Advances in Biology & Earth Sciences
Vol.10, No.2, 2025, pp.289-302
https://doi.org/10.62476/abes.102289

Jomard Publishing

TOXIC ELEMENTS (As^{3+}, Pb^{2+}, Hg^{2+}, Cd^{2+}) IN WASTEWATER: A CASE STUDY ON ENVIRONMENTAL THREATS AND HEALTH RISKS

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Abstract. This study investigates the concentrations of toxic elements, including arsenic (As^{3+}), lead (Pb^{2+}), mercury (Hg^{2+}) and cadmium (Cd^{2+}), in water and sludge samples from the Dicle River and wastewater treatment facilities in Diyarbakir, Turkey, while assessing their environmental implications. Samples were collected from wastewater influent, effluent, sludge, upstream and downstream river locations and the organized industrial zone. Analyses were conducted using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) following EPA Method 200.7. Results reveal that influent wastewater contained As^{3+} (0.13 mg/L) and Hg (0.03 mg/L) concentrations above regulatory limits, whereas all metal levels in treated effluent complied with these thresholds. Sludge samples exhibited accumulation of As^{3+} (0.15 mg/L) and Hg (0.05 mg/L), indicating potential environmental risks. River water metal concentrations were generally within permissible limits. These findings align with existing literature, which reports persistent heavy metal accumulation in the Dicle River's sediments and biota. The results underscore the efficacy of wastewater treatment processes while highlighting the necessity for improved sludge management and ongoing monitoring of river pollution.

Keywords: *Dicle River, heavy metals, ICP-MS, toxic elements, wastewater, contamination.*

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Received: *26 April 2025;* ***Accepted:*** *18 June 2025;* ***Published:*** *6 August 2025.*

1. Introduction

Rapid urbanization and industrialization place considerable pressure on water resources, making wastewater contamination a significant challenge for environmental sustainability (Gleick, 2003). Heavy metals, which accumulate in aquatic ecosystems, threaten biodiversity and human health (Järup, 2003). Arsenic (As^{3+}), lead (Pb^{2+}), mercury (Hg^{2+}) and cadmium (Cd^{2+}) are of particular concern due to their pronounced toxicological effects (Naujokas *et al*., 2013; Needleman, 2004; Clarkson & Magos, 2008; Bernard, 2008). These metals enter water bodies via industrial effluents, agricultural runoff and urban wastewater (Varol, 2011). Global research indicates that heavy metal concentrations in rivers and lakes have risen from the 1970s to the 2010s, evolving from single-metal to complex multimetal contamination (Zhou *et al*., 2020).

Located in Turkey's Southeastern Anatolia Region, Diyarbakir depends on the Dicle River to meet its agricultural, industrial and potable water needs. However, increasing population and industrial activities have adversely affected the river's water quality (Varol *et al*., 2010) Industrial and domestic wastewater discharges introduce heavy metal pollution into the river's ecosystem (Karadede-Akin & Unlu, 2007). Recent studies confirm persistent heavy metal contamination in the Dicle River, with detrimental impacts on biota (Töre *et al*., 2021). Globally, heavy metal pollution remains a critical issue for water resources. Research demonstrates an increase in heavy metal concentrations in rivers and lakes from the 1970s to the 2010s, shifting toward multi-metal pollution (Zhou *et al*., 2020). In Turkey, studies have documented heavy metal accumulation in the Dicle River's sediments and biota (Varol, 2011; Karadede-Akin & Unlu, 2007). For example, Varol (2011) reported elevated levels of As^{3+}, Cd^{2+}, Co, Cr, Cu, Mn, Ni, Pb^{2+} and Zn in the river's sediments, primarily associated with metallic waste from the Ergani Copper Mine (Varol, 2011). Similarly, Karadede-Akin and Ünlü (2007) identified high concentrations of Cu, Ni and Zn in fish from the Dicle River, indicating potential human health risks through bioaccumulation. More recently, Töre et al. (2021) investigated toxic metal levels in edible fish species from the Dicle River, revealing carcinogenic risks associated with Cr, Ni and As in certain species.

Wastewater treatment plants (WWTPs) are critical in mitigating the release of heavy metals into water bodies. However, some WWTPs in Turkey have been reported to discharge effluents containing trace elements (Akdemir, 2024). For instance, Arslan-Alaton et al. (2007) found low levels of Cr and Ni in the effluent of WWTPs in coastal cities, which may pose health risks (Akdemir, 2024). Global literature underscores that heavy metals, even at low concentrations, can induce neurological, cardiovascular and carcinogenic effects (Tchounwou *et al*., 2012; Mood *et al*., 2021). Advances in wastewater treatment technologies have promoted the adoption of both conventional and biotechnological methods for heavy metal removal (Razzak *et al*., 2022; Qasem *et al*., 2021). The effectiveness and sustainability of these technologies are essential for enhancing WWTP performance. Consequently, the efficacy of WWTPs and the environmental impacts of sludge disposal warrant thorough examination.

Toxic elements, including arsenic (As^{3+}), lead (Pb^{2+}), mercury (Hg^{2+}) and cadmium (Cd^{2+}), accumulate through industrial activities, agricultural practices and natural processes, posing significant risks to human health and the environment.

Arsenic, element 33, is a metalloid found in minerals and water sources. Inorganic arsenic, present in soil and water, is highly toxic, associated with skin lesions, lung and bladder cancers and other health issues (Smith *et al*., 2019). Organic arsenic in seafood is generally non-toxic. Contamination typically originates from pesticides, industrial waste and natural sources.

Lead, element 82, a heavy metal, is released from industrial processes, lead-based fuels, paints and aging pipes. It causes severe health effects, including neurological damage, developmental disorders and kidney dysfunction, particularly in children and pregnant women. Lead accumulates in soil and water, necessitating stringent regulations and remediation strategies.

Mercury, element 80, a liquid metal found in coal and minerals, is released through coal combustion, industrial processes and waste management, transforming into toxic methylmercury in aquatic ecosystems. Exposure impairs neurological and cardiovascular systems, particularly affecting brain development in fetuses and children. Rigorous emission controls are essential.

Cadmium, element 48, occurs in soil and minerals and is used in metal processing, battery production and fertilizers. It causes kidney dysfunction, bone loss and respiratory issues. Entering the food chain via contaminated soil and water, cadmium requires robust industrial regulations and waste management strategies.

Effective waste management and environmental protection strategies are critical to mitigate the health and ecological impacts of these toxic elements.

Arsenic exposure leads to acute and chronic health issues, including skin lesions, skin cancer and internal organ cancers (e.g., bladder, lung) due to high concentrations in drinking water. It is also linked to cardiovascular diseases, diabetes and neurotoxic effects, potentially causing developmental issues in children.

Lead exposure severely affects the nervous system, particularly in children, resulting in developmental delays and learning difficulties. It impairs kidney function, increases cardiovascular risks and disrupts hemoglobin production, leading to anemia. Children and pregnant women are especially susceptible, with lead poisoning impacting mental and cognitive development.

Mercury, particularly methylmercury, accumulates in the body, causing neurological damage. It is associated with developmental disorders and cognitive decline in children, as well as toxic effects on the nervous system and kidneys. Mercury exposure may also elevate cardiovascular and hypertension risks, with early symptoms including tremors, memory issues and motor skill deficits.

Cadmium exposure harms kidney function, leading to proteinuria and potential renal failure. It accumulates in bones, contributing to osteoporosis and is linked to increased cardiovascular and respiratory disease risks. Its toxic effects intensify with long-term exposure, significantly impacting health (Ali *et al*., 2019).

These toxic elements underscore the need for robust human health protection strategies and policies. Reducing exposure and mitigating their effects are vital for preventing long-term health consequences.

In Diyarbakir, the Dicle River serves as a vital resource for agricultural irrigation and drinking water supply. However, discharges of industrial and urban wastewater threaten its water quality (Varol & Şen, 2012) This study aims to quantify the concentrations of As^{3+}, Pb^{2+}, Hg^{2+} and Cd^{2+} in samples collected from wastewater treatment plants in Diyarbakir, evaluate their environmental and health impacts and assess the efficiency of these treatment facilities. Furthermore, it seeks to contextualize the pollution status of the Dicle River by comparing it with existing literature and to propose recommendations for sustainable water management.

2. Material and Method

2.1. Study Area and Sampling

Table 1. Physicochemical parameters of wastewater and river samples

Sampling Location	pH	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Temperature (°C)
Wastewater Influent	9.4	3850	1.4	27
Wastewater Effluent	7.3	1100	3.9	24
Downstream River	7.6	1300	4.2	25
Upstream River (Control)	7.2	1200	5.7	24
Organized Industrial Zone Outlet	6.9	1380	4.3	24.5
Reference Range	6.5–8.5	1000–4000	2–8	20–30

This study was conducted at the Dicle River and an advanced biological wastewater treatment facility in Diyarbakir, Turkey. Samples were collected from the following locations: wastewater influent, effluent, sludge, upstream river (control), downstream river and the wastewater discharge from the organized industrial zone. Samples were obtained using 1-liter sterile plastic containers, stabilized with HNO_3 and transported to the laboratory under cold chain conditions (4°C). During sampling, in-situ measurements of pH, temperature, electrical conductivity and dissolved oxygen were performed (Table 1).

2.2. Analytical Procedure

Sample preparation followed EPA Method 200.7. For wastewater samples, 10 mL aliquots were treated with 10 mL of concentrated HNO_3 in a microwave digestion system and diluted to a final volume of 50 mL with ultrapure water. Sludge samples, consisting of 2 g, underwent the same digestion and dilution process. Analyses were performed at the Diyarbakir Environmental Control Laboratory using a Perkin Elmer NexION 2000 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Instrument calibration was conducted with standard solutions ranging from 0 to 20 ppm.

2.3. Data Analysis

The collected data were compared against EPA regulatory thresholds and analyzed using statistical methods. Results were presented visually through graphs and tables.

2.4. Statistical Analysis Methods

Given the small sample size and the presence of values near detection limits, non-parametric statistical methods were employed instead of assuming a normal distribution. The adoption of non-parametric approaches aligns with the typical characteristics of environmental datasets, which often exhibit small sample sizes and non-normal distributions. These methods yield robust results for small datasets and skewed distributions (Gibbons & Chakraborti, 2020). The Spearman correlation coefficient was utilized to evaluate monotonic relationships, a method well-suited for environmental studies involving heterogeneous distributions of heavy metal concentrations (Helsel *et al*., 2020).

- **Descriptive Statistics:** Mean, median and standard deviation were calculated.
- **Limit Value Comparison:** Each measurement was compared against the specified limit values (Hg^{2+}: 0.06, As^{3+}: 0.1, Pb^{2+}: 2.4, Cd^{2+}: 0.12 mg/L).
- **Treatment Efficiency:** The percentage reduction in concentration between influent and effluent was determined.
- **River Impact:** Differences in concentrations between upstream and downstream river locations were analyzed.
- **Correlation Analysis**: Relationships between elements were evaluated using the Spearman correlation coefficient.

2.5. Descriptive Statistics

Summary statistics of concentrations for each element are presented in Table 2:

Table 2. Summary statistics of element concentrations

Element	Mean (mg/L)	Median (mg/L)	Standard Deviation (mg/L)
Hg^{2+}	0.0135	0.00035	0.0218
As^{3+}	0.0487	0.0055	0.0710
Pb^{2+}	0.0518	0.0100	0.0747
Cd^{2+}	0.0300	0.0005	0.0460

The mean concentrations of toxic elements (Hg: 0.0135 mg/L, As^{3+}: 0.0487 mg/L, Pb^{2+}: 0.0518 mg/L, Cd^{2+}: 0.0300 mg/L) reflect their overall distribution, while the median values (Hg^{2+}: 0.00035 mg/L, As^{3+}: 0.0055 mg/L, Pb^{2+}: 0.0100 mg/L, Cd^{2+}: 0.0005 mg/L) better indicate central tendency, revealing a skewed distribution. Lower median values suggest most concentrations cluster at low levels, with high-concentration outliers, likely from wastewater influent or sludge, inflating the means (Forstner & Wittman, 2012; Tchounwou *et al*., 2012). This reflects heterogeneous pollution sources and effective treatment processes reducing concentrations.

Standard deviations (Hg^{2+}: 0.0218 mg/L, As^{3+}: 0.0710 mg/L, Pb^{2+}: 0.0747 mg/L, Cd^{2+}: 0.0460 mg/L) show variability, with high values for As and Pb^{2+} indicating heterogeneous distribution in environmental matrices, driven by natural and anthropogenic sources (Ali *et al*., 2019). Lower variability for Hg^{2+} and Cd^{2+} suggests more consistent concentrations, though elevated levels occur in specific samples.

High mean concentrations are driven by wastewater influent and sludge, while low medians highlight the efficacy of treatment processes (e.g., sedimentation, filtration) in reducing toxic elements in effluent and river water (Fu & Wang, 2011). However, outliers indicate occasional treatment limitations or persistent point-source pollution. Ecologically, low medians are positive for river ecosystems, but high standard deviations and outliers suggest risks to biodiversity (Forstner & Wittman, 2012). Future research should identify outlier sources and optimize treatment processes.

Descriptive statistics underscore the skewed distribution of toxic elements, with low post-treatment concentrations dominating but high variability highlighting point-source pollution. These insights guide environmental monitoring and pollution control strategies.

2.6. Limit Value Comparison

The comparison with limit values was conducted for water samples (sludge was evaluated separately), as shown in Table 3:

Table 3. Comparison of element concentrations with limit values

The place that sample was taken	Hg^{2+}> 0.06	As^{3+}> 0.1	Pb^{2+}> 2.4	Cd^{2+}> 0.12
Wastewater influent	No (0.03 ≤ 0.06)	Yes (0.13> 0.1)	No (0.16 <2.4)	No (0.08 <0.12)
Wastewater effluent	No (<DL)	No (<DL)	No (<DL)	No (<DL)
River water downstream	No (<DL)	No(<DL)	No (<DL)	No (<DL)
River water upstream	No (<DL)	No (<DL)	No (<DL)	No (<DL)
Outlet	No (<DL)	No (<DL)	No (<DL)	No (<DL)

Sludge:

- Hg^{2+}: 0.05 mg/L < 0.06 mg/L

• As^{3+}: 0.15 mg/L > 0.1 mg/L
• Pb^{2+}: 0.16 mg/L < 2.4 mg/L
• Cd^{2+}: 0.1 mg/L < 0.12 mg/L

In wastewater influent, arsenic (As^{3+}) concentration (0.13 mg/L) exceeds the 0.1 mg/L limit, suggesting contamination from industrial discharges, agricultural runoff, or geochemical sources (Smedley & Kinniburgh, 2002). This indicates a right-skewed distribution with high-concentration outliers. Other elements (Hg^{2+}, Pb^{2+}, Cd^{2+}) remain below their limits, marking As^{3+} as the primary pollutant.

In wastewater effluent, river water (upstream and downstream) and industrial discharge, all element concentrations are below detection limits (<DL), confirming effective treatment processes in reducing toxic elements and minimizing river ecosystem risks (Fu & Wang, 2011). These <DL measurements suggest near-zero central tendency and minimal variance.

In sludge, As^{3+} concentration (0.15 mg/L) exceeds the water-specific 0.1 mg/L limit, indicating accumulation during treatment (Babel & Kurniawan, 2003). This highlights the need for further analyses (e.g., sequential extraction) to assess pollution load, as water-specific limits may not suit sludge's distinct matrix. Investigation into As^{3+}'s chemical form and sedimentation/filtration efficacy is warranted.

The findings reveal significant As^{3+} contamination in influent and sludge, while affirming treatment effectiveness for water samples. Influent As^{3+} exceedance calls for source investigation and sludge As^{3+} levels underscore the need for matrix-specific regulations. These insights inform environmental monitoring, pollution control and treatment optimization, emphasizing further research into As^{3+} sources and sludge management.

2.7. Treatment Efficiency

The reduction in concentrations between wastewater influent and effluent is presented in Table 4:

Table 4. Concentration reduction between wastewater influent and effluent

Elementary	Wastewater Influent (mg/L)	Wastewater Effluent (mg/L)	Reduction (%)
Hg^{2+}	0.03	0.00005	99.83
As^{3+}	0.13	0.0005	99.62
Pb^{2+}	0.16	0.005	96.88
Cd^{2+}	0.08	0.0005	99.38

The wastewater treatment facility achieves high removal efficiencies for toxic elements: 99.83% for Hg^{2+}, 99.62% for As^{3+}, 96.88% for Pb^{2+} and 99.38% for Cd^{2+}, indicating effective treatment technologies (e.g., chemical precipitation, ion exchange, biological treatment) and compliance with regulations (Fu & Wang, 2011). Removal efficiencies above 96% confirm consistent performance.

Slight variations in efficiency reflect chemical behaviors and influent concentrations:

• Hg^{2+} and As^{3+}: High efficiencies (99.83% and 99.62%) suggest effective binding to sludge via precipitation or ion exchange, aided by low Hg^{2+} influent (0.03 mg/L).

- Pb^{2+}: Lower efficiency (96.88%) may result from higher influent (0.16 mg/L) or resistant chemical forms (e.g., organic complexes).
- Cd^{2+}: 99.38% efficiency indicates effective removal via sulfide precipitation or adsorption.

Influent concentrations (Hg^{2+}: 0.03 mg/L, As^{3+}: 0.13 mg/L, Pb^{2+}: 0.16 mg/L, Cd^{2+}: 0.08 mg/L) vary significantly, reflecting diverse pollution sources (e.g., industrial discharges, geochemical factors). Uniformly low effluent concentrations show treatment mitigates this variability, ensuring consistent water quality.

The facility's >96% removal rates demonstrate optimized technologies and effective pollution control. However, Pb^{2+}'s lower efficiency may warrant enhancements (e.g., adsorption materials, pH optimization). Low effluent concentrations minimize river ecosystem risks, but metal accumulation in sludge highlights the need for robust sludge management (e.g., stabilization, hazardous waste disposal) to reduce environmental risks (Kurniawan *et al*., 2006).

2.8. River Impact

Concentration differences between upstream and downstream river locations are presented in Table 5.

Table 5. Concentration differences between upstream and downstream river locations

Elementary	River Upstream (mg/L)	River Downstream (mg/L)	Differences Between Upstream And Downstream (mg/L)
Hg^{2+}	0.00005	0.00065	0.0006
As^{3+}	0.0005	0.0105	0.0100
Pb^{2+}	0.005	0.015	0.0100
Cd^{2+}	0.0005	0.0005	0.0000

2.9. Evaluation of Concentration Differences

The table indicates slight increases in concentrations downstream for Hg^{2+} (0.0006 mg/L), As^{3+} (0.0100 mg/L) and Pb^{2+} (0.0100 mg/L), with no difference observed for Cd^{2+} (0.0000 mg/L). These increases suggest that wastewater discharge or other environmental sources (e.g., surface runoff or sediment resuspension) may have a limited impact on river water quality. However, both upstream and downstream concentrations remain well below environmental limit values (e.g., Hg^{2+}: 0.06 mg/L, As^{3+}: 0.1 mg/L, Pb^{2+}: 2.4 mg/L, Cd^{2+}: 0.12 mg/L), supporting low environmental risk and minimal impact of discharges on water quality.

Statistically, concentration differences were calculated using the formula:

$$\text{Difference (mg/L)} = C_{\text{Downstream}} - C_{\text{Upstream}}$$

where $C_{\text{Downstream}}$ and C_{Upstream} represent downstream and upstream concentrations, respectively. Positive differences for Hg^{2+}, As^{3+} and Pb^{2+} indicate an increase downstream, while the zero difference for Cd^{2+} suggests stable concentrations.

2.10. Statistical Significance of Differences

Evaluating the statistical significance of concentration differences is critical forunderstanding the impact of wastewater discharge on the river. However, the table provides only a single pair of measurements (upstream and downstream), limiting the application of statistical tests. Despite small absolute differences, relative increases (e.g., 1200% for Hg^{2+}, 2000% for As^{3+}, 200% for Pb^{2+}) are notable. These suggest that discharges or other sources may elevate concentrations at low levels, but absolute values remain well below environmental limits, indicating low risk.

2.11. Element-Specific Differences

Concentration differences reflect variations in chemical and environmental behaviors:

• Hg^{2+}: The concentration increases from 0.000 05 mg/L upstream to 0.000 65 mg/L downstream, representing a 1200% relative increase. This may result from wastewater discharge or processes like sediment resuspension, though the value remains well below the limit of 0.06 mg/L.

• As^{3+}: The concentration rises from 0.0005 mg/L to 0.0105 mg/L, a 2000% relative increase, suggesting influence from discharges or anthropogenic sources (e.g., agricultural runoff). The value remains below the 0.1 mg/L limit.

• Pb^{2+}: The concentration increases from 0.005 mg/L to 0.015 mg/L, a 200% relative increase, potentially due to discharges or sediment sources. The value is well below the 2.4 mg/L limit.

• Cd^{2+}: Identical concentrations (0.0005 mg/L) upstream and downstream indicate no impact from discharges or stable concentrations at the detection limit.

These differences may be attributed to the chemical form of elements (e.g., dissolved or particulate-bound), river transport mechanisms, and discharge composition. The limited impact of wastewater discharge on river water quality, with all concentrations below limit values, supports low environmental risk. However, high relative increases for As^{3+} and Hg suggest potential accumulation at low levels, which could have long-term ecological impacts via bioaccumulation (e.g., in fish or benthic organisms). Long-term monitoring and bioavailability testing are recommended.

2.12. Correlation Analysis

The relationships between elements were evaluated using the Spearman correlation coefficient (non-parametric, suitable for small datasets), as shown in Table 6:

Table 6. Spearman correlation coefficients between elements

	Hg^{2+}	**As^{3+}**	**Pb^{2+}**	**Cd^{2+}**
Hg^{2+}	1.00	0.94	0.89	0.94
As^{3+}	0.94	1.00	0.94	0.89
Pb^{2+}	0.89	0.94	1.00	0.83
Cd^{2+}	0.94	0.89	0.83	1.00

2.13. Interpretation of High Correlations

The correlation coefficients, ranging from 0.83 to 0.94, indicate strong monotonic relationships between elements. The Spearman method, suitable for non-normal data or small datasets, confirms robust associations:

• High correlations for Hg^{2+}-As^{3+} (0.94), Hg^{2+}-Cd^{2+} (0.94) and As^{3+}-Pb^{2+} (0.94) suggest that these elements share common environmental sources (e.g., wastewater influent) or accumulate through similar chemical/physical processes, consistent with pollution dynamics in wastewater and sludge.

• The lowest correlation, Pb^{2+}-Cd^{2+} (0.83), still reflects a strong relationship but suggests slightly different sources or processes. For instance, Pb^{2+} may originate from fuel additives, while Cd^{2+} may be linked to fertilizers.

These correlations provide valuable insights for environmental pollution monitoring and management. The high Hg^{2+}-As^{3+} correlation suggests that monitoring one element may predict the presence of the other. Treatment processes should account for the tendency of these elements to accumulate in sludge, employing technologies like chemical precipitation or ion exchange. Further analyses (e.g., factor analysis, principal coponent analysis) could explore whether these elements exhibit similar bioavailability or toxicity.

3. Discussion and Conclusion

The analysis of heavy metal concentrations in water and wastewater samples provides critical insights into the distribution, treatment efficiency and environmental impact of toxic elements, namely mercury (Hg^{2+}), arsenic (As^{3+}), lead (Pb^{2+}) and cadmium (Cd^{2+}). The findings underscore the heterogeneous nature of heavy metal pollution, the effectiveness of treatment processes and the need for targeted environmental management strategies to address residual risks.

The descriptive statistics reveal a skewed distribution of heavy metal concentrations, as evidenced by the significant disparity between mean and median values. Mean concentrations (Hg^{2+}: 0.0135 mg/L, As^{3+}: 0.0487 mg/L, Pb^{2+}: 0.0518 mg/L, Cd^{2+}: 0.0300 mg/L) are consistently higher than median values (Hg: 0.00035 mg/L, As^{3+}: 0.0055 mg/L, Pb^{2+}: 0.0100 mg/L, Cd^{2+}: 0.0005 mg/L), indicating the presence of high-concentration outliers, likely originating from wastewater influent or sludge. This skewness is consistent with environmental pollution studies, where point-source discharges, such as industrial effluents, contribute to elevated concentrations. The high standard deviations, particularly for As^{3+} (0.0710 mg/L) and Pb^{2+} (0.0747 mg/L), reflect significant variability, suggesting diverse pollution sources and varying treatment efficiencies across samples. In contrast, the relatively lower standard deviations for Hg^{2+} (0.0218 mg/L) and Cd^{2+} (0.0460 mg/L) indicate more uniform concentrations, though outliers still occur in specific matrices like influent or sludge.

The low median concentrations in treated effluent and river water highlight the efficacy of treatment processes in reducing heavy metal levels. However, the presence of outliers suggests that certain point sources, such as industrial discharges or agricultural runoff, may overwhelm treatment systems in specific scenarios. From an ecological perspective, the low median concentrations are encouraging for river ecosystems, but the high variability and outliers underscore potential risks to biodiversity, particularly in areas with heavy metal accumulation. These findings underscore the importance of identifying sources and optimizing treatment technologies to address high-concentration inputs.

The comparison of heavy metal concentrations with regulatory limit values (Hg^{2+}: 0.06 mg/L, As^{3+}: 0.1 mg/L, Pb^{2+}: 2.4 mg/L, Cd^{2+}: 0.12 mg/L) reveals arsenic as the primary pollutant of concern. In wastewater influent, arsenic concentrations (0.13 mg/L) exceed the limit, likely due to industrial discharges or geochemical sources. Similarly, arsenic in sludge (0.15 mg/L) exceeds the water-specific limit, indicating accumulation during treatment processes. However, applying water-specific limits to sludge may not be entirely appropriate, as sludge represents a distinct matrix with unique accumulation mechanisms. This suggests the need for matrix-specific regulatory standards for sludge management.

Table 7. Toxic element concentrations in Diyarbakir wastewater (mg/L)

The Place That Sample Was Taken	Hg^{2+}	As^{3+}	Pb^{2+}	Cd^{2+}
Wastewater İnfluent	0.03	0.13	0.16	0.08
Wastewater Effluent	<0.0001	<0.001	<0.01	<0.001
Sludge	0.05	0.15	0.16	0.1
River Water Downstream	<0.0013	<0.021	<0.03	<0.001
River Water Upstream	<0.0001	<0.001	<0.01	<0.001
Outlet	<0.0001	<0.001	<0.01	<0.001
Limit Value	0.06	0.1	2.4	0.12

All elements in wastewater effluent, river water (upstream and downstream) and outlet samples were below detection limits, confirming the effectiveness of treatment processes in reducing heavy metal concentrations to safe levels. This aligns with previous studies highlighting the efficacy of technologies such as sedimentation, filtration and chemical precipitation in wastewater treatment. The exceedance of arsenic in influent and sludge underscores the need for targeted investigations into pollution sources and enhanced treatment strategies, such as advanced oxidation or adsorption, to mitigate arsenic contamination.

The wastewater treatment facility demonstrates exceptional removal efficiencies, ranging from 96.88% for Pb^{2+} to 99.83% for Hg^{2+}. These high efficiencies indicate robust performance of treatment technologies, including chemical precipitation, ion exchange and biological processes. The slight variation in removal rates, with Pb^{2+} showing the lowest efficiency (96.88%), may be attributed to its higher influent concentration (0.16 mg/L) or chemical forms (e.g., dissolved organic complexes) that resist precipitation. In contrast, Hg^{2+} and As^{3+} exhibit near-complete removal, likely due to effective binding to the sludge phase or lower influent concentrations facilitating higher percentage reductions.

The findings indicate that the concentrations of As^{3+} (0.13 mg/L) and Hg (0.03 mg/L) in wastewater influent exceed the regulatory limits (As^{3+}: 0.1 mg/L, Hg^{2+}: 0.06 mg/L). These elevated levels suggest potential pollution from industrial and agricultural activities, particularly from sources such as the Ergani Copper Mine (Smedley & Kinniburgh, 2002). Post-treatment metal concentrations fall below the regulatory limits (As^{3+}: <0.001 mg/L, Hg^{2+}: <0.0001 mg/L), demonstrating the effectiveness of wastewater treatment plants in metal removal (Metcalf & Eddy, 2014). However, accumulation of As^{3+} (0.15 mg/L) and Hg^{2+} (0.05 mg/L) in sludge has been observed, necessitating careful management during sludge disposal processes (Tytła, 2019). Heavy metals accumulated in sludge may leach into soil and groundwater, potentially causing secondary pollution (Feng *et al*., 2023).

The low effluent concentrations confirm that the treatment facility successfully mitigates environ- mental risks to receiving water bodies. However, the accumulation of heavy metals in sludge highlights the importance of proper sludge management practices, such as stabilization or controlled disposal, to prevent secondary pollution. The findings suggest that while the treatment plant performs effectively, optimizing processes for Pb^{2+} removal (e.g., through pH adjustment or specialized adsorbents) could further enhance overall efficiency.

The slight increases in downstream concentrations for Hg^{2+} (0.0006 mg/L), As^{3+} (0.0100 mg/L) and Pb^{2+} (0.0100 mg/L) suggest a limited impact of wastewater discharge or other environmental sources, such as sediment resuspension or runoff. Despite notable relative increases (e.g., 2000% for As^{3+}), all downstream concentrations remain well below regulatory limits, indicating minimal ecological risk. The absence of a concentration difference for Cd^{2+} suggests stable environmental conditions or effective treatment preventing downstream impacts.

The high relative increases for Hg^{2+} and As^{3+}, though small in absolute terms, warrant attention due to their potential for bioaccumulation in aquatic organisms. Long-term monitoring and bioavailability studies are recommended to assess whether these low-level increases pose cumulative risks to river ecosystems. Additionally, the influence of external factors, such as agricultural runoff or sediment dynamics, should be investigated to better understand concentration changes.

The Spearman correlation coefficients (0.83-0.94) indicate strong monotonic relationships between heavy metal concentrations, suggesting shared pollution sources or similar chemical behaviors during treatment. The high correlations between Hg^{2+}-As^{3+} (0.94), Hg^{2+}-Cd^{2+} (0.94) and As^{3+}-Pb^{2+} (0.94) imply that these elements may originate from common industrial or geochemical sources and accumulate similarly in sludge. The slightly lower Pb^{2+}-Cd^{2+} correlation (0.83) suggests some divergence in sources or treatment dynamics, possibly due to Pb^{2+}'s association with fuel additives versus Cd^{2+}'s link to fertilizers.

These correlations provide valuable insights for environmental monitoring, as monitoring one element (e.g., Hg^{2+}) could predict the presence of others (e.g., As^{3+}). Treatment strategies should leverage these relationships by employing technologies that target multiple elements simultaneously, such as ion exchange or chemical precipitation. Further multivariate analyses, such as principal component analysis, could elucidate underlying pollution patterns and guide management strategies.

These findings align with the thesis results, highlighting the persistent impact of industrial waste on the river. From a health perspective, As^{3+} exposure is associated with cancer and cardiovascular diseases, while Hg^{2+} exposure may cause neurological developmental disorders in children (Naujokas *et al*., 2013; Grandjean & Landrigan, 2014). Therefore, continuous monitoring of pollution levels in the Tigris River and assessment of public health risks are of critical importance. Effective strategies must be developed for sludge management in wastewater treatment plants to prevent the release of heavy metals into the environment.

This study highlights the effectiveness of wastewater treatment in reducing heavy metal concentrations, with low effluent and river water concentrations indicating minimal environmental risk. However, arsenic contamination in influent and sludge, coupled with high variability and outliers, underscores the need for targeted source control and enhanced treatment processes. The strong correlations between elements suggest shared pollution dynamics, offering opportunities for integrated monitoring and treatment strategies. Future research should focus on identifying specific pollution sources, optimizing Pb^{2+} removal and developing matrix-specific standards for sludge management to further mitigate environmental risks.

4. Results

This study evaluated the concentrations of toxic elements (As^{3+}, Pb^{2+}, Hg^{2+}, Cd^{2+}) in water and sludge samples from the Dicle River and wastewater treatment facilities in Diyarbakir, assessing environmental and health risks. Statistical analyses elucidated treatment efficiency, pollution sources and impacts on the river ecosystem.

In the wastewater influent, As^{3+} (0.13 mg/L) exceeds the limit value (0.1 mg/L), while Hg^{2+} (0.03 mg/L), Pb^{2+} (0.16 mg/L) and Cd^{2+} (0.08 mg/L) remain below their respective limits (0.06 mg/L, 2.4 mg/L, 0.12 mg/L). Post-treatment, all concentrations are below detection limits (Hg^{2+}: <0.0001 mg/L, As^{3+}: <0.001 mg/L, Pb^{2+}: <0.01 mg/L, Cd^{2+}: <0.001 mg/L), demonstrating high removal efficiencies (Hg^{2+}: 99.83%, As^{3+}: 99.62%, Pb^{2+}: 96.88%, Cd^{2+}: 99.38%). Descriptive statistics reveal that mean concentrations (Hg^{2+}: 0.0135 mg/L, As^{3+}: 0.0487 mg/L, Pb^{2+}: 0.0518 mg/L, Cd^{2+}: 0.0300 mg/L) are influenced by high values in influent and sludge, while median values (Hg^{2+}: 0.000 35 mg/L, As^{3+}: 0.0055 mg/L, Pb^{2+}: 0.0100 mg/L, Cd^{2+}: 0.0005 mg/L) reflect low post-treatment concentrations. High standard deviations (Hg^{2+}: 0.0218 mg/L, As^{3+}: 0.0710 mg/L, Pb^{2+}: 0.0747 mg/L, Cd^{2+}: 0.0460 mg/L) highlight the heterogeneity of pollution sources and the presence of high-concentration outliers.

Sludge analyses show As^{3+} (0.15 mg/L) exceeding the limit and Hg^{2+} (0.05 mg/L) near the limit, indicating accumulation risks, while Pb^{2+} (0.16 mg/L) and Cd^{2+} (0.1 mg/L) remain below limits. Water-specific limits may not be suitable for sludge, necessitating matrix-specific regulations. Concentration differences between upstream and downstream river points show slight increases for Hg^{2+} (0.0006 mg/L), As^{3+} (0.0100 mg/L) and Pb^{2+} (0.0100 mg/L), with no change for Cd (0.0000 mg/L). All concentrations remain well below limits, supporting low environmental risk. Spearman correlation analysis reveals strong relationships between elements (Hg^{2+}-As^{3+}: 0.94, Hg^{2+}-Cd^{2+}: 0.94, As^{3+}-Pb^{2+}: 0.94, Pb^{2+}-Cd^{2+}: 0.83), indicating common pollution sources and similar chemical behaviors.

The findings confirm the wastewater treatment facility's effectiveness in removing toxic elements, but highlight arsenic contamination in influent and sludge accumulation risks. Low river concentrations are positive, but the biomagnification potential of As^{3+} and Hg^{2+} necessitates long-term monitoring. Future studies should investigate arsenic pollution sources, develop matrix-specific sludge standards and assess bioavailability. Strict oversight of industrial and agricultural activities is critical for preserving the Dicle River's ecological balance.

References

Akdemir, T. (2024). Trace element concentrations in effluent of municipal wastewater treatment plants along the Turkish coasts and assessment of human health risk. *Frontiers in Marine Science,* 11, 1521449. https://doi.org/10.3389/fmars.2024.1521449

Ali, H., Khan, E. & Ilahi, I. (2019). Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity and bioaccumulation. *Journal of Chemistry*, 1, 6730305. https://doi.org/10.1155/2019/6730305

Babel, S., Kurniawan, T.A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *Journal of Hazardous Materials, 97*(1-3), 219-243. https://doi.org/10.1016/S0304-3894(02)00263-7

Bernard, A. (2008). Cadmium & its adverse effects on human health. *The Indian Journal of Medical Research, 128*(4), 557-564.

Clarkson, T.W., Magos, L. (2008). The toxicology of mercury and its chemical compounds. *Critical Reviews in Toxicology, 36*(8), 609-662. https://doi.org/10.1080/10408440600845619

Feng, J., Burke, I.T., Chen, X. & Stewart, D. (2023). Assessing metal contamination and speciation in sewage sludge: Implications for soil application and environmental risk. *Reviews in Environmental Science and Bio/Technology, 22*(7), 1037-1058. https://doi.org/10.1007/s11157-023-09675-y

Förstner, U., Wittman, G. (2012). *Metal Pollution in the Aquatic Environment*, 2nd edition. Berlin: Springer-Verlag.

Fu, F., Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management, 92*(3), 407-418. https://doi.org/10.1016/j.jenvman.2010.11.011

Gleick, P.H. (2003). Water use. *Annual Review of Environment and Resources*, 28, 275-314.

Grandjean, P., Landrigan, P.J. (2014). Neurobehavioural effects of developmental toxicity. *The Lancet Neurology, 13*(3), 330-338. https://www.thelancet.com/journals/laneur/article/PIIS1474-4422(13)70278-3/fulltext

Järup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin, 68*(1), 167-182. https://doi.org/10.1093/bmb/ldg032

Karadede-Akin, H., Unlu, E. (2007). Heavy metal concentrations in water, sediment, fish and some benthic organisms from Tigris River, Turkey. *Environmental Monitoring and Assessment,* 131, 323-337. https://doi.org/10.1007/s10661-006-9478-0

Kurniawan, T., Chan, G., Lo, W. & Babel, S. (2006). Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, *118*(1-2), 83-98. https://doi.org/10.1016/j.cej.2006.01.015

Metcalf & Eddy (2014). *Wastewater Engineering: Treatment and Resource Recovery*, 5th edition. New York: McGraw-Hill.

Mood, M.B., Naseri, K., Tahergorabi, Z., Khazdair, M.R. & Sadeghi, M. (2021). Toxic mechanisms of five heavy metals: Mercury, lead, chromium, cadmium and arsenic. *Frontiers in Pharmacology,* 12. https://doi.org/10.3389/fphar.2021.643972

Naujokas, M.F., Anderson, B., Ahsan, H., Aposhian, H., Graziano, J.H., Thompson, C. & Suk, W. A. (2013). The broad scope of health effects from chronic arsenic exposure: Update on a worldwide public health problem. *Environ Health Perspect, 121*(3), 295-302. https://doi.org/10.1289/ehp.1205875

Needleman, H. (2004). Lead poisoning. *Annual Review of Medicine*, 55, 209-222. https://doi.org/10.1146/annurev.med.55.091902.103653

Qasem, N.A., Ramy, M.H. & Lawal, D.U. (2021). Removal of heavy metal ions from wastewater: A comprehensive and critical review. *npj Clean Water,* 36. https://doi.org/10.1038/s41545-021-00127-0

Razzak, S.A., Faruque, M.O., Alsheikh, Z., Alsheikhmohamad, L., Alkuroud, D., Alfayez, A., ... & Hossain, M.M. (2022). A comprehensive review on conventional and biological-driven heavy metals removal from industrial wastewater. *Environmental Advances*, 7, 100168. https://doi.org/10.1016/j.envadv.2022.100168

Smedley, P.L., Kinniburgh, D.G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry, 17*(5), 517-568. https://doi.org/10.1016/S0883-2927(02)00018-5

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K. & Sutton, D.J. (2012). Heavy metals toxicity and the environment. *Molecular, Clinical and Environmental Toxicology,* 3, 133-164. https://doi.org/10.1007/978-3-7643-8340-4_6

Töre, Y., Ustaoğlu, F., Tepe, Y. & Kalipci, E. (2021). Levels of toxic metals in edible fish species of the Tigris River (Turkey); Threat to public health. *Ecological Indicators,* 123, 107361. https://doi.org/10.1016/j.ecolind.2021.107361

Tytła, M. (2019). Assessment of heavy metal pollution and potential ecological risk in sewage sludge from municipal wastewater treatment plant located in the most ındustrialized region in Poland - case study. *International Journal of Environmental Research and Public Health, 16*(13), 24-30. https://doi.org/10.3390/ijerph16132430

Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous Materials,* 195, 355-364. https://doi.org/10.1016/j.jhazmat.2011.08.051

Varol, M., Gökot, B. & Bekleyen, A. (2010). Assesment of water pollution in the Tigris River in Diyarbakir, Turkey. *Water Practice & Technology, 5*(1), wpt2010021. https://doi.org/10.2166/wpt.2010.021

Varol, M., Şen, B. (2012). Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *Catena,* 92, 1-10. https://doi.org/10.1016/j.catena.2011.11.011

Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H. & Yao, X. (2020). Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. *Global Ecology and Conservation,* 22. https://doi.org/10.1016/j.gecco.2020.e00925