654 ± 4.169 , 7.700 ± 6.251 , 2.551 ± 3.898 , 2.292 ± 3.996 , and 18.236 ± 5.583 µg/L, respectively. All the sampling sites showed an overall rising trend in the presence of heavy metals from upstream (ST7) to downstream (ST1) (Fig. 1). The first station (ST1) had the highest average

concentrations of the six heavy metals of Fe, Co, Mn, Ni, Cd, and Cu, which were 25.70417, 11.73083, 11.90917, 13.15833, 12.67583, and 13.06667 μ g/L, respectively. The concentrations decreased in the order of Fe > Cu > Ni > Cd > Mn > Co.

There were significant differences in heavy metals abundance between sampling periods (Fig. 2). The Fe had the highest concentrations during study periods, and its concentration decreased in the following order: P4 > P2 > P5 > P1 > P6 > P3. While nickel was in the following order in terms of concentration: P1 > P2 > P3 > P5 > P4 > P6, as the second rank after Fe. For Cu, the highest concentration was during periods 1 and 6. The highest concentration of Cd was during periods 4 and 3 and the highest concentrations of Mn and Co were found during periods 4 and 3, respectively.

Discussion

A spatial and temporal distribution of the surface water temperatures of the Shatt Al-Arab River, showed typical seasonal variability, reflecting changes in air temperature and dynamics of the river flow. The pH value did not alter seasonally, but there was some spatial variability along the Shatt Al-Arab River. These values were within the range of the USEPA (1999) criterion for surface water (6.5-9). Salinity in Shatt Al-Arab is mostly caused by seawater entering the river from Iraqi marine waters. Salinity variation across seasons and sites can be correlated with flow regimes and seasonal influences (Al-Asadi et al., 2019). Chemical ions entering the river from its major tributaries and sea salt entering from the sea both impact the quality of the Shatt Al-Arab River. The mean salinity concentration is due to the loss of most tributaries of the freshwater flow in the river combined with increases in seawater intrusion from Iraqi marine waters (Moyel and Hussain, 2015; Abdullah, 2016). Thus, the mean salinity values at all studied sites along Shatt Al-Arab River were increased from Qurna (ST7) (5.31 g/L) to Fao Sea (ST1) (34 g/L). These results indicate a tendency toward water stress due to rising demand by population growth, water the development of irrigated land, the building of dams within river basins, and other factors. Reduced runoff and increased water evaporation losses have also been caused by climate change.

Heavy metals are highly persistent in the environment and can be toxic for living organisms. The current study showed that trace metal concentrations are below WHO recommendations (WHO, 2011). According to the salinity, the river

can be divided into two regions. These regions could also be easily recognized due to their heavy metal concentrations. Extremely low heavy metals were found in the first region, which comprised the Qurna (ST7), Harth (ST6), Sidebaed Island (ST5), and Basrah city (ST4). The second region, which includes Abu Al-Khaseeb (ST3), Fao city (ST2), and Fao Sea (ST1), had the highest concentration. Therefore, there was clear evidence that seawater intrusion influenced the levels of heavy metals. Salinity, pH, geological environment, and terrestrial runoff are a few variables that might have affected metal changes (Raknuzzaman et al., 2016). Cd, Cu, and Pb in lake water can be decreased by raising pH levels because proton binding decreases as pH rises, reducing the metal-binding capacity (Tokalioglu et al., 2000). Water volume and velocity are positively correlated with the level and distribution of heavy metals in surface water (Alloway and Steinnes, 1999).

Heavy metals in the surface water were diluted by the high-water volume and velocity, decreasing their concentration. One of the factors causing a decrease in the concentrations of heavy metals in the surface water is rainwater entering the surface of the water body in a short period (Shamsuzzaman et al., 2012). The levels of heavy metals in the Shatt Al-Arab River surface waters during the summer (P3, P4, and P5) showed a slight increase compared to the rest of the year. The Shatt Al-Arab River experiences a major decrease in water volume and velocity during the dry seasons, and the physical and chemical characteristics of the water body differ noticeably from those during the rainy season. While land use patterns and levels of human activity on both banks of the Shatt Al-Arab River have remained mostly unchanged throughout this period, the residual concentration of heavy metals in the surface water has increased dramatically. Hence, to monitor and ecological assess local and environmental conditions, it is essential to know the spatial distribution of heavy metals in surface water (Mohiuddin et al., 2011).

In conclusions, the primary causes of the salinity

of Shatt Al-Arab waters are from Marin water. This work provided baseline data on some toxic heavy metal concentrations in the surface water of this river at various times and locations following seawater intrusion. The results showed that heavy metal concentrations are below WHO recommendations. All the sampling sites showed an overall rising trend in the presence of heavy metals from upstream (ST7) to downstream (ST1). Furthermore, there is a correlation between seawater intrusion and the concentrations highest at sites with the highest salinity levels.

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