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High pollutant levels of produced water around Al-Ahdab oil field in Wasit governorate (Iraq)

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Abstract. Exploration activities of the oil and gas industry generate loads of formation water called produced water (PW) up to thousands of tons each day. Depending on the geographic area, formation depth, oil production techniques, and age of oil supply wells, PW from different oil fields contain different chemical compositions. Currently, PW is also known as industrial waste water containing heavy metals that are toxic to humans and the environment, requiring special processing so that they can be disposed of in the environment. To determine the heavy metals content in PW from the Al-Ahdab oil field (AOF), the Ministry of Science and Technology/Agricultural Research Department determined some parameters including the concentrations of Cd, Co, Cr, Pd, and Ni using instrument inductively couple plasma (ICP-OES). Results of this study showed high concentrations of Cd (0.51-2.05, Cr (0.06-1.81), Co (0.11-0.72), Ni (0.12-0.22) and Pb (5.52-20.6) in the AOF compared to concentrations in water bodies about 16 km outside the field; Cd (0.01-0.32), Cr (0.01-0.11), Co (0.03-0.18), Ni (0.02-0.11) and Pb (0.04-1.73). These findings indicate there are increased levels of pollutants in the PW within the AOF of the Main Outfall Drain (MOD). The PW could not be as a source of drinking water and other daily activities, including fisheries and crop planting, unless advanced treatment, to remove the heavy metal content.

Keywords: Heavy Metals (Cd, Co, Cr, Pd, and Ni), Al-Ahdab oilfield in Wasit, Iraq, the Main Outfall Drain (MOD), produced water (PW), inductively couple plasma (ICP-OES).

1. Introduction
Produced water (PW) is water that is brought to the surface during oil and gas explorations, trapped in subsurface formations. For millennia, this water has been in contact with the hydrocarbon-bearing formation, and therefore, it contains some characteristic hydrocarbons. PW is sometimes referred to as brine or formation water [1, 2] and may include water from the reservoir, and any chemicals or surfactants which could be added during the production and treatment processes. Depending on the geographic location of production area, there are different chemical compositions of the PW. The influence of the subsurface, with which PW has been in contact for centuries and the nature of hydrocarbons being produced. The PW volume also varies during a reservoir's exploration period. The chemical composition of PW can differ even more dramatically if water and chemical or surfactant injections are carried out to increase oil production. The metals concentration of the PW depends on the age and geology of the reservoir from which oil and gas are extracted. Zn, Pb, Mn, Fe, and Ba are common metals in the PW [3]. Discarding PW without proper treatment can lead to serious environmental damage affecting communities [4].
Many heavy metals are harmful and carcinogenic and damage humans and other living organisms. Heavy metal at concentrations above the controlled threshold can cause severe health effects, including growth defects and cell growth, nervous system damage and, in worse cases, death. Autoimmune

diseases, such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and fetal brain development may develop when exposed to certain metals, such as Hg and Pb.[5]
PW is as a waste produced by the oils and gases industries, which generate more than 250 million barrels of PW per day [6]. Industries dispose of such waste by discharging it into water bodies after treatment or by injection into the subsurface [7]. Thus, this study aims to describe the water produced from the AL-Ahdab oil field (AOF) and determine the concentration of heavy metals in PW inside and outside the field, in the MOD river near the field, which feeds several wetlands those intended to be protected by a national agreement and then to be included in the Ramsar Convention [8].

2. Methods

2.1. Sample collection

The PW samples of AOF were taken from inside the field at three different sites and five different sites on the public wastewater with 3 replications during January 2018 to November 2019. Samples were handled as mentioned in the SM 1060 standard method [9]. The samples were collected, properly preserved and analyzed on the same day of experiment. Description and coordination of the sampling areas in and around the AOF is shown in Table (1). The Geographic Positioning System (GPS) satellites was used to provide spatial information and data about the location and time in all weather conditions and anywhere on or near the Earth (often coordinates length, width, altitude and time).

Table1. Locations and Descriptions and coordination of the sampling areas inside and around the AOF.

No.	Description	Forms site	Coordinates	
			Latitude (N)	**Longitude** (E)
1	PW within the AOF	PW before treatment	32 49 16 1	45 66 78 6
2		PW after treatment	32 49 14 7	45 66 94 5
3		PW surplus in evaporation ponds	32 48 79 1	45 66 78 4
4	PW outside the AOF from the Main Outfall Drain (MOD)	Just before Al-Ahdab Injection water supply line from MOD	32 44 99 3	45 10 41 8
5		Just before Al-Ahdab Injection water supply line 5 km from point 4 from MOD	32 43 63 1	45 16 05 6
6		Al-Ahdab Injection water supply line from MOD	32 40 333	45 20 66 6
7		After Al-Ahdab Injection water supply line from MOD	32 40 09 7	45 20 89 5
8		Hor Al-Dalmaj entrance	32 37 89 4	45 23 53 1

2.2. Analysis of Produced Water

PW samples were analyzed in the laboratory of the Ministry of Science and Technology, Department of Agricultural Research in Iraq, accredited to ISO 17025 for data quality analysis of cobalt (Co), cadmium (Cd), chromium (Cr), lead (Pb) and nickel heavy metals (Ni). Samples were filtered via 0.45 mm filter paper and acidified using HNO3(conc.) to afinal pH of less than 2 and then directly pumped into SHIMADZU-9000 Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES). Standard reference materials (SRM) were calibrated and accredited reference materials (PAHs (Low Level) - WP, Sigma-Aldrich) were used to ensure the precision and reliability of measurements.

2.3. Statistical analysis

GraphPad PRISM 7 was used for student` t-test analysis of a significance level $p<0.05$ with 1 tail and 2 tails hypothesis.

3. Result and discussion

A series of concentration measurements were taken over the year at 8 separate locations and were collated with respect to the months of February, April, August, October. The concentrations of the heavy metals in PW are shown in Tables 2-5, respectively and represented in Figure 1. Table 2 also highlights the acceptance limit of heavy metals for Iraqi Government (No. 25 of 1967) on the Management of Water Quality and Control of Water Pollution[10]. The heavy metal concentration of PW within the Ahdab oil field were from three locations (No_1, No_2, No_3). The average range of the concentration level was: Cd (0.51-2.05 µg /ml), Cr (0.06-1.81µg /ml), Co (0.11-0.72 µg /ml), Ni (0.12- 0.22 µg /ml) and Pb (5.52-20.6 µg /ml). Different concentrations outside the field were determined in bodies of water near the field at five locations and for all seasons (No_4, No_5, No_6, No_7, No_8): Cd (0.01-0.32 µg /ml), Co (0.03-0.18 µg /ml), Cr (0.01-0.11 µg /ml), Pb (0.04-1.73 µg /ml) and Ni (0.02-0.11 µg /ml), see Tables 2-5. However, no significant differences between measurements of heavy metals in one session than another at level of significance $p<0.05$ with 2 tails or 1 tail hypothesis, see also Figure 1.

Table 2. Analysis of pollutants in produced water in Winter**.**

Metals	Sample (µg /ml) in winter									Contamination Limits in Pursuance of Law no.25 of 1967 for Protection of Rivers [10]
	No_1	No_2	No_3	Criteria for values of heavy elements in produced water [11]	No_4	No_5	No_6	No_7	No_8	
Cd	1.40	0.54	0.69	0.03-0.2	0.01	0.01	0.01	0.01	0.02	0.1
Co	0.18	0.72	0.21	0.03-0.2	0.05	0.05	0.05	0.04	0.03	0.1
Cr	0.49	1.65	0.66	0.1-1	0.01	0.01	0.01	0.01	0.01	0.1
Pd	7.75	20.61	8.76	0.1-19.5	0.96	0.90	1.07	1.73	1.57	0.1
Ni	0.21	0.15	0.25	2.3-17.4	0.06	0.06	0.06	0.07	0.06	0.1

Table 3. Analysis of pollutants in produced water in Spring.

Metals	Sample (µg /ml) in spring							
	No_1	No_2	No_3	No_4	No_5	No_6	No_7	No_8
Cd	2.05	0.54	0.64	0.03	0.02	0.02	0.02	0.01
Co	0.15	0.75	0.27	0.05	0.05	0.06	0.04	0.03
Cr	0.48	1.62	0.56	0.05	0.04	0.04	0.04	0.07
Pd	6.55	19.64	7.79	0.68	0.61	0.87	0.89	1.07
Ni	0.11	0.11	0.19	0.02	0.03	0.06	0.07	0.06

Table 4. Analysis of pollutants in produced water in Summer.

Metals	Sample (µg /ml) in summer							
	No_1	No_2	No_3	No_4	No_5	No_6	No_7	No_8
Cd	1.55	0.77	0.97	0.15	0.17	0.29	0.30	0.27
Co	0.26	0.73	0.21	0.05	0.06	0.06	0.11	0.08
Cr	0.53	1.71	0.08	0.09	0.13	0.16	0.24	0.29
Pd	7.88	18.03	8.45	0.33	0.45	0.82	1.01	1.01
Ni	0.19	0.17	0.21	0.06	0.07	0.07	0.07	0.11

Table 5. Analysis in pollutants produced water in Autumn**.**

Metals	**Sample (µg /ml) in the autumn**							
	No$_1$	**No$_2$**	**No$_3$**	**No$_4$**	**No$_5$**	**No$_6$**	**No$_7$**	**No$_8$**
Cd	1.09	0.78	0.77	0.16	0.18	0.27	0.31	0.32
Co	0.31	0.69	0.23	0.04	0.04	0.05	0.18	0.15
Cr	0.46	1.80	0.06	0.03	0.03	0.11	0.11	0.12
Pd	5.52	19.73	7.78	0.04	0.48	0.81	0.91	0.94
Ni	0.15	0.17	0.18	0.05	0.04	0.04	0.07	0.07

Owing to the deposition of heavy metals in soils and the absorption of plants, the ingestion of heavy metals has long-term detrimental effects on human health [12], such as damage to the nervous system [13], fetal impair development [14] carcinogenicity and impaired immune function [15]. A major environmental impact has also been demonstrated by heavy metals; the effect of Cd is greater than that of other heavy metals. Cd is thus more mobile in the soil, more bioavailable in general, and appears to bioaccumulate. In certain plants and animals, it is readily accumulated inside tissues rather than in muscles or blood. Acute and chronic effects in mammals similar to those seen in humans are caused by chronic exposure to Cd [16]. Pb, on the other hand, has no vital role in the human body, but could cause many side effects, such as kidney failure of high blood pressure, neuron cell damage, low fertility in males, learning disabilities and erratic behaviour [17]. The heavy components and effects of Iraqi water sources have also been studied. [18] [19].

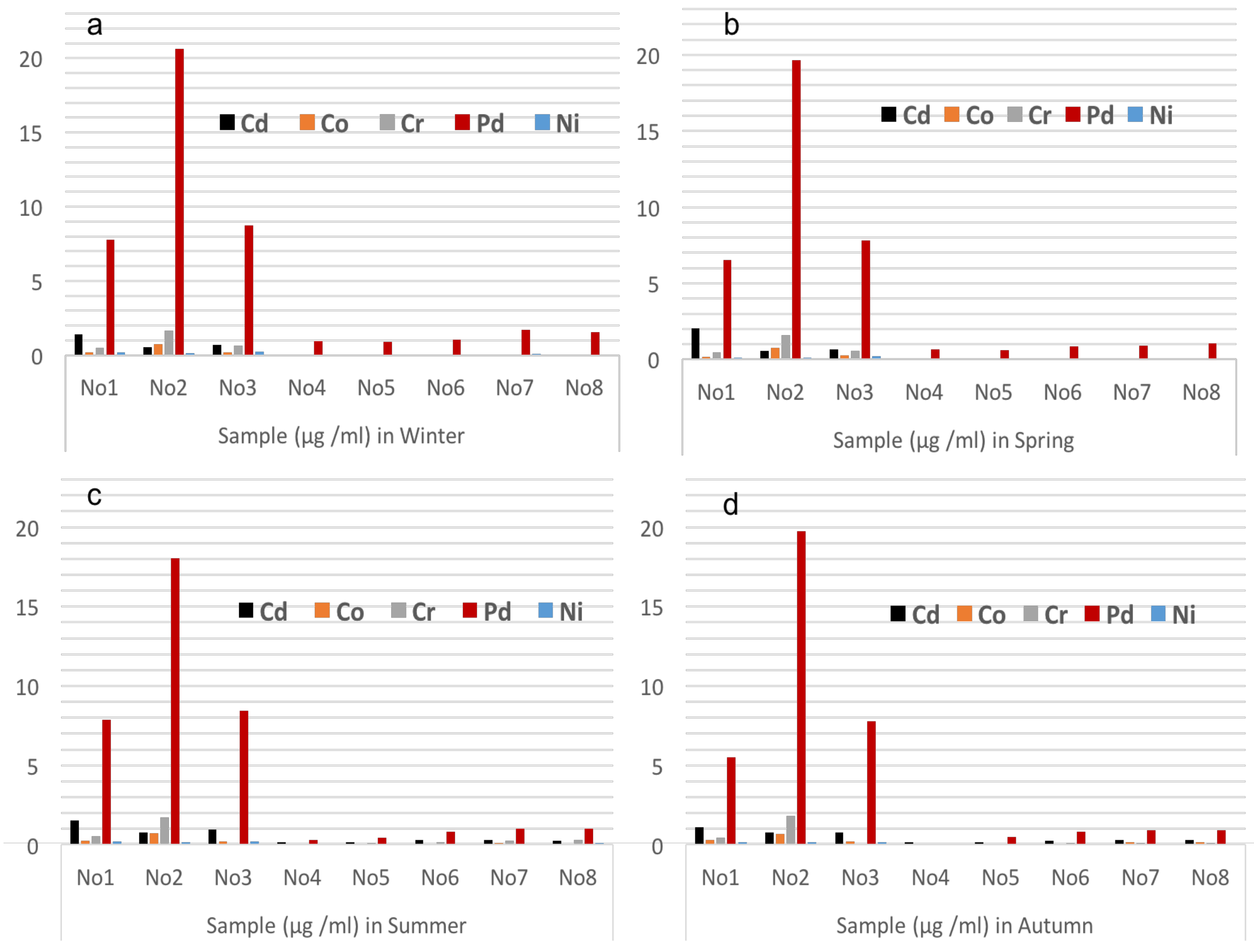

Figure 1. Analyses of pollutants of produced water in all locations (No_1- No_8) of the AOF in all seasons. a) in Winter, b) in Spring, c) in Summer and d) in Autumn.

4. Conclusion:

This study suggests that the Al-Ahdab Oilfield in Wasit Governorate of Iraq contains high levels of water pollutants, heavy metals which are above the regular limits. Based on Iraqi Government No. 25 of 1967 on the Management of Water Quality and Control of Water Pollution the PW at Al-Ahdab Oilfield is considered to be a poor source of drinking water and other routein activities, such as fishing or planting, unless adequate treatment, to remove the content of heavy metals. For the time being, the injection of PW into the oil production reservoir to enhance oil recovery (EOR) is the best practice for controlling the contamination of the generated water to protect people and the environment.

Conflict of interest

The authors declare no conflict of interest, financial or otherwise.

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Ethics approval and consent to participate

Ethical Approval was given by the Ethics committee of College of Science at Mustansiriyah University (Iraq).

Availability of data and materials

Authors can declare that data generated or analyzed during this study are all included in this article.

Authorship

All authors have read and approved this version of the manuscript.

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