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ORIGINAL ARTICLE

Investigating the Seasonal Variability of Arsenic Levels in the Tigris River Tributaries and Its Correlation with Water Quality Parameters

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KEYWORDS

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ABSTRACT: This study presents a comprehensive analysis of arsenic contamination in the Tigris River, Iraq, with a focus on seasonal variations and their relationship with water quality parameters. Conducted from November 2022 to July 2023, this research involved quarterly sampling at ten stations along the river and its tributaries. Arsenic levels were measured using a Shimadzu AA-6300 atomic absorption device, and water quality parameters such as dissolved oxygen (DO), total hardness, total dissolved solids (TDS), electrical conductivity (EC), and pH were assessed. This study revealed significant seasonal fluctuations in arsenic concentrations, with the highest levels detected during the winter season. Eight out of ten stations exceeded the World Health Organization's guideline limit of 10 μg L^{-1} for arsenic in drinking water during winter, with concentrations at the more contaminated stations reaching up to 16 times this limit. The research found no significant correlation between arsenic concentration and the water quality parameters measured, suggesting that these parameters are not reliable predictors of arsenic contamination. The highest arsenic concentrations were consistently observed at the first three stations, indicating a localized source of contamination likely due to the dissolution of arsenic from arsenic-rich soil layers. This study also noted the potential for bioremediation, as evidenced by the reduced arsenic levels at station 4 during the winter, which correlated with the presence of arsenic-absorbing Chara algae. The findings highlight the urgent need for targeted remediation efforts to mitigate arsenic pollution and protect public health in the region.

INTRODUCTION

Arsenic is an element that naturally exists and is identified by the atomic number 33. It's classified as a metalloid due to its shared characteristics with both metals and non-metals. Arsenic has multiple allotropes, but the grey one, which resembles a metal, is of the greatest industrial significance. This grey variant of

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arsenic possesses a specific gravity of 5.73 and melts at a temperature of 817°C [1,2].

Arsenic, a naturally occurring element, is present in numerous minerals, typically in conjunction with sulfur and metals, but it can also exist as a pure elemental crystal. Its industrial applications are diverse, including its use as an alloying component, in the manufacture of glass, pigments, textiles, paper, metal glues, wood preservatives, and ammunition. Additionally, arsenic plays a role in the hide tanning process and is used to a lesser degree in pesticides, feed additives, and pharmaceuticals [3–5].

Arsenic, in its inorganic state, is highly poisonous. Individuals are subjected to high levels of inorganic arsenic via several routes - consumption of contaminated water, use of such water in food preparation and crop irrigation, industrial activities, ingestion of tainted food, and tobacco smoking [6]. Chronic arsenic poisoning can result from long-term exposure to inorganic arsenic, primarily through the intake of water and food. The most common manifestations of this condition are skin lesions and skin cancer [7].

The primary public health risk from arsenic stems from polluted groundwater. Several countries, including Vietnam, the United States of America, Pakistan, Mexico, India, China, Chile, Cambodia, Bangladesh, and Argentina, have naturally high levels of inorganic arsenic in their groundwater (Figure 1) [8–10].

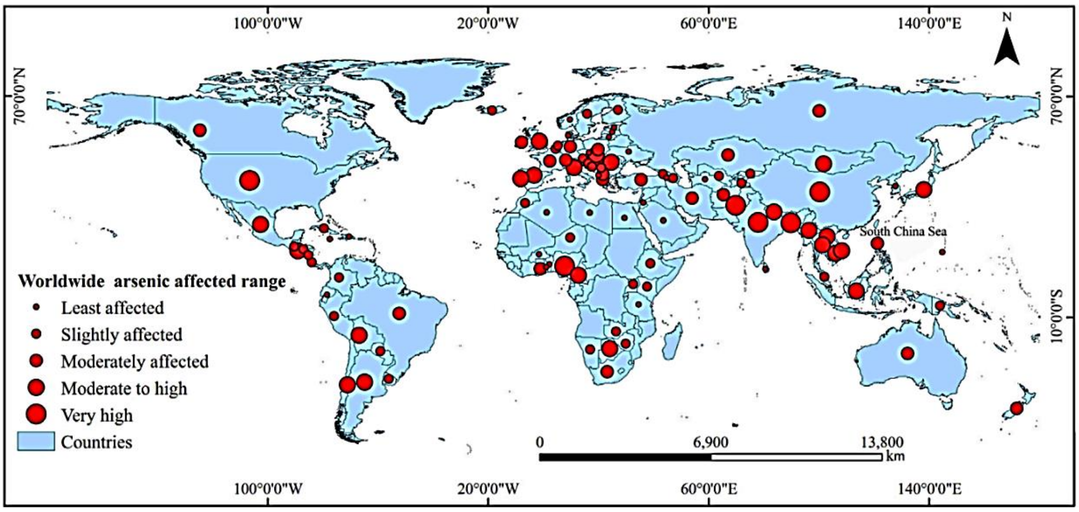

Figure 1. Global distribution of arsenic contamination: intensity indicated by plot sizes.

The World Health Organization (WHO) has set a safe limit of 10 µg L^{-1} (10 ppb) of arsenic in water supplies [11]. However, water supplies with an arsenic concentration exceeding 50 ppb are utilized by 57 million people, while 137 million individuals consume water with a higher arsenic content [12].

Studies have shown that prolonged intake of water contaminated with arsenic poses a significant risk to human health, leading to various forms of cancer, including those affecting the kidney, liver, skin, and spleen [13–15]. Additionally, it can cause skin conditions such as keratosis and pigmentation [16].

Research conducted over the years has confirmed the presence of arsenic contamination in the Tigris River in Iraq [17–19]. It is fed by more than 17 tributaries, which significantly contribute to its water flow. The river's flow can be effectively managed through the operation of a series of dams located on these tributaries. This allows for a high degree of control over the river's flow, ensuring optimal use and distribution of its water resources [20]. The Tigris River is the primary water source for the region, serving both agricultural and domestic needs. Many men, who work outside the village and on the land, directly consume the polluted river water for drinking and tea brewing, thereby exposing themselves to the pollution.

The contamination originates from the weathering and subsequent changes in arsenic-containing minerals in the region. The concentration of arsenic in the contaminated soil of the study area is significantly higher than that in uncontaminated soil, ranging from 220 to 28×10^6 ppm [17]. The primary objective of this research is to investigate the concentration of dissolved arsenic in the region's water across different seasons. Additionally, measurements were taken for factors such as Dissolved Oxygen (DO), pH, hardness, electrical conductivity (EC), total dissolved solids (TDS), and water temperature (T) to determine any significant relationship with the concentration of arsenic in the region's water.

MATERIAL AND METHODS

To evaluate arsenic levels in the Tigris River in Iraq, a study was conducted with 10 designated sampling stations, evenly spaced along the river and its tributaries. The stations closest to the pollution source were stations 1, 2, and 3. Sampling was carried out between 11:00 am and 3:00 pm at quarterly intervals, starting from November 2022 and concluding in July 2023. All stations were sampled in each season, except for stations 1 and 2 during the summer due to drought-induced water shortage. During each sampling phase, on-site measurements were taken for pH using a digital pH meter (Instrument Model: DPH-500, Global make), and for DO and T using an Orion Star A213 RDO/DO Meter [21].

Water hardness was determined via complexometric titration with ethylenediaminetetraacetic acid (EDTA) [22]. EC and TDS were measured in a laboratory setting using a WPA model CMD-200 model and a TDS meter [23]. The sampling stations' locations are depicted in Figure 2.

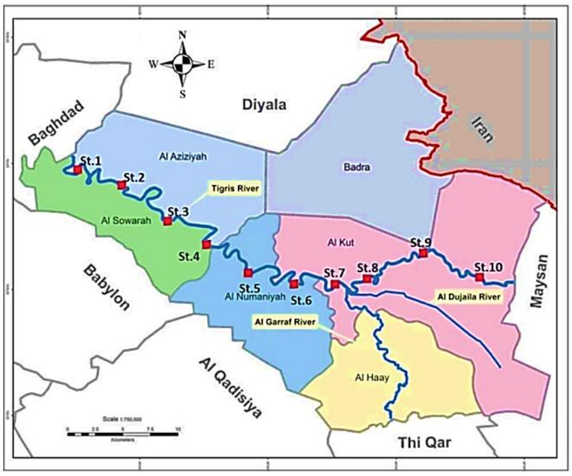

Figure 2. Sampling locations along the Tigris River in Wasit province.

Water samples were collected using polyethylene containers that had been thoroughly cleaned with 10% acetic acid [24]. During each sampling phase, three water samples were obtained from each station by submerging the containers at least 15 cm below the water surface. The samples were then refrigerated and swiftly transported to the laboratory for analysis.

Various methods are employed to analyze different forms of organic and inorganic arsenic across different matrices, such as water, food, and biological samples like blood, nails, and hair. These methods are continually evolving and improving.

In this study, arsenic levels were determined using a Shimadzu AA-6300 atomic absorption device equipped with a hydride generation system. The hydride generation method is a highly sensitive technique for measuring arsenic in water samples. It involves the conversion of inorganic arsenic species to arsine gas (AsH3) using a reducing agent such as sodium borohydride (NaBH4). The arsine gas is then introduced into the atomic absorption spectrometer for quantification. This method can achieve detection limits as low as 0.2 µg L^{-1}, making it suitable for measuring arsenic at the levels typically found in water samples [25]. The Shimadzu AA-6300 atomic absorption device, when coupled with the hydride generation system, can measure arsenic levels with a detection limit of 0.2 µg L^{-1} and an accuracy of ±5%. To ensure the reliability of the results, a standard reference material (NIST SRM 1643f) was analyzed alongside the water samples. Recoveries of arsenic from the reference material were within the acceptable range of 90-110%, confirming the accuracy of the analytical method [26]. At this point, the data gathered from measuring the selected parameters was inputted into the SPSS version 23.0 database. Subsequently, the required statistical analyses and tests were conducted.

RESULTS

The water analysis results, as shown in Figure 3, reveal that the highest arsenic concentrations were observed during the winter season. Out of the 10 stations examined, eight exceeded the WHO's guideline limit for arsenic contamination (10 μg L^{-1}) during the winter.

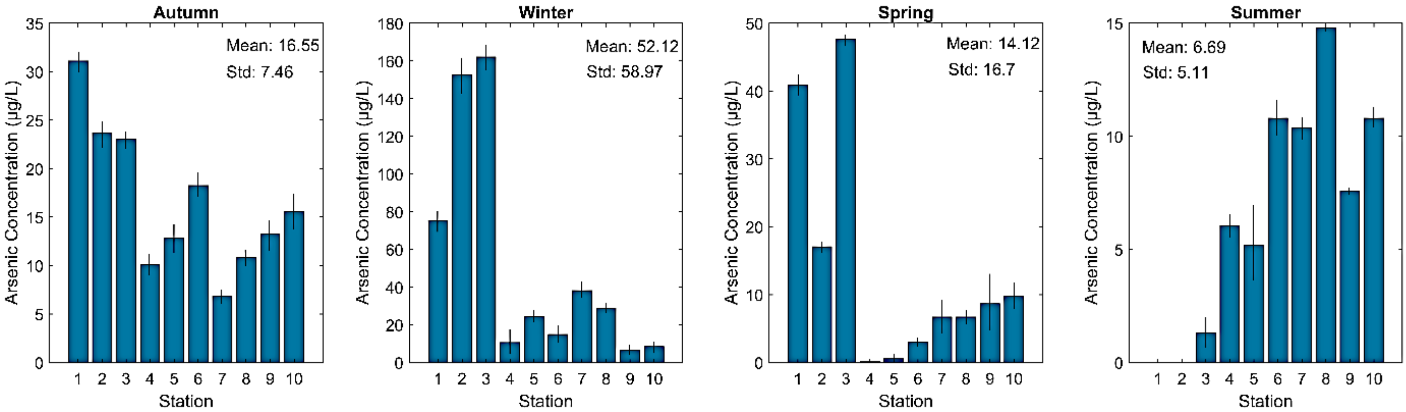

Figure 3. Seasonal variations in arsenic concentration across water stations in the Tigris River.

The substantial number of contaminated stations suggests a unique geological structure and widespread arsenic contamination in the region, further evidenced by the high arsenic concentration in the local soil. Notably, the arsenic levels at the more contaminated stations during winter were 16 times the WHO guidelines. This underscores the severity of the contamination issue in this region.

The concentration of arsenic in the water stations of the Tigris River exhibits significant seasonal fluctuations. In most stations, the arsenic concentration is notably higher during the winter season compared to other seasons. However, an exception to this trend is observed at station 10, where the arsenic concentration is found to be higher during other seasons. These fluctuations in arsenic concentration could potentially be influenced by several environmental factors. One such factor is the amount of precipitation, which can affect the infiltration of water from various layers of the earth. Another factor is the activity of living organisms, which can absorb arsenic and thereby affect its concentration in the water.

The first three stations consistently show the highest concentrations of arsenic across all seasons. This is likely due to their proximity to arsenic layers located in the upper parts of the earth's crust. As water passes through these areas, it dissolves the arsenic, leading to higher concentrations. As we move further away from these arsenic-rich areas, some of the dissolved arsenic becomes insoluble and precipitates, resulting in a decrease in arsenic concentration in the lower stations. The activity of organisms, which can change the form of arsenic and absorb it, also contributes to this decrease. However, there are exceptions to this general trend. For instance, stations 7 and 8 show an increase in arsenic concentration during the winter season. This could be due to the influx of water from other areas. Similarly, at station 4, the growth of certain plants, such as the Chara algae, which has been proven to absorb arsenic [27], leads to a reduction in arsenic concentration during the winter season. During the summer season, the region experiences severe drought and a lack of rainfall. This results in a decrease in the amount of arsenic in the water, as the reduced water flow limits the dissolution and transport of arsenic.

Variations in arsenic concentration across different water sources is a phenomenon that has been noted in various studies [28–30]. While the focus of the current research is on surface water, it's important to note that the primary source of contamination is the arsenic-laden soil layers. As water percolates through these contaminated layers, it dissolves the arsenic, leading to elevated concentrations in the water.

The water quality data for the stations, as summarized in Table 1, reveals distinct characteristics across different seasons. The waters under study exhibit an alkaline pH, with values ranging from 7.95 to 9.36. Interestingly, the pH levels remain relatively stable across all seasons, suggesting that there are no major chemical alterations occurring in the environment. On the other hand, EC varies significantly across different seasons and stations, with values ranging from 575.40 µs to 5995.50 µs. This variation in EC is mirrored in the TDS levels, as TDS is a direct function of conductivity, with values ranging from 271.95 mg L^{-1} to 2551.50 mg L^{-1}. When it comes to water hardness, the studied waters fall within the semi-hard to very hard range. The hardness values span from a minimum of 131.25 mg L^{-1} to a maximum of 2572.50 mg L^{-1}, with an average value of 588.03 mg L^{-1}. The standard deviation, based on calcium carbonate ($CaCO_3$), is 567.11 mg L^{-1}. These variations in hardness could potentially be attributed to seasonal changes in rainfall and the dissolution of solutes from upper soil layers into the water.

Table 1 also presents the statistical correlations between the concentration of arsenic in water and various other water quality parameters. According to the data in this table, arsenic concentration does not exhibit a significant correlation with pH, EC, TDS, total hardness, and DO. This suggests that these parameters may not directly influence the levels of arsenic in the water.

Table 1. Comprehensive overview of water quality metrics for Tigris River stations and correlation analysis of arsenic concentration with other quality parameters

Parameter	Min	Max	Mean	Std.	Correlation coefficient	Sig.
pH	7.95	9.36	8.72	0.38	-0.12	0.53
EC (µs)	575.40	5995.50	1968.38	1287.84	0.13	0.50
TSD (mg L^{-1})	271.95	2551.50	957.33	580.26	0.14	0.48
Total hardness (mg L^{-1} as $CaCO_3$)	131.25	2572.50	588.03	567.11	0.07	0.73
DO (mg L^{-1})	4.73	12.50	8.98	1.84	0.42	0.02
T (^{o}C)	4.20	27.30	16.76	7.21	-0.45	0.01

DISCUSSION

This study provides a comprehensive analysis of arsenic contamination in the water of Tigris River, with a particular focus on seasonal variations and their relationship with various water quality parameters. The results indicate a significant seasonal fluctuation in arsenic concentration, with the highest levels observed during the winter season. This finding is consistent with the global understanding of arsenic mobility and distribution in aquatic environments, as highlighted by [29], who reported that arsenic contamination in groundwater is a widespread issue with serious implications for public health.

The elevated arsenic concentrations during the winter season, exceeding the WHO guideline limit of 10 µg L^{-1} at eight out of ten stations, suggest that the Tigris River is subject to considerable geogenic contamination. This is likely due to the unique geological structure of the region, which is rich in arsenic-bearing minerals. The high arsenic levels in local soil, as evidenced by the study, corroborate this hypothesis and align with findings from [30], who emphasized the impact of water pollution on public health in Bangladesh, a country with similar geogenic arsenic issues.

This study's observation of the highest arsenic concentrations at the first three stations, irrespective of the season, points to a localized source of contamination. This is indicative of arsenic layers in the upper parts of the earth's crust, as water passing through these areas dissolves arsenic and increases its concentration. The phenomenon of arsenic-rich areas leading to higher concentrations in nearby water bodies has been documented in various studies [9,31,32], and the current research adds to this body of knowledge by providing specific data for the Tigris River. Interestingly, this study found no significant correlation between arsenic concentration and water quality parameters such as pH, EC, TDS, total hardness, and DO. This suggests that while these parameters are essential for understanding the overall water quality, they may not directly influence the levels of arsenic in the water. This finding is in line with [12], who noted that arsenic exposure through contaminated water is not necessarily linked to other water quality metrics. The presence of certain plants, like the Chara algae, which absorb arsenic and reduce its concentration, as observed at station 4 during the winter season, is a noteworthy aspect of this study. This bioremediation potential has been explored in various contexts, and the current research provides a practical example of its occurrence in the natural environment [27].

While this study provides valuable insights into the seasonal dynamics and spatial distribution of arsenic contamination in the Tigris River and its tributaries, it is important to acknowledge its limitations. Firstly, the sampling was conducted over a one-year period, which may not fully capture long-term trends in arsenic levels. Future studies should consider extending the sampling period to gain a more comprehensive understanding of the temporal variations in arsenic contamination.

Secondly, the study focused on surface water and did not investigate groundwater, which is another potential source of arsenic exposure for the local population. Future research should include groundwater sampling to assess the extent of arsenic contamination in the region's aquifers and its potential impact on public health.

Thirdly, the study did not explore the bioaccumulation of arsenic in aquatic organisms and the potential for transfer through the food chain. This is an important aspect to consider, as the consumption of arsenic-contaminated fish and other aquatic products may pose an additional health risk to the local population. Future studies should investigate the levels of arsenic in aquatic biota and assess the potential for human exposure through dietary intake.

Based on the findings and limitations of this study, several areas for future research can be proposed. Firstly, a more extensive investigation of the geological sources of arsenic in the region is needed to better understand the mechanisms of arsenic mobilization and transport in the Tigris River system. This could involve detailed geochemical analyses of soil, sediment, and rock samples, as well as the use of advanced techniques such as isotope tracing to identify the origin and fate of arsenic in the environment.

Secondly, the potential for bioremediation, as evidenced by the reduced arsenic levels at station 4 during the winter season, warrants further exploration. Future studies should focus on identifying the specific organisms responsible for arsenic absorption and investigating ways to enhance their growth and activity in the river system. This could lead to the development of nature-based solutions for mitigating arsenic contamination in the Tigris River and other affected water bodies.

Thirdly, the long-term health impacts of arsenic exposure on the local population need to be thoroughly investigated. This could involve epidemiological studies to assess the incidence of arsenic-related diseases, such as skin lesions and various forms of cancer, in communities relying on the Tigris River for their water supply. Such studies would provide valuable data to inform public health interventions and guide the development of targeted remediation strategies.

CONCLUSIONS

The comprehensive investigation of arsenic contamination in the tributaries of the Tigris River in Iraq, as presented in this study, underscores a significant environmental and public health concern. This research, conducted over a year with seasonal sampling at ten designated stations, has revealed alarmingly high levels of arsenic in the region's water, particularly during the winter months. The findings indicate that the highest concentrations of arsenic were observed in the colder season, with eight out of ten stations exceeding the WHO guideline limit of 10 $\mu g\ L^{-1}$ for arsenic in drinking water. This seasonal variation in arsenic levels suggests that environmental factors such as precipitation and biological activity play a crucial role in the mobilization and distribution of arsenic in the river system.

This study also examined the correlation between arsenic concentration and other water quality parameters such as pH, EC, TDS, total hardness, and DO. The lack of a significant correlation between these parameters and arsenic levels indicates that they are not reliable predictors of arsenic contamination in the water. This finding emphasizes the need for direct measurement of arsenic to assess the contamination levels accurately.

The consistent detection of high arsenic concentrations near the source of contamination highlights the influence of local geology on water quality. The dissolution of arsenic from arsenic-rich soil layers into the water as it flows through these areas is a primary contributor to the elevated levels observed. This study also notes that certain biological activities, such as the growth of arsenic-absorbing organisms, can affect arsenic concentrations, as seen in the reduced levels at station 4 during the winter season.

The implications of these findings are profound, considering the Tigris River's role as a critical water source for agriculture and domestic use in the region. The presence of arsenic at concentrations far exceeding safe limits poses a severe risk to human health, with potential long-term effects including various forms of cancer and skin conditions. The data presented in this study serve as a clarion call for immediate action to address the contamination issue.

In conclusion, this research provides valuable insights into the seasonal dynamics of arsenic contamination in the Tigris River and its tributaries. It highlights the urgent need for targeted strategies to mitigate arsenic pollution, protect water resources, and safeguard the health of the local population. The establishment of regular monitoring programs, the development of effective water treatment methods, and the implementation of policies to prevent further contamination are critical steps toward ensuring the safety and sustainability of water supplies in the region.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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