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Assessment of Heavy Metals Contamination of Groundwater at Sana'a Basin along the Wastewater Channel, Yemen.

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KEYWORDS

Assessment, groundwater, heavy metals, ICP-OES, contamination.

ABSTRACT:

Introduction: Given the great importance of water in various aspects of human life, whether drinking, industry or agriculture, various studies must be conducted to determine freedom from harmful pollutants, and to find appropriate methods for purifying and treating it. Heavy metals are considered one of the most important pollutants of groundwater resulting from the seepage of water contaminated with sewage into the lower ground layers, Which leads to pollution.

Objectives: This study aimed to detect groundwater contamination with heavy metals caused by wastewater in the northern part of the Sana'a Basin for the area extending along the sewage canal in Sana'a City.

Methods: Heavy metal contamination assessment was conducted in 42 groundwater wells along the sewerage canal. Samples were analysed using the standard method using the ICP-OES program, and the results were analysed using the SPSS statistical analysis program.

Results: The results of the statistical analysis showed high concentrations of some heavy metals that had led to groundwater pollution, including Cd, Mn and Pb.The Cd appeared in four wells, and this value exceeded the permissible limits in Yemeni specifications and the World Health Organization. The Mn appeared in ten wells and its values were within the permissible limits in the Yemeni specifications and exceeded the permissible specifications in the World Health Organization. Pb appeared in 3 wells and its value exceeded permissible limits according to World Health Organization specifications, but it was within the limits allowed by Yemeni specifications.

Conclusions: The study showed that 40% of the wells studied were polluted with three heavy elements (Cd, Mn and Pb). The results showed that groundwater is contaminated with heavy metals and is not suitable for drinking in that studied wells . Therefore, it is recommended in this area to take precautionary measures, such as avoiding the use of wastewater in agriculture.

1. Introduction

Natural water on earth has two important sources: surface water (lakes, ponds, rivers, streams, etc.) and groundwater (wells and well water). Water plays an important role in human life. This importance is represented as a source of human drinking and an important supply for industry and irrigation around the world. Increasing population growth, industrialization and urbanization are considered an important cause of groundwater pollution **(Bhatnagar and Sillanpa, 2010)**.

Good quality water ensures a healthy life for people. For this reason, emphasis is placed on water quality and reducing contamination with pathogens and toxic substances **(Alexakis D.E., 2021)**.

Among the toxic pollutants, heavy metals are of great importance in water pollution. Heavy elements are those minerals that have a mass or density greater than water. Heavy elements are classified into essential and non-essential metals, the essential heavy metals include Zn, Fe, etc., and the non-essential metals are As, Pb, Cd, Co, Ni, Hg, and Cr **(Amin N., *et al*., 2014)**.

Environmental pollution by heavy metals is becoming an increasing problem and has become a major concern due to the harmful effects it causes worldwide. These inorganic pollutants are mostly eliminated in water, soil and the atmosphere due to the rapid growth of agriculture and mineral industries and the improper disposal of waste, fertilizers and pesticides. Some metals affect biological functions and growth, while other metals accumulate in one or more different organs, causing many serious diseases such as cancer. Each bioaccumulation of heavy metals produces many physiological and biochemical effects in humans (Briffa J, et al., 2020).

Groundwater contamination with heavy metals is associated with serious health effects, including kidney damage, neurodegenerative conditions, respiratory disease, cardiovascular disease, and cancer (Rehman, K, et al., 2018; Mohammadi A.A., et al., 2019).

Groundwater contamination with heavy metals in particular indicates serious health problems. In general, some minerals such as copper, iron, manganese, zinc and cobalt are essential, but increased concentrations of them cause serious health problems - the most toxic heavy metals include arsenic, lead, mercury, cadmium, chromium, copper, nickel, silver and zinc. Groundwater contamination with heavy metals causes serious health and environmental problems (**Fernandez and Olalla, 2000; Ogoyi, *et al*., 2011)**.

Groundwater contamination leads to poor drinking water quality, loss of water supply, high cleaning, sterilization, and desalination costs, and potential health problems Restoring polluted groundwater is not easy and requires a high cost. Therefore, it was necessary to protect the quality of groundwater **(Kumar M. and Puri A., 2012)**.

The pollution in the groundwater reservoir, the northern part of the Sana'a Basin, in the Bani Al-Harith and Arhab regions, located along the sewage canal, comes as a result of sewage being released without adequate treatment as a result of repeated malfunctions in the sewage treatment plant in Sana'a, where repeated large flows of treated sewage have led to Insufficiently, it leaked into the ground layers of soil and led to groundwater pollution in the Sana'a Basin **(Al-Kharbash B, *et al*., 2023)**.

2. Objectives

This study aimed to evaluate the quality of groundwater in the northern part of the Sana'a Basin for the area extending along the sewage canal in terms of its contamination with heavy metals as a result of sewage seepage into the aquifer in the study area.

3. Methods

Study area: the study was conducted in the northern area of Sana'a Basin located along the sewage channel of the wastewater treatment plant north of the capital Sana'a and on an estimated length of about 20 km north **(Merghem K, *et al*., 2016)**. About 95 % of irrigation in the study area depends upon the wastewater produced from the Sana'a Wastewater Treatment Plant (WWTP), with 5 % coming from groundwater (boreholes) that farmers use to directly irrigate the cultivated areas. The reason for this relates to the high cost of well water and the resultant decrease in economic income in comparison to irrigation with sewer water (**Al-Sharabee, 2009 and Merghem, *et al*. 2016**).

Wastewater passage in the Sana'a basin starts at the outlet of the Sana'a City's

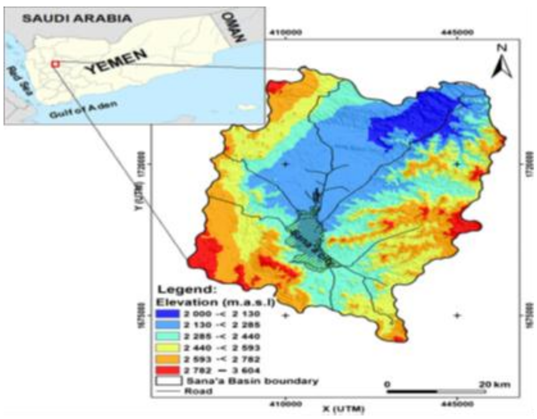

Figure (1): Location and topographic map of the Sana'a Basin (digital elevation map from a satellite dataset) (Abdulla and Assa'd, 2006).

Wastewater Treatment Plant (WWTP) at northern edge of the Sana'a basin (Arhab and Bani Al-Harith

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areas). Treated and untreated wastewater flow together in the channel, figure (1). This channel is about 2.5 m in width and 20 km the length. The passage runs across agricultural land and very critical geological features, including major faults, and encounters significant geological variations, including volcanic and limestone outcrops (**Hydrosult, 2003**).

Sampling sites: The sampling sites was between latitudes and longitudes that were 29.3656^{0}15'N - 42.8765^{0}15'N and 04413.8741^0'E - 04413.8755^0'E. The total numbers of the wells were 42 governmental and private wells, figure (2).

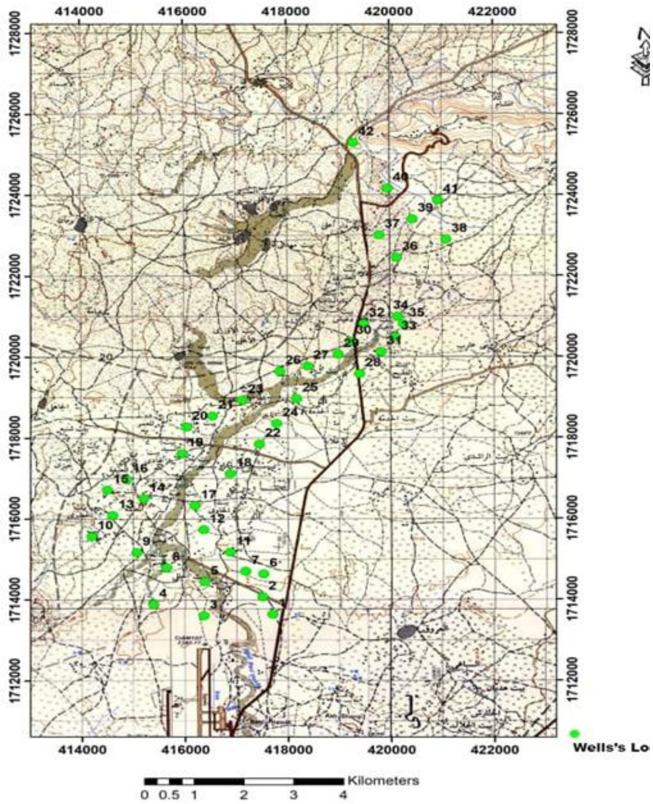

Figure (2): Topographic map of the study area and samples collection sites (National Water Resources Data Management Center- Sana'a, 2018).

Heavy metals analysis: heavy metals analysis were carried with special precautions were taken during the collection of samples, before collecting the samples, the sample containers are soaked overnight in 2% nitric acid and washed with deionized water. Eight of the heavy metals (Cd, Cr, Mn, Ni, Cu, Co, Pb and Zn,) were analysed by direct aspiration of water samples into Inductively Coupled Plasma – Optical Emission Spectrometer Vista-MPX (ICP-OES) (Varian) system in Yemeni Standradization Organization, Meterology and Quality Control according to **(Bhattacharya, *et al*., 2002)**. 50 ml of water samples were taken from the study sites and placed in a clean 100 ml glass beaker and 5 ml of concentrated nitric acid were added (to digest the samples). The beaker was heated on a hot plate and leaved it on the hot plate to continue heating to the pre-drying phase. Then 5 mL of concentrated nitric acid was added to the sample and continue heating to obtain a precipitate. After cooling, the volume was completed to 25 ml with dionized water and it was filtered with a 0.20 µm filteration membrane. To get the sample ready to estimate the concentrations of heavy metales in it according to **(Bhattacharya, *et al*., 2002)**, then the absorbance of these digested samples was measured using a device ICP- OES. The data were analysed using SPSS (one sample test and Pearson Correlation) program. to study the effect of the depth of the wells and the distance between the studied wells and the source of pollution represented by the sewage channel.

4. Results

Table (1) revealed the presence of heavy metals identified in the samples of the studied wells according to the depth of these wells and the distance between them and the wastewater channel. The results were showed the concentrations of heavy metals that detected in the groundwater samples that were analyzed in this study for 8 heavy metals Cd, Cr, Mn, Ni, Cu, Co, Pb and Zn. 3 of the studied heavy metals (Cd, Mn and Pb) appeared in 11 wells, Cd appeared in wells 1, 7, 14 and 29, exceeding the permissible limits of the Yemeni and the WHO standards, where the concentrations reached 0.01294 ppm, 0.01687 ppm, 0.00710 ppm and 0.05671 ppm respectively.

Mn also appeared in Well 1, 2, 3,7,14,15,16,22,25 and 33, exceeding the permissible limit of WHO, as its concentration was 0.01655 ppm, 0.01626 ppm, 0.01620 ppm, 0.01621 ppm, 0.01652 ppm, 0.01619 ppm,0.01638 ppm, 0.01615 ppm, 0.01628 ppm, 0.01694 ppm and 0.01604 ppm respectively, and it were within the permissible limits in the Yemeni specifications, as well as the other metals within the permissible limits of the Yemeni specifications and the WHO and the rest of the metals were mostly below the detection limits and within most of the wells studied.

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Pb also appeared in Well 1, 7, and and 33, exceeding the permissible limit of WHO, as its concentration were 0.01531, 0.01695 and 0.02337 respectively, and it was within the permissible limits in the Yemeni specifications. The results showed no correlation between depth and distance and the results obtained for heavy metals in the wells studied table (2).

Table (1): Heavy metals determined in water samples of the wells with the depth and distance.

WHO S.L	Yemeni S.L	Highest value (ppm)	Distance (m)	Depth (m)	Well No.	Heavy metal
0.003 ppm	0.005 ppm	0.01294	800	140	W1	Cd
		0.01687	900	100	W7	
		0.0071	600	70	W14	
		0.05671	1000	100	W29	
0.004 ppm	0.2 ppm	0.01655	800	140	W1	Mn
		0.01626	1000	150	W2	
		0.0162	700	90	W3	
		0.01621	900	100	W7	
		0.01652	600	70	W14	
		0.01619	1600	50	W15	
		0.01638	1100	60	W16	
		0.01615	1100	50	W22	
		0.02128	900	70	W25	
		0.01794	1000	100	W29	
		0.01604	700	60	W33	
0.01 ppm	0.05 ppm	0.01531	800	140	W1	Pb
		0.01695	900	100	W7	
		0.02337	1600	50	W15	

Table (2): The correlation between depth, distance, and heavy metals of the studied wells .

Correlations		Cd	Cr	Mn	Ni	Cu	Co	Pb	Zn	Depth	Distance
Cd	Pearson Correlation	1									
	Sig. (2-tailed)										
Cr	Pearson Correlation	.387*	1								

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	Sig. (2-tailed)	0.011									
Mn	**Pearson Correlation**	.432**	.983**	1							
	Sig. (2-tailed)	0.004	0								
Ni	**Pearson Correlation**	.362*	.970**	.946**	1						
	Sig. (2-tailed)	0.019	0	0							
Cu	**Pearson Correlation**	.364*	.963**	.969**	.944**	1					
	Sig. (2-tailed)	0.018	0	0	0						
Co	**Pearson Correlation**	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}	.^{c}				
	Sig. (2-tailed)	.	.	.	.	.					
Pb	**Pearson Correlation**	0.144	.809**	.763**	.777**	.717**	.^{c}	1			
	Sig. (2-tailed)	0.363	0	0	0	0	.				
Zn	**Pearson Correlation**	.325*	.433**	.447**	.414**	.446**	.^{c}	.492**	1		
	Sig. (2-tailed)	0.035	0.004	0.003	0.006	0.003	.	0.001			
Depth	**Pearson Correlation**	- .157-	- .531-**	- .526-**	- .506-**	- .527-**	.^{c}	- .434**	- .161-	1	
	Sig. (2-tailed)	0.32	0	0	0.001	0	.	0.004	0.307		
Distance	**Pearson Correlation**	0.013	0.152	0.076	0.104	0.094	.^{c}	0.285	- .128-	-.156-	1
	Sig. (2-tailed)	0.936	0.336	0.631	0.513	0.556	.	0.067	0.418	0.323	

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5. Discussion

The study showed that 40% of the wells studied were polluted with three heavy elements (Cd, Mn and Pb). Cd appeared in four wells and its value exceeded the permissible limits in Yemeni and international specifications. Mn appeared in ten of the wells studied, and its values were within the permissible limits in the Yemeni specifications and exceeded the permissible limits in the international specifications of the World Health Organization.

Pb appeared in 3 wells, where its value exceeded the permissible limits in the international specifications of the World Health Organization, and the values were within the permissible limits in the Yemeni specifications. The result of the use of wastewater, sludge, and municipal waste on agricultural lands in the study area, or the reuse of wastewater for irrigation, which ultimately led to groundwater pollution. The results of this study differ with the results of the study conducted by (**Abdullah S. Q. S., 2021)** in the groundwater of the city of Al Bayda, Yemen.

The Cd pollution that exceeded the permissible limits in the Yemeni and international specifications of the World Health Organization. And that results were agreed with the results of the study by (**Thamer M. B., (2021)** and were agreed with the study conducted by **(Lotfi S *et al*. 2020)**.

The results showed a high and linear correlation relationship of Mn and Cr that was 0.983 at a significance level less than 0.01, high and linear correlation relationship of Ni with Cr and Mn that were 0.970 and 0.946 respectively at a significance level less than 0.01. , high and linear correlation relationship of Cu with Cr, Mn and Ni that were 0.963, 0.969 and 0.944 consecutively, at a significance level less than 0.01, high and linear correlation relationship of Pb with Cr, Mn, Ni and Cu that were 0.809, 0.763, 0.777 and 0.717 consecutively, at a significance level less than 0.01, medium and liner correlation of Zn with Cr, Mn, Ni, Cu and Pb that were 0.433, 0.447, 0.414, 0.446 and 0.492 consecutively, at a significance level less than 0.01 and inverse and medium correlation of the depth with Cr, Mn, Ni, Cu and Pb that were -0.531, -0.526, -0.506, -0.527 and -0.434 consecutively, at a significance level less than 0.01.

These results agreed from the study carried out by **(Oyoh and Evbuomwan, 2008)** and **(Al-Sabahi, *et al*., 2009)** and contradicted the results of the study that carried out by **(Saleh S M, *et al*., 2020).** These correlation values indicate that these elements come from the same sources and multivariate statistical analyses revealed that the release of these heavy metals into the groundwater system is primarily influenced by anthropogenic inputs rather than natural processes. There was no correlation of the distance with the studied heavy metals that was due to the surface drilling of wastewater, which was widespread in the study area, and also to the intention of the farmers to dig ponds containing wastewater adjacent to drinking water. This study differed from the study that was carried out by (**Mohamed R, *et al*., 2011**).

Heavy metals, uncontrolled in the water and exceeding the permissible limits, can lead to adverse health effects such as poor growth and development, cancer, nervous system damage, and death, and contact with some heavy metals including Pb that may cause autoimmune diseases affecting the immune system of the body **(Barakat, 2011)**. Lead rarely exist in nature and could be found in different forms such as organic and inorganic compounds **(Akinbile C and Yusoff, M, 2011)**. The presence of Pb may also affect the gastrointestinal tract, kidneys, and the central nervous system. Exposure to lead could lead to loss of memory, nausea, insomnia, anorexia, and weakness of the joints, failures of reproduction, inhibition of haem synthesis, irritation and producing tumor **(Srinivasamoorthy K., *et al*, 2009)**. Cd is a metal found naturally in the environment. It is a toxic metal even at low levels small quantities of Cd cause adverse changes in the arteries of human kidney and replaces zinc biochemically and causes high blood pressures and kidney damage **(Williams P.L., *et al*, 2000)**.

Mn is found in many, widely scattered minerals and Mn is an essential plant mineral nutrient, playing a key role in several physiological processes, particularly photosynthesis. Mn toxicity in humans mainly affects the respiratory tract and the brain; Symptoms include hallucinations, forgetfulness and nerve damage. It could also cause lung embolism, Parkinson's disease and bronchitis, it is more common than toxicity, and causes impaired reproduction and growth **(Mor S., *et al*., 2010)**.

6.Conclusions

The study showed that 40% of the wells studied were polluted with three heavy elements (Cd, Mn and Pb). Cd appeared in four wells and its value exceeded the permissible limits in the Yemeni and international specifications. Mn appeared in ten of the wells studied, and the values were within the permissible limits in Yemeni specifications and exceeded the permissible limits in the WHO international specifications. Pb appeared in 3 wells, where its value exceeded the permissible limits in the WHO international specifications, and the values were within the permissible limits in the Yemeni specifications.

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