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Multivariate Assessment of Heavy Metal Contamination and Ionic Composition in Groundwater near Industrial Zone: Environmental and Health Evaluation.

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ABSTRACT
Ionic composition and heavy metal contamination were measured in groundwater collected in some Iraqi industrial zones. Analysis studies highlighted that areas adjacent to industrial facilities are characterized by an excess of ions and heavy metals. IC and physiochemical measurements indicate that Pb, Cd, and Cr represent the main contaminations in groundwater, likely originating from anthropogenic and industrial processes. Statistical methods like principal component analysis (PCA) and Pearson's correlations were also carried out to determine contamination sources and patterns, revealing that Pb, Cd, Ni, As, and Cr are positively correlated with EC TDS. Risk assessment done through the Water Quality Index (WQI), considering contact exposure methods, revealed that these metals posed toxic effects, exceeding WHO and BIS thresholds. The findings show strong links between industrial discharges and groundwater contamination.

1. INTRODUCTION:

Industrial operations and agriculture mainly depend on groundwater sources, which play an important role in human consumption in some arid areas, mostly in the Middle East and African countries. Due to its movement through rocks and soil, which acts as a filtration process, groundwater is deemed a safer option for human and agricultural usages. However, groundwater has become increasingly deteriorated due to industrialization and urban expansion in recent years. Thus, it is important to understand the contributing factors that affect the quality of groundwater and then employ long-term strategies to preserve its safety and sustainability [1]. These harmful factors are manifested by industrial practices and urban developments. Such elements lead to severe problems in the environment by discarding untreated wastes directly in underground and other bodies of water. These run-offs are then persistent in the environments and bioaccumulate in living organisms, causing neurotoxicity and kidney damage [2]. Primarily industrial loading of salts and heavy metals (HMs) is imposing great threats. These pollutants remain in the environment, bioaccumulate in animals, and can have negative health impacts—such as neurotoxicity and kidney problems—even at trace levels. Therefore, the occurrence in groundwater is a significant public health risk [3].Groundwater pollution not only has a negative impact on public health but also affects crop production and soil structure. Accumulation of certain solute ions in solution can destroy soil texture, fertility, and vegetation. When irrigated with polluted groundwater, it could lead to food contamination with the risk of having various negative impacts on both humans and animals [4]. The natural and man-made origins of groundwater pollution are diverse. Natural rock weathering processes are responsible for the baseline chemistry of groundwater but are being intensified by discharge from industrial activities, mismanagement, and surface runoff from urban settings. Source and transport pathways of pollutants are key information for the management of water resources [5]. Although people are becoming more environmentally aware, a lot of the

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groundwater contamination goes unnoticed until damage is widespread and the impact is irreversible. In contrast to surface water CWC, which is frequently observed after the environmental pollution has already begun progressing, evidence on groundwater CWC is usually accumulating slowly and might remain unnoticed for a long time until the damage gets permanently affected [6]. Implementation of preventive groundwater protection is necessary in order to secure sustainable access to water resources and health protection. This includes tightened environmental regulations, the promotion of cleaner industrial technology, and raising public awareness [7]. The extent and paths of industrial wastewater encroachment into groundwater systems and their effects on human health have been studied in other regions. In another work, 86 groundwater and wastewater samples were studied for heavy metals along with physicochemical parameters. The contamination levels were found to be greater than national and international standards, which emphasizes poor health hazards. Nevertheless, the survey was limited to one geographical location and did not take seasons into consideration or record cases of chronic exposure [8] [9]. Another study Soil and groundwater samples were analyzed for nine heavy metals by atomic adsorption spectrophotometry. The indices applied include Enrichment Factor (EF), Geo-accumulation Index (Igeo), Contamination Factor, and Pollution Load Index. Assessments showed higher contamination in soil than the acceptable limits, with concentrations of the groundwater samples within safe levels. These analyses are especially pertinent to consolidated rock aquifers and could vary in alluvial systems. Eight heavy metal contents were also determined using Monte Carle simulation and multivariate statistical analysis in order to estimate possible health risks [10]. The concentrations of chromium (Cr), arsenic (As), and iron (Fe) exceeded the WHO safety levels in most abstractions, and Cr and As were also highly carcinogenic. The study only focused on local shallow groundwater systems, and seasonal or long-term variations were not considered. Results of the investigation showed the environment and public health were under threat due to heavy metal pollution in groundwater [11]. The scarcity of field data and significant local variability still limited the reliability and generalizability of findings, despite the proposed different remediation strategies. Hence statistical measures such as Spearman correlation, principal component analysis (PCA) and cluster analysis were used to evaluate the risks liked to heavy metals in industrial groundwater. Quantitative indices were used to assess risk levels and identify these sources of pollution. Both non-carcinogenic exposures and carcinogenic, specifically through dermal constancy, were estimated using Monto Carlo simulations. There were high levels of contamination and evident health risks, particularly for children. However, since the evaluation of both surface water and groundwater contamination was primarily focused on a rural community, Orwari, the study's goegraphic scope was limited as seasonal variation was included in the study. [12] [13]. Additionally, Atomic Absorption Spectroscopy (AAS) was used to assess fifteen water samples that were taken from wells, rivers and streams. Non-carcinogenic risks were nonetheless significant even though some metals, such as Nickel , Cadmium, and Iron, were found below advised hazardous limits. However, PFAS compounds were not investigated, which led to additional research.

[14]. In a separate study, sixty-three groundwater samples from both sedimentary and hard rock aquifers were assessed using geochemical and pollution index methods, alongside statistical analysis. The study also examined the contamination levels and health hazards associated with artisanal industrial operations. The study found elevated concentrations of Ba, Zn, Fe, and Ni with higher pollution indices and carcinogenic risks linked to sedimentary aquifers with anthropogenic contributions were low, while site-specific seasonal variability was prominent [15].

Moreover, another research was conducted on all fifteen borehole water samples to evaluate heavy metals such as Cd, Cr, As, Zn, Pb, and Cu and toxic metalloid levels in groundwater from an intensive agricultural zone. Although the study was geographically and seasonally limited, it indicated concentrations of Cd and Cr exceeded WHO safety limits, making the groundwater in this region unsafe for consumption, especially for young generations. [16]. Furthermore, two separate studies were performed, one being investigated during various seasons with a lack of dermal absorption or bioaccumulation, focusing on both trace metals (TMs) and carcinogenic and non-carcinogenic risk, while the other was being investigated during one season without alternative exposure pathways such as dermal absorption or food chain transfer. While TMs levels and most metal concentrations remained within acceptable safety thresholds in both studies, potential health impacts were still apparent, as Cr levels exceeded acceptable limits in both studies, posing a potential carcinogenic threat [17][18]. Another investigation was performed to collect groundwater samples from eleven locations during both the wet and dry seasons. These patches were tested for thirteen physicochemical parameters, and Atomic Absorption Spectroscopy (AAS) was employed to determine the concentration of heavy metals. Health risks were estimated using pollution indices, in particular for Cd in this study. It was found that the elevated levels of Fe and As due to anthropogenic sources (industrial and agricultural) were observed in the wet season, while domestic contamination was associated with subsurface waters during the dry one. However, the results of the study were very site-specific, and the results could not necessarily be generalized to more general groundwater availability in the region [19]. This paper seeks to assess the impact of industrial activities on ion concentration and heavy metal contamination in groundwater, apportion sources of pollution, evaluate health risks, and validate the level of pollution through physicochemistry as well as statistical methods.

2. METHODOLOGY:

Seven samples were obtained from different sites near industrial areas like the Baiji industrial complex and the Al-Dora refinery zone (Baghdad) industrial area complex and then were analyzed with the help of various instruments. Both pH and Total Dissolved Solids (TDS) measurements were conducted using a Hanna HI 98129 multi-parameter meter, while electrical conductivity was done using a Thermo Scientific Orion Star A212 Conductivity Meter. Atomic Absorption Spectroscopy (AAS) was used to find the amounts of heavy metals like lead Pb2+, Cd2+, Cr2+ , Arsenic As2+, Nickel and Zinc Zn2+. I used a PerkinElmer Analyst 400 with an air-acetylene flame to measure the metal ions. Ion Chromatography (IC) with a Metohm 883 Basic IC plus system was used to measure the concentrations of major ions such as Ca^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-}. The Water Quality Index (WQI) was computed to sort the overall quality of groundwater. In addition, multivariate statistical tools, such as Principal Component Analysis (PCA) and Pearson's Correlation Coefficient, were used to find possible pollution sources and pattern determination among variables. IBM SPSS Statistics v26 and OriginPro 2022 were also employed for data visualization and analysis. Sample collections were conducted near industrial zones, such as the Baiji industrial complex and the Al-Dora refinery zone (Baghdad) industrial area complex. These industrial locations were directly influenced by industrial waste discharge; thus, sampling was done during the dry season to reduce dilution effects from rain. Figure 1 shows the spatial presentation of the process of groundwater assessments.

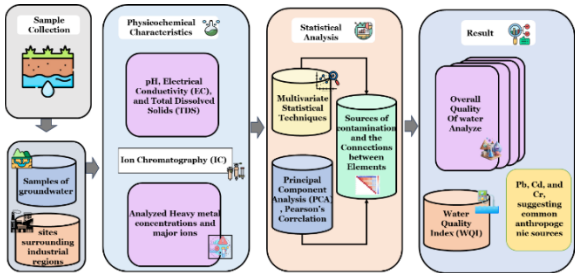

Figure 1: Schematic Representation of Groundwater Quality Assessment

3. RESULTS AND DISCUSSION:

Heavy metal contamination in the industrial area exceeded limits set by WHO and BIS five times for lead, ten times for mercury, but zero for nickel. As these elements are highly intercorrelated, it is clear that they are man-made in origin. The Water Quality Index values for the study area indicated that most samples fell into the categories 'poor' or 'very bad.' In both PCA and Pearson correlation cluster analyses of pollutants therein, particularly that of industrial emissions, it becomes the top cause with regard to underground drinking water, which calls for removal measures.

3.1 Principal Component Analysis (PCA):

The aim of this study was to reduce the dimensionality of the data set and to identify some dominant variables associated with underground water pollution around industrial zones, using Analysis of Principal Components (ACA). Four factors (PC1-PC4) were retained, which explain different patterns of contamination and hydrogeochemical behaviors as well as connected clusters of correlated variables.

3.1.1 PC1 Impact of Anthropogenic Activities and Salinity:

PCI exhibits the highest variance in the dataset, with strong positive loadins for lead (0.088), Cadmium (0.05), and Chromium (0.082) as well as salinity-related parameters including TDS(0.74), EC (0.76), Chloride ion (0.69) and Sodium ion (0.74). This section mirrors the unexpected anthropogenic influence, primarily from waste and industrial release.

The presence of massive positive negative charged and ions poisonous heavy metals and means that Groundwater quality is greatly impacted by industrial operations like petrochemical manufacturing, metal plating, and other trash. High TDS and EC reading are indicative of high ionic content for untreated wastewater or saline intrusion.

3.1.2 PC2 Geological Sources and Lithological

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Ingredients

PC2 is primarily rich in mercury and arsenic, along with major elements; nonetheless, with the exception of zinc and nitrogen, these elements are clearly indicative of natural geogenic sources, such as the sediments of rocks rich in high concentrations of mercury and arsenic and weathering processes. This segment mostly shows background geochemistry, however human influences should be not ignored. These patterns are good fit with the possibility that GW was in contact with rocks, in which arsenic has high concentration or was in a region with a strong heat gradient.

3.1.3 PC3 Mixed Trace Metal and Fertilizer Contributions

PC3 in column 3 presents positive loadings for Ni (0.76) and Zn (0.78) along with low values for Mg2+ (0.16) and K+ (0.24). These elements are often stemmed from both agricultural and industrial wastes, which mean there are two options of contamination sources. The latter pollution source is mostly responsible for high levels of zinc and Nickel as these elements are generated from chemically treated products, paints, or agrochemicals. Contribution from cities in peri-industrial area may be included in this part.

3.1.4 PC4 Carbonate Buffering and Water Chemistry

PH (0.84) significantly affects PC4, with HCO- (0.41), K (0.30) and SO(0.59), making dominant contributions. The statistical data from PC4 with PH, sulfate, bicarbonate and potassium loadings is interapted as evidence that carbonate association and cations probably raised the PH levels in the sample that were collected, controlling the groundwater's chemistry in term metal mobility and toxicity. Table 1 shows the results.

Table 1: Key Component Loadings of Ions and Metals in Industrial Zone Groundwater

Parameter	PC1	PC2	PC3	PC4
Pb	0.88	0.23	0.15	0.08
Cd	0.85	0.18	0.14	0.11
Cr	0.82	0.25	0.21	0.10
EC	0.76	0.43	0.19	0.10
TDS	0.74	0.46	0.17	0.15
Na^+	0.71	0.48	0.23	0.12
Cl^-	0.69	0.45	0.18	0.16
As	0.30	0.83	0.12	0.07
Hg	0.22	0.78	0.25	0.13
Zn	0.28	0.29	0.78	0.14
Ni	0.35	0.18	0.76	0.20
pH	0.10	0.13	0.19	0.84
SO_4^{2-}	0.51	0.36	0.21	0.59
Ca^{2+}	0.60	0.39	0.15	0.32
Mg^{2+}	0.63	0.34	0.16	0.28
K^+	0.48	0.42	0.24	0.30
HCO_3^-	0.46	0.30	0.19	0.41

3.2 Pearson's Correlation

Pearson's correlation analysis was calculated using the core function in R and presented as heatmaps. The statistical results from this part indicated the significant correlation between continuous variables. These variable are ionic constituents (Cl^- and Na^+) and heavy metal concentrations (Cd^{2+}, Pb^{2+}, and Cr^{3+}). The coefficient of the Pearson correlation (r) is shown in Equation (1).

$$r = \frac{\sum(b_j - \bar{b})(a_j - \bar{a})}{\sqrt{\sum(b_j - \bar{b})^2 + (a_j - \bar{a})^2}}$$

Figure 2 shows a visual matrix of the linear relationships of these correlations.

Category	Water Samples (%)	Range of WQI	Quality of Water Status
A	19	0 – 25	Excellent
B	32	26 – 50	Good
C	22	51 – 75	Poor
D	10	76 – 100	Very Poor
E	17	>100	Not Suitable for Drinking

It can be absorbed from figure 2 that both electrical conductivity (EC) and dissolved solids (TDS) were positively correlated (r=0.96). Heatmap analysis indicates EC is a decisive factor for salinity and total ionic concentrations. In addition, Ca+2 (0.85), Mg+2 (0.83), and Na+ (0.78) are highly correlated with EC. Therefor the analysis shows these positively charged ions are in relation to salinity in the groundwater samples. There are also positive moderate correlations between Pb (0.71) and Cd (68), Ni (0.79), and EC. The results denote that the concentrations of such metals could be influenced similar industrial or agricultural sources. Moreover, As and Cr display a strong reciprocal relationship (0.79), supporting theories of origin and mobilization pathways, likely accounting for industrial discharges and waste leaching, while Ni exhibits a strong correlation with Cr (0.76) and a mild one with Zn (0.59), meaning possible contamination from electroplating and metal processing sources. Although heavy metals such as Cd and Cr show a positive strong relationship with Na^+, Cl^-, and SO_4^{-2} (all >0.65) as a possible cause of geochemical or industrial discharges, As and Zn show lower correlations with most other parameters, which is attributed to clear source behavior or geochemical mobility. However, pH displays inadequate correlations with other parameters ($r < 0.15$), suggesting the lowest effect on the solubility or mobility of charged species and metals within the sample.

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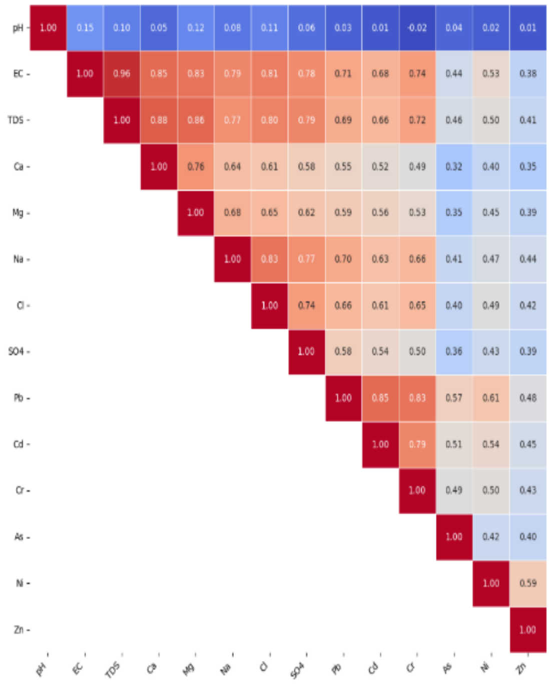

Figure 2: Pearson Correlation of Groundwater Parameters

As a result, Pearson's matrix supports the hypothesis of common pollution sources by confirming interdependence among contaminations and informing possible solutions as well as giving rise to the major contamination mechanisms in industrial groundwater locations.

3.3 Water Quality Index (WQI).

The Water Quality Index (WQI) is a common method to incorporate multiple physicochemical variables into one major score to evaluate the overall groundwater suitability for human consumption. In this study, this indicator was calculated using major ion concentrations such as Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-} and main water quality parameters such as pH, EC, and TDS, as they have a potential impact on human health. The WQI values are

classified into four classes, three of which are a sign of the level of contamination and health risks in the obtained samples. Table 1 shows main ions and heavy metals have negligible traces, which account for about 19% of the samples. However, the range of 26-50 WQI corresponds to 32% of sampling, showing limited industrial activities and suggesting tolerable concentrations of ionic species. Category C illustrates 22% of the samples and the WQ1 51-75 range. This value highlights high concentration and contamination risks possibly from anthology practices. Subsequently, the quality of water status is projected as very poor in category D, with 10% of the samples and is of WQ1 76-100 ranges. This part highlights untreated industrial wastes, indicative of heavy metals (e.g., lead, cadmium, and chromium) and high levels of TDS and EC. However, an larming 17 percent of groundwater tests are expected to be unsafe for drinking because they show harsh contamination from being nearby industrial locations, where toxic metals and non-biodegradable pollutants are commonly found.

Table 2: Using WQI and Sample Distribution to Classify Groundwater Quality

Category	Water Samples (%)	Range of WQI	Quality of Water Status
A	19	0 – 25	Excellent
B	32	26 – 50	Good
C	22	51 – 75	Poor
D	10	76 – 100	Very Poor
E	17	>100	Not Suitable for Drinking

The high scores of WQI in D and E categories are about one-third and show significant pollution levels. The strong relationship between high WQI and industrial vicinity indicates that chemical manufacturing, metal plating, and waste disposal are the main contributors. Hence, the results of this study are consistent with the PCA and Pearson's correlation data, revealing clear patterns among heavy metals and dissolved ions. The water quality characteristic shown in Table found to be suitable for the classification of groundwater properties and can lay foundations for recovery programs and monitoring programs for environmental legislations in industrial Iraqi areas.

3.4 Descriptive Statistics

Variability, central tendency, and dispersion of important physicochemical parameters and major ions in the groundwater of the industrial area were studied through descriptive statistics. The standard deviation T (obtained by Equation 2) indicates the degree of variation in each water quality parameter around its mean and reflects differences between sampling sites.

$$T = \sqrt{\frac{\sum (w - \bar{w})^2}{m - 1}}$$

The minimum, maximum, mean, and standard deviation (SD) of the parameters were presented in Table 3.

Table 3: Summary of Groundwater Ion and Heavy Metal Concentrations with Statistical

Parameter	Minimum	Maximum	Mean	Standard Deviation (SD)
pH	6.3	8.1	7.4	0.5
EC	450	1920	1060	320
TDS	290	1210	730	210
Ca^{2+}	28	140	72.6	24.1
Mg^{2+}	12	88	38.4	15.9
Na^{+}	32	170	96.7	28.5

K^+	2.1	14.6	6.4	2.7
Cl^-	55	280	145.3	48.9

Table 3 shows the PH range 6.3 to 8.1, with with a mean and low standard deviation (0.5) of 7.4 is indicative of close to neutral to an alkaline environment. The mean and standard deviation for EC and TDS were greater (1060 µS/cm and 730 mg/L respectively). That means variation in space, due to anthropogenic factors and characteristic goegenic causes changes in the EC and TDS values. Calcium and magnesium ions had the average concentrations of 72.6 mg/L and 38.4 mg/L, respectively, with dispersion (SD: 24.1 and 15.9).This findings indicates underground water has come naturally to contact with rocks contained such metals. Na^+ particularly exhibited high variability (SD = 28.5) with the mean value of 96.7 mg/L, which might have been due to industrial effluents or surface activity pollution. The concentration of chloride ion is 145.3 mg/L with a standard deviation of 48.9. This data services as an indicator such as human wastewater and industrial discharges.

4. CONCLUSION

The results obtained in this study indicate like lead (Pb^{2+}), cadmium (Cd^{2+}), chromium (Cr^{2+}) chloride (Cl^-), and sodium (Na^+) ions, which originated from humans activities and industrial discharge released into surroundings close to some Iraqi industrial zones, present the main contaminations in underground water. These chemical ions were evaluated by principle analysis, electrical conductivity and total dissolved solid methods, and were found to be the dominant pollutants in the samples collected for this study. The Water Quality Index indicates some water statuses are deemed as unsuitable for human consumption and may cause adverse health outcomes for children through direct exposure routes. These findings represent the first evidence of the connections between industrial activities and groundwater contamination and risk assessment in some industrial facilities, like Bajii and Al-Dora in Iraq. The study hence gives scientific advice to policy makers and stakeholders for future-oriented solutions.

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