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Fate and Management of Pollution of Hexavalent Chromium Cr(VI) and Heavy Metals in the Zarqa River Basin in Jordan

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ABSTRACT

This paper focused on the fate of pollution and management of hexavalent chromium Cr(VI) and heavy metals in the Zarqa River Basin in Jordan. The Zarqa River basin was selected in this research because it contains the majority of Jordanian industries, which are the main source of pollutants including Cr(VI) and heavy metals. This will help in assisting water resource management organizations in decision making when coping with pollution. Industries related to sources and impacts of Cr(VI) and heavy metals were identified, and the administration measures were highlighted according to their role in improving water quality. An analysis of water samples along the Zarqa River was conducted between 2016–2019 to evaluate the heavy metals concentrations and compare the results with the Jordanian standards. Findings showed that Cr(VI) was below the allowable limits (<5 µg/l), and the heavy metals were within the allowed limits set forth in the Jordanian Standard. The ranges of water analysis values (µg/L) were; DO 4640–6480, Fe <40–80, Mn 20–128, Co <20–30, Pb 80–190, Zn 70–100, and Cu <80–190, Al 700–730, V <70–100, B <300–351, Si 1100–1800, Ni 30, and Cd <10. These findings indicated that the quality of the Zarqa River would not cause hazardous effects. However, this was not the case few years ago due the current protection measures. At present some industries have been relocated from the Zarqa Basin to an area that does not pose any environmental hazards, while the rest of industries remained in the basin, but they have established an on-site treatment plant for industrial waste under the control of Jordanian government, and the enforcement of the environmental protection law. These measures must be monitored and updated by decision makers in a sustainable manner to prevent any water pollution.

Keywords: Zarqa River Basin, industrial activities, water pollution, hexavalent chromium Cr(VI), heavy metals, decision makers.

INTRODUCTION

The fate of pollutants in the environment depends upon the 'compartment' in which they occur: air, water, soil, sediment or living organisms. The water compartment may include groundwater, surface water, or pore water. Within each compartment, the environmental contaminant may remain unaltered, but more often is altered by living or nonliving components of the environment [Wexler 2014]. Industries, agriculture, wastewater, mining and metallurgical processes and runoffs also lead to the release of pollutants to different environmental compartments. Heavy metals are known to be naturally occurring compounds, but anthropogenic activities introduce them in large quantities in different environmental compartments. This leads to the environment's ability to foster life being reduced as human, animal, and plant health become threatened. Remediation of heavy metals requires special attention to protect soil quality, air quality, water quality, human health, animal health and all spheres as a collection. Developed physical and chemical heavy metal remediation technologies are demanding costs which are not feasible, time-consuming, and release additional waste to the environment [Masindi and Muedi 2018].

Therefore, pollution management and care must be taken when planning and operating wastewater treatment systems to ensure proper management of wastewater and sources of heavy metals pollution [Tracy et al. 2020].

Pollution with hexavalent chromium Cr(VI) and other heavy metals is a major concern due to heavy metals toxicity, bioaccumulation, abundance and persistence [Huang et al. 2020]. The major source of heavy metals such as lead, zinc, nickel, copper, chromium and cadmium is from industrial wastewater [Al-a'qarbeh et al. 2020]. The rivers in urban areas are most likely to have high concentrations of heavy metals due to industrial effluent discharge [Islam et al. 2015].

One of the most prominent heavy metals is Cr(VI) [Shammout and Shatanawi 2021]. It has high solubility, mobility and oxidizing potential and hence it is deemed the most toxic chromium form [Shadreck and Mugadza 2013]. Baral et al. [2006] showed that Cr(VI) has a certain maximum concentration limit in water. Cr(VI) is a priority pollutant and has numerous effects on health and the environment [Mongelli et al 2019]; most notably Cr(VI) is carcinogenic; exposure to it increases the risk of sinus, nasal, or lung cancer. It is also genotoxic and its compounds may induce gene mutation or DNA damage [Mishara and Bharagava 2016]. Other health effects include ulcers, kidney abnormalities, perforation of the nasal spectrum and the eardrum, and skin and eye irritations [Sharma et al. 2021; Yoshinaga et al. 2018]. Cr(VI) compounds are used in several industries including petroleum refining, leather tanning, pulp producing, paints, textiles, iron and steel, electroplating and wood preservation [Kerur et al. 2021; Saha et al. 2011; Wang and Shen 1995]. Chromic trioxide and chromates of zinc, strontium, calcium, sodium, and barium are used in anti-corrosion coatings. Chromates of lead, zinc, calcium, sodium, and barium are used in pigments for plastics, paints and ink [Saha et al. 2011].

In the case of treating water polluted with Cr(VI) and heavy metals to be used for agricultural or other uses, the cost for treatment depends on the level of pollution and the quantity of water that must be treated. There are plenty of methods to treat polluted water such as adsorption, ion-exchange and reverse osmosis [Awwad et al. 2021]. The most reasonable alternative to ensuring safe water within allowable concentration limits is the in situ treatment of industrial wastewater effluent. This alternative must be monitored through institutional measures and restrictive regulations because some of the pollutants like metals are not effectively removed in conventional wastewater treatment processes. Preventive measures should be adopted to minimize the difficult-to-treat pollutants from entering the municipal sewer system through various point and non-point source. In China, the government has set quality requirements for utilizing reclaimed wastewater; consequently, the quality of reclaimed wastewater is constantly improved, making it suitable for many uses other than land applications [Yi et al. 2011]. In Malaysia, [United Nations Environment Program 2009], the regulations set forth procedures for the design and construction of industrial effluent treatment systems, and acceptable conditions of the discharge of industrial or mixed effluent. The regulations provide: monitoring of discharge of industrial effluent or mixed effluent; point of discharge of industrial or mixed effluent; containment measures for spills or accidental discharge of industrial or mixed effluent; prohibition of discharge of industrial effluent containing certain substances; license fees and penalties. In Poland, pollution of freshwater resources was a result of negligence in wastewater management in the past, but the Water Framework Directive (WFD) (2000/60/EC) introduced a legal framework to protect and restore the water environment across Europe and ensure its long-term, sustainable use, which take into account many water parameters indicated by the guidelines of the WFD [European Parliament and Council 2000; Vlachopoulou et al. 2014]. Essential EU legislation regarding water and wastewater management was implemented into the Polish law already in 2001 [Mikosz 2013]. Poland achieved significant progress in the approximation of Polish legislation with the EU environmental law. The implementation of the European Union Framework Directive 2000/60/EC on water policy has made the competent authority in the governmental administration responsible for managing water and facing problems related to the implementation, enforcement of the law and monitoring the implementation process in the field of improving the status of water resources, in terms of quantity and quality.

In Jordan, water quality problems are emerging strongly due to climate change, intensive agricultural activities and the development of industries that require water resources monitoring in a sustainable manner by decision makers through a water policy approach [Shammout and Shatanawi 2021; Shammout et al. 2013]. Physical development planning was generally insufficient and until 2003 there was little concern for the environment. Mohsen and Jaber [2003] showed that there are many signs of significant pollution and environmental degradation, where industrial enterprises had been constructed without provisions for adequate treatment of wastewater effluent. For this purpose, the Jordanian Environmental Protection Law was issued in 2006 after the establishment of Ministry of Environment in 2003 [Ministry of Environment 2006; World Bank 2009]. According to the Ministry of Environment was deemed the competent party to protect the environment and the reference for all environmental matters in Jordan. The Ministry of Environment was assigned a set of environmental duties such as, setting a policy for environmental protection and sustainable development, preparing the standards and specifications for the elements of the environment, as well as setting the principles of handling hazardous and harmful materials. A set of regulations emerged from this law, which are, the regulation of harmful and hazardous materials management such as; the regulation of soil protection (regulation no. 25/2005), the regulation of environmental protection from pollution in emergency cases (regulation no. 26/2005), the regulation of natural reserves and national parks (regulation no. 29/2005), the regulation of environmental impact assessment (regulation no. 30/2005), and the regulation of marine and coastal protection (regulation no. 51/1999). However, some environmental regulations have not been sufficiently implemented, and some wastewater effluent from industrial enterprises have not been adequately managed which may have led to pollution of water resources.

This research was conducted between 2016–2019 for the Zarqa River Basin in Jordan due to the industrial activities, which are the main source of pollutants including Cr(VI) and other heavy metals. In this research paper, the main objective is to highlight and describe the fate of pollution and management of hexavalent chromium Cr(VI) and other heavy metals in the Zarqa River Basin. The specific objectives were (1) to identify the industrial activities and sources of Cr(VI) and heavy metals in the Zarqa River Basin, (2) to analyse the water samples from different sampling sites in the Zarqa River between the years 2016–2019, and (3) to evaluate the heavy metals concentrations in the Zarqa River by comparing their concentrations to that of the Jordanian Standard [Jordanian Standard 2006) for irrigation purposes.

METHODOLOGY

Study site and industries

The area of the Zarqa River Basin basin is about 4120 km^2 from the upper northern point to its outlet near King Talal Dam. This area hosts three major cities, namely; Amman, Jerash and Zarqa, and it is the largest urban center in Jordan with more than half the population of the Kingdom. The basin faces problems related to water availability, water quality and ecological degradation because of over-abstraction of groundwater, discharge of treated wastewater effluents and other non-point sources pollution. In addition, the basin is experiencing rapid increase in population and associated social and economic development that will increase water demand and pollution load. The Zarqa River Basin is also the most complex resource system in Jordan. At the lower end of the basin King Talal Dam (KTD) is located with a capacity of 75 MCM. The reservoir of KTD receives runoff from the basin and wastewater from treatment plants, i.e. the flow of the Zarqa River mixed with treated effluents from WWTPs and is finally stored in King Talal Dam, where the dam's water is used for irrigation in the Jordan valley [Al-Taani et al. 2018; Shammout et al. 2018]. The reservoir also control water releases to the central part of the Jordan valley where it is mixed with the canal water diverting water from upstream sources. Upstream from the release point to the canal, a water diversion supplies fresh water back to the municipal system in Amman [Shammout et al. 2021]. This complex exchange represents the spectrum of water sources, uses and issues related to water problem as polluted water.

The Zarqa River Basin has the majority of Jordanian industries [Mohsen and Jaber 2003]. Since early 1990s, tremendous industrial development took place in the basin where the industrial enterprises had been constructed without provisions for adequate treatment of wastewater. The main industrial activities in the basin are: Al-Hussein thermal power plant, petroleum refinery, electroplating, textile manufacturing, paper and carton processing, painting, plastic industry, leather tanning, spinning and weaving, optical and hearing aid industries, food stuff industries, ice and aerated water, beer, dairy cattle and poultry farms, Amman municipality slaughterhouse, poultry processing, yeast industry, Jordan mills, intermediate pharmaceutical and chemical industries, aluminum industry, intermediate petro-chemicals, and mining industries. Basin industries are located in the Zarqa industrial center and represent more than 50% of Jordanian factories and are a source for pollution.

The basin also includes four wastewater treatment plants (WWTPs), namely, Khirbet As-Samra, Abu Nsair, Baqa'a, and Jerash, whose treated wastewater sometimes does not meet Jordanian standards for reusing water for irrigation [Jordanian Standard 2006]. Although, the Environmental Protection Law [Ministry of Environment 2006] has established a set of rules to protect the various aspects of the environment and imposed penalties on any violations

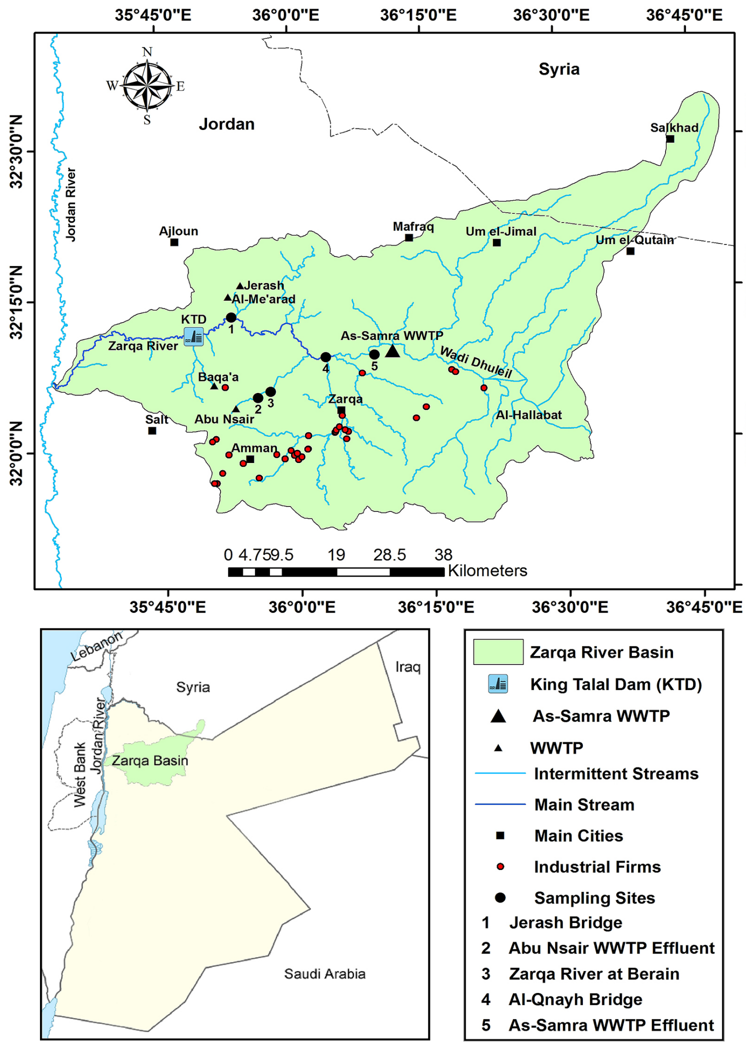

Figure 1. Zarqa River Basin and sampling sites

Table 1. Parameters and methods of analyses [American Public Health Association 2012]

Parameter	Symbol	Method Used	Method Number
Power of Hydrogen	pH	pH-Meter at Field	4500 H B
Electrical Conductivity	EC	Conductivity at Field	2510 B
Total Dissolved Solids	TDS	Drying at 180 °C	2540 C
Dissolved Oxygen	DO	Membrane Electrode at Field	4500-O G
Chromium, Iron, Manganese, Cobalt, Lead, Zinc, Copper, Aluminum, Vanadium, Boron, Silicon, Nickel, and Cadmium	Cr, Fe, Mn, Co, Pb, Zn, Cu, Al, V, B, Si, Ni, and Cd	Inductively Coupled Plasma/Atomic Emission Spectroscopy	3120 B
		Atomic absorption spectrometry	3111 B

of them, some environmental regulations have not been sufficiently implemented, and some wastewater effluent from industrial enterprises have not been adequately managed. This leads to pollution of the water resources of the Zarqa River Basin.

Zarqa River water sampling and analyses

To study the concentrations level of Cr(VI) and other heavy metals in the Zarqa River water, five samples were collected from Zarqa River between the years 2016–2019 as shown in Figure 1. The targeted sampling sites of the Zarqa River water are: (1) Jerash Bridge, (2) Abu Nseir Wastewater Treatment Plant effluent, (3) Zarqa River at Berain, (4) Al-Qnayh Bridge, and (5) As-Samra Wastewater Treatment Plant effluent.

Analyses were conducted at the laboratory of the Water, Energy, and Environment Centre (WEEC) at the University of Jordan, and the Ministry of Water and Irrigation according to the Standard Methods of the American Public Health Association [2012]. Many parameters reflect pollution with heavy metals. These parameters and methods are shown in Table 1. These parameters are pH, EC, TDS, DO, Cr, Fe, Mn, Co, Pb, Zn, Cu, Al, B, Si, Ni, and Cd. Table 1 shows the parameters and methods of analyses.

RESULTS AND DISCUSSION

To evaluate the level of heavy metals concentration in the Zarqa River, water samples from five targeted sites were collected, analyzed and evaluated by comparing their concentrations with the Jordanian Standard for irrigation purposes. Table 2 shows the average values of water analysis of Zarqa River during the period 2016–2019 and the permissible limits set forth in the Jordanian Standard [2006]. The water at Jerash Bridge, Abu Nseir Wastewater Treatment Plant effluent, Zarqa River at Berain, Al-Qnayh Bridge, and As-Samra Wastewater Treatment Plant effluent is used for irrigation purposes.

Table 2 shows the value variations in pH, EC, and TDS. At the Jerash Bridge site, the pH 8.57, EC 1850 µS/cm and TDS 1101 mg/L. Abu Nsair WWTP Effluent, the pH 7.74, EC 1750 µS/cm, and TDS 1064 mg/l. Zarqa River at Berain site, pH 7.93, EC 1710 µS/cm, and TDS 1052 mg/l. The pH at the Al-Qnayh Bridge is 8.23, the EC is 1700 µS/cm, and the TDS is 1019 mg/l. At As-Samra WWTP Effluent site, pH 7.43, EC 1700 µS/cm and TDS 1050 mg/L. By comparing these values of these targeted sites with the Jordanian Standard 2006, results showed that the pH, EC, and TDS value were within the limits of the Jordanian Standard.

Table 2. Average values of water analysis of Zarqa River during the period 2016–2019 and the permissible limits set forth in the Jordanian Standard [2006]

Site	X WGS 84	Y WGS 84	Water Use	Water Kind	pH	EC µS/cm	TDS mg/L
1. Jerash Bridge	35.882211°	32.217236°	Irrigation	Surface	8.57	1850	1101
2. Abu Nsair WWTP Effluent	35.927826°	32.083072°	Irrigation	Surface	7.74	1750	1064
3. Zarqa River at Berain	35.951618°	32.092780°	Irrigation	Surface	7.93	1710	1052
4. Al-Qnayh Bridge	36.056984°	32.147867°	Irrigation	Surface	8.23	1700	1019
5. As-Samra WWTP Effluent	36.147922°	32.149785°	Irrigation	Surface	7.43	1700	1050
Permissible Limits (JS 893/2006)	-	-	-	-	6–9	-	1500 mg/L
Site	**DO µg/L**	**Cr(VI) µg/L**	**Fe µg/L**	**Mn µg/L**	**Co µg/L**	**Pb µg/L**	**Zn µg/L**
1. Jerash Bridge	6480	<5	<40	20	30	180	70
2. Abu Nsair WWTP Effluent	4640	<5	<40	80	<20	80	100
3. Zarqa River at Berain	5360	<5	80	80	30	120	100
4. Al-Qnayh Bridge	5600	<5	<40	128	30	190	100
5. As-Samra WWTP Effluent	4950	<5	60	50	30	160	100
Permissible Limits (JS 893/2006)	>2000 µg/L	100 µg/L	5000 µg/L	200 µg/L	50 µg/L	200 µg/L	5000 µg/L
Site	**Cu µg/L**	**Al µg/L**	**V µg/L**	**B µg/L**	**Si µg/L**	**Ni µg/L**	**Cd µg/L**
1. Jerash Bridge	110	710	100	<300	1600	30	<10
2. Abu Nsair WWTP Effluent	190	700	<70	309	1800	30	<10
3. Zarqa River at Berain	<80	730	100	<300	1100	30	<10
4. Al-Qnayh Bridge	85	730	100	351	1500	30	<10
5. As-Samra WWTP Effluent	<80	710	<70	347	1400	30	<10
Permissible Limits (JS 893/2006)	200 µg/L	5000 µg/L	100 µg/L	1000 µg/L	-	200 µg/L	10 µg/L

It can be seen from Table 2 that the average values of water analysis of Zarqa water varies according to the targeted sites. The average values (μg/L) are as follows: DO 4640–6480, Cr(VI) <5, Fe <40–80, Mn 20–128, Co <20–30, Pb 80–190, Zn 70–100, and Cu <80–190, Al 700–730, V <70–100, B <300–351, Si 1100–1800, Ni 30, Cd <10. For these sites, findings showed that Cr(VI) was below the allowed limits (<5 μg/l), and the other heavy metals; Fe, Mn, Co, Pb, Zn, Cu, Al, B, Si, and Cd were also fall below or within the permissible limits set forth in the Jordanian Standard which would not cause hazardous effects.

These results of this research showed that the concentration of Cr(VI) and other heavy metals did not exceed the allowable limit [Jordanian Standard 2006] and therefore does not pose any hazard on water resources of the Zarqa River Basin. However, that was not the case a few years ago as reported in a review of other literature [Mohsen and Jaber 2003], as well as the efforts made by the Ministry of Environment and the Ministry of Water and Irrigation. Mohsen and Jaber [2003] indicated that the quantities of metals of Cr, Zn, Cu, Pb, Ni, Cd, Fe and Al must to be controlled. They recommended that further studies be conducted to determine what type of wastewater pre-treatment strategies are needed to introduce cleaner technology in the industries. The decrease in Cr(VI) and heavy metals pollution in the Zarqa Basin is attributed to many factors; the reinforcement of laws and regulations and imposing penalties on violations, more industries started building on-site treatment for their effluents. Some industries had migrated from the Zarqa River Basin region to other industrial regions. Furthermore, some industries in the region had shut down their businesses due to financial difficulties.

Comparing the results of this research results to other historical studies conducted on the quality of the Zarqa River; in 2001, the Ministry of Water and Irrigation, in Water Resource Policy Support, reported that the pollutants of industries wastewater effluent, including heavy metals, showed persistent heavy metals concentrations in many industries in the Zarqa Basin such as in the Jordan Yeast Company; the concentration Cr was 250 μg/L and the Permissible Limits set forth in the Jordanian Standard of (JS 893/2006) should not exceed 100 μg/L. Also, Fe, Mn, Pb, and Ni were in excess of the permissible limits [Ministry of Water of Irrigation 2001]. The Ministry of Environment [2015], conducted a national project for monitoring water quality in Jordan in order to analyze and control pollution of industries including heavy metals. It has been shown that concentration of heavy metals has been reduced. As for the Jordan Yeast Company, Cr was 55 μg/L, and other heavy metals as Zn 375 μg/L and Ni 40 μg/L were within the allowed limits set forth in the Jordanian Standard. Another example of industries that has been relocated from the Zarqa River Basin to other industrial areas is Jordan Rotografia, which specializes in printing and packaging. Where, Ministry of Environment [2015], reported that Cr was 210 μg/L, and other heavy metals as Cu, Mn, and Ni were in excess of the permissible limits for this industry, But, after the year 2016, it was relocated to industrial zone that will not affect soil and water resources.

CONCLUSIONS

The Zarqa River Basin was chosen as a case study for this research due to the necessity of monitoring the problem of river water pollution. The basin is considered as one of the most significant basins in the country with respect to its economic, agricultural and industrial importance. It contains the majority of the Jordanian industry. Industrial categories represented in the basin are from small food industries to a large Jordan petroleum refinery and a power plant. In addition, leather and garment products followed by chemical, agricultural and pharmaceutical products, constituted a vital part of Jordan's exports. Some of industries use heavy metals and hazardous substances in significant quantities in their production process.

Physicochemical analysis of water samples in the Zarqa River Basin of Jordan was conducted between the years 2016–2019 in order to evaluate the heavy metals concentrations and compare the results to the Jordanian standards; JS 893/2006. The river water quality water must comply with the permissible limits set forth in the Jordanian Standard [2006].

The analysis showed no pollution of Cr(VI) and other heavy metals. This was not the case a few years ago, when Cr(VI) and pollutant water heavy metals has been observed in industrial center of the Zarqa River Basin where more than 50% of Jordanian factories are located, and it has been observed that the concentration of pollutants in industrial effluent did not meet the permissible limit.

More specifically, at present some industries have been relocated from the Zarqa River Basin to an area that does not pose any environmental hazards; while for the rest of industries remained in the Zarqa River Basin, where, on-site treatment plants were constructed for industrial wastewater under the control of Jordanian government, enforcement of the environmental protection law and penalties.

It is recommended to update laws and regulations related to the enforcement of the protection of water resources, including industrial wastewater, and the municipal water. Actions measures must be monitored by decision makers in a sustainable manner in order to prevent water pollution.

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