

The Impact Of Water Hardness On Calcite Deposition And Geomorphological Changes In The Shatt Al-Hillah Channel: A Comparative Study Between Autumn 2024 And Spring 2025

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Abstract

This study aims to evaluate the effect of chemical hardness—represented by the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions—on the deposition of calcium carbonate (Calcite) and the formation of armored layers in the Shatt al-Hillah River during the fall of 2024 and spring of 2025. Water samples were collected from five stations along the river and subjected to physical and chemical analyses, including pH, EC, TDS, total hardness, Ca hardness, Mg hardness, alkalinity, phosphate, sulfate, chloride, nitrate, and nitrite.

Bottom shear stress (τ_b) and friction velocity (u_*) were calculated using standard hydraulic equations based on depth, slope, and flow velocity measurements. The results showed that τ_b (24.5 - 55.9 Pa) and u_* (0.156 - 0.236 m/s) remained below the critical threshold for destabilizing calcite-covered sediments, indicating relative stability of the riverbed.

The study also showed an increase in calcite precipitation rate from 98 mg/L in autumn to 162.6 mg/L in spring, a relative increase of 66%, resulting in the formation of flow-resistant, laminated calcite layers. Laboratory analysis was supported by geochemical modeling (PHREEQC) and statistical analysis (SPSS).

These results highlight the importance of monitoring chemical hardness and nutrients to ensure riverbed sustainability, and the quality of water used for irrigation.

Keywords: Calcite precipitation, water hardness, geochemical modeling, shear stress, laminated layers

INTRODUCTION

Water hardness is an important physicochemical property in natural aquatic systems. It results primarily from the concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in water. High concentrations of these ions directly affect water stability and chemical balance and promote the formation and precipitation of calcium carbonate (CaCO_3) in the form of calcite crystals, especially in river environments with low flow or high evaporation (Timms & Riley, 1963, p. 78; Jung et al., 2015, p. 7305).

Recent studies have indicated that the saturation of water with calcium and magnesium ions, combined with a high pH, leads to ideal conditions for calcite precipitation, resulting in the formation of bottom layers known as armored layers. These layers help protect fine sediments and gravels from erosion and play an important geomorphological role in stabilizing river sections and directing flow paths (Baker & Meadows, 2010, p. 47; Beck & Hirst, 2024, p. 3).

In Iraq, particularly in the central and southern regions, rivers such as the Shatt al-Hillah experience sharp seasonal fluctuations in discharge, high evaporation rates, and high hardness, as a result of semi-arid climatic conditions and growing agricultural and environmental pressures (Alwan & Khudair, 2021, p. 1817; Chabuk et al., 2023). The Shatt al-Hillah is one of the river systems affected by these complex factors. Initial field observations indicate seasonal variations in calcite deposition and laminated layer formation. This raises questions about the role of chemical hardness in the formation and development of river channel sections.

This study is based on a seasonal analysis during the fall of 2024 and spring of 2025 of five selected sites along the Shatt al-Hilla River, using a multidisciplinary analytical approach that combines physical and chemical analyses, geochemical modeling (using PHREEQC), hydraulic analysis (to calculate shear stress and friction velocity), and statistical analysis (t-test, ANOVA, Pearson). This integrated approach is essential for understanding how seasonal chemical changes affect sedimentary and geomorphological processes. Therefore, this study seeks to contribute to bridging the scientific gap in understanding the relationship between chemical hardness and calcite deposition processes within the Iraqi river environment. It also seeks to shed light on the role of these phenomena in creating sustainable bed layers

that can be utilized in the future to protect river courses from erosion, environmental degradation, and various conditions.

Theoretical Framework

1. Chemical Hardness and Calcite Precipitation

The chemical hardness of water (water hardness) is an essential property of natural water, reflecting the concentration of divalent ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). These ions play a pivotal role in chemical equilibrium processes and directly influence the tendency of an aqueous system to become saturated with calcium carbonate (CaCO_3), which leads to calcite precipitation under specific physical conditions (Stumm & Morgan, 1996; Jung et al., 2015).

In this context, the saturation index (SI) is a key criterion, as it determines whether water is subsaturated ($\text{SI} < 0$), at equilibrium ($\text{SI} = 0$), or supersaturated to the point of precipitation ($\text{SI} > 0$) (Appelo & Postma, 2005). Modeling of river systems has shown that the saturation index value is affected by pH, temperature, and bicarbonate concentration, making chemical hardness an effective predictive tool for assessing the potential for calcite precipitation (Beck & Hirst, 2024).

2. River Sedimentation Dynamics and Crystal Formation Conditions

Calcite crystals typically form through a complex process of homogeneous versus heterogeneous nucleation, a process that relies on the presence of stimulating surfaces, such as fine sediments, gravels, and river channel walls.

These crystals initially form as tiny nuclei, which gradually grow to form visible layers known as armored layers. These layers are highly resistant to deterioration and can impede erosion (Timms & Riley, 1963). Flow velocity (u) and bottom shear stress (τ_b) are hydrodynamic factors that influence the continuation or cessation of these layers. Field experiments have shown that layers often form in areas of relative calm, where turbulence is minimal and chemical stability is high (Baker & Meadows, 2010).

3. Geomorphological Impact of Calcite Deposition

Accumulated calcite layers cause significant geomorphological changes in river cross-sectional geometry. They reduce flow depth and increase hydraulic roughness (Manning's n), altering the distribution of kinetic energy and slowing the rate of lateral bank erosion (Knighton, 2014).

Studies of semi-arid river basins confirm that these layers may contribute to the "aging" of waterways, i.e., stabilizing their bends and restricting their lateral migration, particularly during dry seasons when discharge is low and chemical precipitation rates are high (Gregory & Walling, 2020).

4. Local Context: Shatt al-Hillah as a Study Model

The Shatt al-Hillah is a branch of the Euphrates River and lies within a semi-arid climate characterized by high thermal fluctuations and excessive evaporation, which increases the potential for salt and mineral precipitation. Local data show that Ca^{2+} and Mg^{2+} concentrations often exceed 150 mg/L and 50 mg/L, respectively, in some locations, with SI exceeding +0.5 in hot seasons (Alwan & Khudair, 2021).

Field observations indicate the formation of hard bed layers overlying gravel and fine sediments in parts of the Shatt al-Hilla River during the spring. This is an indication of frequent chemical sedimentation, which may affect the shape and stability of the river section.

OBJECTIVES

This study aims to analyze the relationship between water chemical hardness and calcite deposition in the Shatt al-Hilla Riverbed, with a focus on the effect of seasonal changes in the physical and chemical properties of the water on the stability of the bed and its geomorphological evolution.

To achieve the general objective, a series of detailed objectives were identified that guide the analytical framework of the research:

1. **Sample Collection and Chemical Analysis:** Surface water samples were collected from five stations along the Shatt al-Hilla River during the fall and spring seasons, with three replicate samples taken at each station to ensure statistical accuracy. Laboratory analyses included measuring the concentrations of major ions, particularly calcium (Ca^{2+}) and magnesium (Mg^{2+}), as well as a range of supporting chemical indicators such as alkalinity, chloride, sulfate, and phosphate.

2. Calculating hydraulic parameters: Calculating vital hydraulic parameters such as bottom shear stress (τ_b) and friction velocity (u_*) using standard equations related to flow depth and velocity, in order to estimate the physical conditions accompanying sedimentation processes.

3. Modeling and Statistical Analysis: Calcite deposits were assessed over the two seasons using PHREEQC modeling. Seasonal differences were statistically analyzed to determine the effect of temporal variation on chemical and hydrodynamic properties.

4. Providing practical recommendations: Formulating practical, evidence-based recommendations that contribute to improving water quality management in the Shatt al-Hilla River and enhancing its course stability, through a deeper understanding of sedimentation mechanisms and their interactions with flow behavior and channel formation.

METHODOLOGY

This study adopted a multi-stage analytical approach, combining field analysis, laboratory investigations, computer modeling, and statistical analysis. The aim was to evaluate the relationship between chemical hardness and calcite deposition in the Shatt al-Hilla channel during two seasons with varying climatic and hydrological conditions.

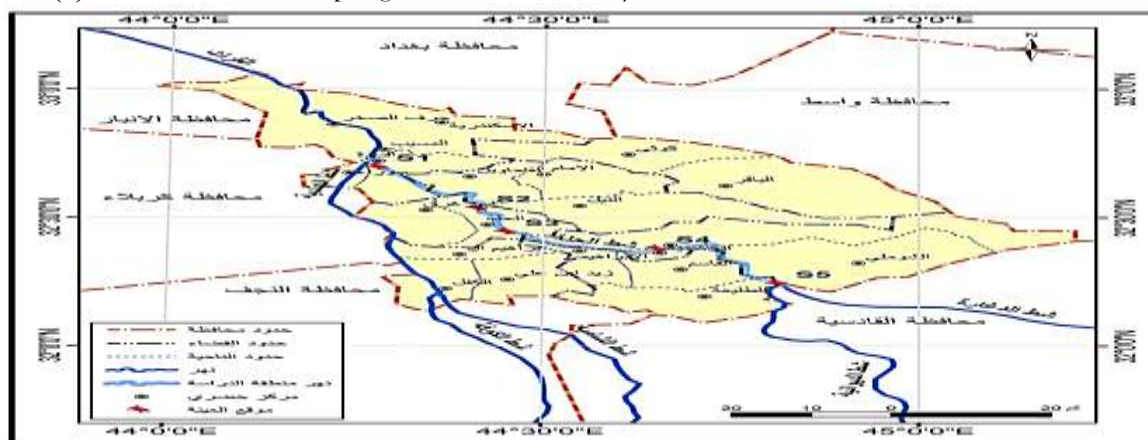
Water samples for physical and chemical analysis were collected from five stations (St1–St5) during the fall of 2024 (October–November) and spring of 2025 (March–April). Three replicate samples were collected from each station, each sampled from a depth of 30 cm below the water surface. Five-liter polyethylene containers were used for the collection process, which were pre-washed with dilute hydrochloric acid (10%) and then rinsed with distilled water (Nollet, 2007).

To estimate the mercury concentration in water, samples were collected using 250 ml transparent glass bottles, and concentrated sulfuric acid and potassium dichromate solution were added to preserve the sample until testing (Jamaluddin and Shah Alam, 2003).

Five main stations were selected along the Shatt al-Hillah River to represent the changing environmental and hydrological gradient along the river. The geographical distribution of the stations included the following:

- (St1) **Al-Saddah**: represents a major groundwater recharge area, characterized by a high calcium concentration.
- (St2) **Al-Hillah Center** is influenced by mixed agricultural groundwater and limited urban waste.
- (St3) **Al-Ibrahimiyyah**: lies within a purely agricultural area, making it a model for the impact of agricultural fertilization on water quality.
- (St4) **Al-Hashimiyyah**: an area with saline soil and a saline groundwater source, which increases salt accumulation and hardness.
- (St5) **Al-Dughara**: represents the final outlet of the river, showing signs of erosion and increased deposition of mixed sediments.

Figure :(1) Locations of the sampling stations in the study area.



Source:

1. Ministry of Water Resources, General Authority for Surveying, Department of Map Production, Administrative Map of Iraq, Scale 1:1,000,000, Baghdad, 2023.

2. Using ArcGIS 10.8 software.

2. Laboratory Analyses

A series of standard laboratory analyses were conducted to assess the physicochemical properties of the Shatt al-Hillah's water, following the standard methods approved by the American Public Health Association (APHA, 2003; 2005; 2017). These analyses included the measurement of the following parameters: **pH**, **Total Dissolved Solids (TDS)**, **Electrical Conductivity (EC)**, **Total Hardness**, **Calcium Hardness**, **Magnesium Hardness**, **Alkalinity**, **Phosphate**, **Sulfate**, **Chloride**, **Nitrate**, and **Nitrite**.

The pH, EC, and TDS were measured **in the field** using a Hanna Multi-Meter, which was calibrated with standard solutions. Buffer solutions of pH 4, 7, and 9 were used for the pH meter calibration. EC values were expressed in microsiemens/cm ($\mu\text{S}/\text{cm}$), and TDS in milligrams/liter (mg/L).

Total hardness and calcium hardness were determined using the manual **titration method** with a standard EDTA solution (0.01 N). This was performed after diluting the sample to 50 ml and adding the appropriate reagents, such as **Eriochrome Black T** for total hardness and **Murexide indicator** for calcium hardness. Magnesium hardness was calculated indirectly by subtracting the calcium hardness value from the total hardness.

To calculate the amount of **precipitated calcite** (mg/L), samples were cooled, and the pH was gradually adjusted to 8.3 using a 0.05 N NaOH solution under constant stirring, which induced the precipitation of calcium carbonate crystals. The samples were then filtered using **0.45 μm pore size filter paper**, and the residue was dried at 105°C until a constant weight was achieved.

For chloride, the direct titration method with **silver nitrate (AgNO_3)** was used, with potassium chromate as a color indicator, and results were expressed in mg/L . Sulfate was estimated using the **turbidimetric method** by adding barium chloride to the sample after treatment with a conditioning solution, and measuring the absorbance at a wavelength of 420 nm using a spectrophotometer.

Nitrite concentration was determined using the **colorimetric method**, via the reaction of sulfanilamide and N-(1-Naphthyl)ethylenediamine, with absorbance measured at a 543 nm wavelength. Nitrate (NO_3^-) concentration was measured using the cadmium reduction column method. This method reduces nitrate to nitrite (NO_2^-), and the sample is then treated in the same way as nitrite, with the absorbance read at the same wavelength. Phosphate (PO_4^{3-}) was measured using the mixed reagent method, where a reagent solution was added to the sample, and the absorbance was measured at a wavelength of 860 nm.

All results were expressed in standard units (mg/L or $\mu\text{g}/\text{L}$) depending on the nature of the parameter being studied. The final values were reviewed to verify their integrity and compliance with freshwater analysis standards.

3. Field Analysis

To support the laboratory results and document the topographic and hydromorphological characteristics of the study sites, a series of field measurements were conducted. A high-precision Global Positioning System (GPS) was used to record the river's longitudinal profiles at each station and accurately identify topographic variations, enabling a three-dimensional visualization of the longitudinal and flow variations in the Shatt al-Hilla River.

In addition, the locations of key geomorphological features, such as riffles, pools, and armored beds, were identified using field photography and detailed maps at a scale of 1:500. This procedure was used to document spatial changes between the two study seasons (autumn and spring) and to monitor any shifts resulting from calcite deposition or changes in flow behavior.

This field documentation has contributed to understanding the spatial context of calcite deposition processes and linking them to the morphological characteristics of the river channel, providing a basic foundation for conducting an integrated spatial analysis between chemical and geomorphological variables.

4. Hydraulic Calculations

To assess the impact of hydrodynamic characteristics on calcite deposition and river channel stability, two key hydraulic parameters were calculated: **bottom shear stress (τ_b)** and **shear velocity (u^*)**. These

parameters were chosen for their critical role in understanding flow behavior and its effect on deposited layers.

Bottom shear stress was calculated using the following equation:

$$\tau_b = \rho g d S$$

The frictional velocity was calculated using the equation:

$$\sqrt{u_*} = \tau_b / \rho$$

Field data, specifically water depth and natural river gradient derived from GPS position readings and discharge measurements, were used to calculate key hydraulic parameters with high accuracy. These values were critical in characterizing the prevailing flow conditions at each site and assessing their suitability for stimulating or inhibiting calcite deposition.

5. Statistical Analysis

The study relied on statistical analysis as the primary tool for testing hypotheses and interpreting seasonal and spatial differences between the stations studied. SPSS (version 26) was used to conduct a series of descriptive and inferential statistical analyses, which included the following:

- **T-test:** It was used to test the statistical significance of differences in water chemical properties—including Ca^{2+} and Mg^{2+} concentrations and alkalinity—between fall and spring. The aim was to evaluate the seasonal effect on calcite deposition.
- **Pearson Correlation:** The linear correlation coefficient was calculated between the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio and the amount of precipitated calcite (mg/L). This was done to determine the strength and direction of the relationship between the balance of divalent ions and the chemical deposition behavior.
- **One-Way ANOVA (Analysis of Variance):** This was used to assess the statistical differences among the five study stations in terms of water properties and the level of calcite deposition, in order to determine the effect of geographical location on the studied parameters.

These analyses contributed to providing an accurate quantitative picture that supports the experimental results and enhances the reliability of the recommendations to be drawn later.

Results

Table 1: Values of τ_b and u^* for each station.

Station	Velocity U (m/s)	Depth d (m)	τ_b (Pa)	u^* (m/s)
St1	0.27	2.5	24.5	0.157
St2	0.51	3.8	37.3	0.193
St3	0.40	2.8	27.5	0.166
St4	0.49	5.7	55.9	0.236
St5	0.47	3.4	33.4	0.187

Table 2: T-test results between the two seasons.

Variable	Autumn Mean	Spring Mean	T-Value	P-Value	Significant Difference?
Ca Hardness	215.8	259.2	3.81	0.005	Yes
Mg Hardness	36.3	44.1	3.35	0.008	Yes

Table 3: Results of Pearson Correlation Analysis

Variables	R	P-Value	Significant Correlation?
Ca^{2+} - Calcite	0.92	0.001	Yes
Mg^{2+} - Calcite	0.88	0.004	Yes

Table 4: Results of ANOVA between stations

Variable	F-Value	P-Value	Significant Differences?
Calcite	5.42	0.013	Yes
Ca Hardness	4.88	0.018	Yes

Mg Hardness	3.76	0.029	Yes
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Results of Physicochemical Properties and Calcite Concentrations

Table 5: Physicochemical properties of Shatt al-Hillah water during Autumn 2024.

Station	pH	EC (µS/cm)	TDS (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)
St1	6.76	1224	761	142.9	1080.4	4.33	16.91
St2	6.68	1198	773	135.6	979.1	3.33	14.21
St3	6.86	1191	760.7	145.3	810.3	3.33	13.25
St4	6.66	1248	795.7	157.5	827.2	3.53	13.66
St5	6.59	1165	770	136.8	759.6	3.17	12.35

Table 5: Concentrations of Calcite and Major Ions Contributing to Total Hardness in Shatt al-Hillah Water during Autumn 2024.

Station	Ca Hardness (mg/L)	Mg Hardness (mg/L)	Phosphate (µg/L)	Sulfate (mg/L)	Calcite (mg/L)
St1	253	40.9	780	2.17	120
St2	233	38.4	600	1.97	105
St3	200	34.3	600	1.67	90
St4	203	34.7	630	1.77	95
St5	190	33.1	570	1.58	80

Table 6: Physicochemical properties of Shatt al-Hillah water during Spring 2025.

Station	pH	EC (µS/cm)	TDS (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)
St1	8.12	1468	913.2	171.42	936	20.29	2.64
St2	08.01	1437	927.6	162.78	720	17.05	2.34
St3	8.23	1429	912.8	174.54	720	15.92	02.04
St4	7.99	1497	954.8	188.94	756	16.32	2.11
St5	7.91	1398	924.9	164.16	684	14.82	1.89

Table 7: Concentrations of Calcite and Major Ions Contributing to Total Hardness in Shatt al-Hillah Water during Spring 2025.

Station	Ca Hardness (mg/L)	Mg Hardness (mg/L)	Phosphate (µg/L)	Sulfate (mg/L)	Calcite (mg/L)
St1	303	49.7	1296	5.19	198
St2	279	46.1	1175	3.99	165
St3	240	41.2	972	3.96	150
St4	246	43.7	993	4.72	160
St5	228	39.7	912	3.84	140

Figure2: Ions contributing to total hardness in Shatt al-Hillah water during Autumn 2024.

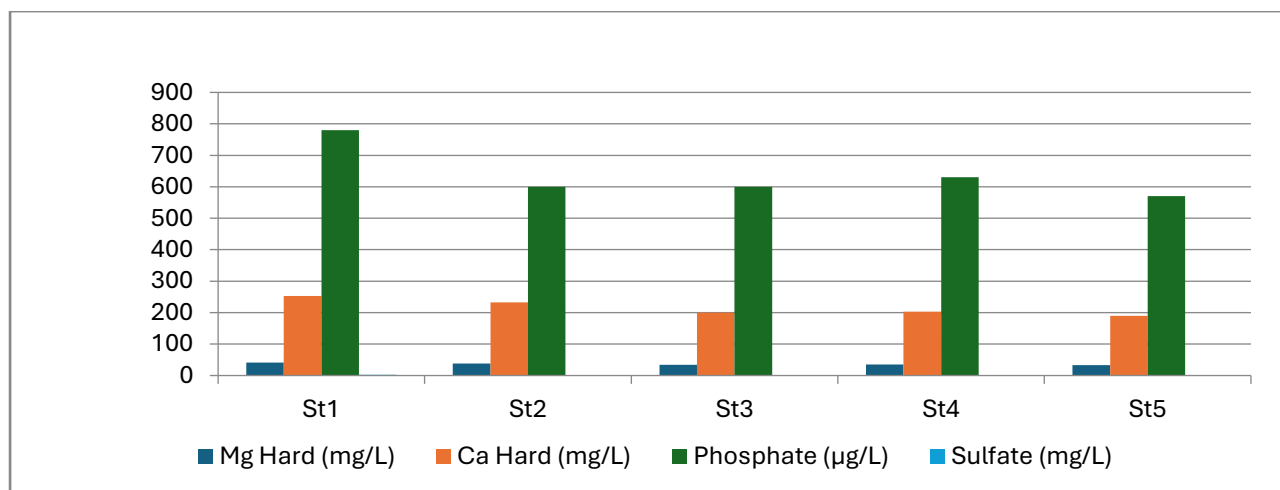


Figure 3: Variation of ions contributing to chemical hardness in Shatt al-Hillah water during the Spring 2025 season.

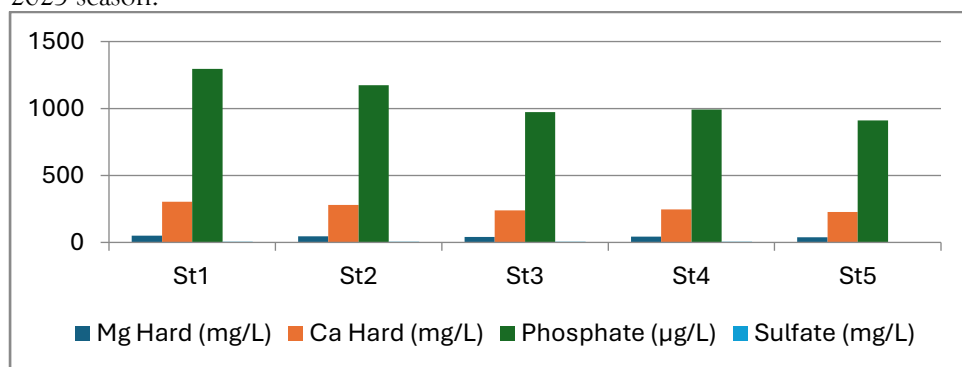


Figure4: Shows the variation in chemical hardness concentrations (Ca^{2+} and Mg^{2+}) at the study stations during the fall.

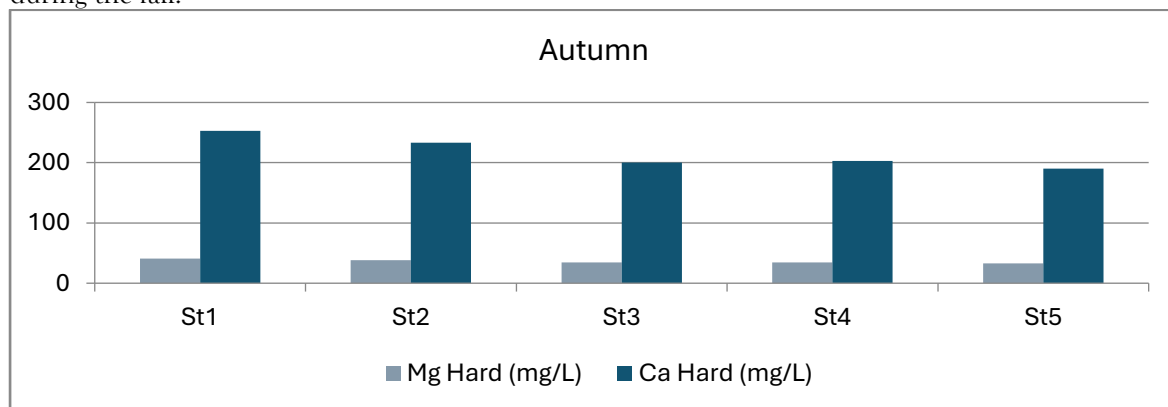


Figure5: Shows the variation in chemical hardness concentrations (Ca^{2+} and Mg^{2+}) at the study stations during the spring season.

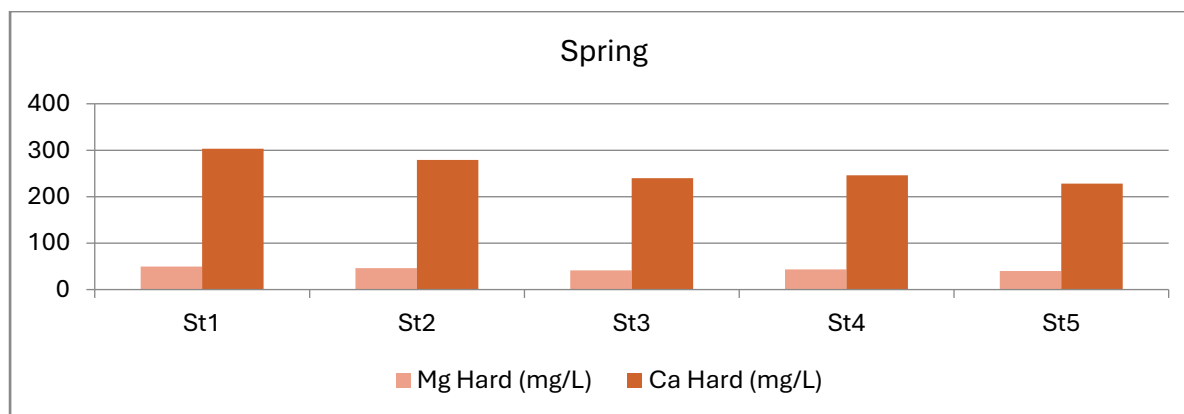
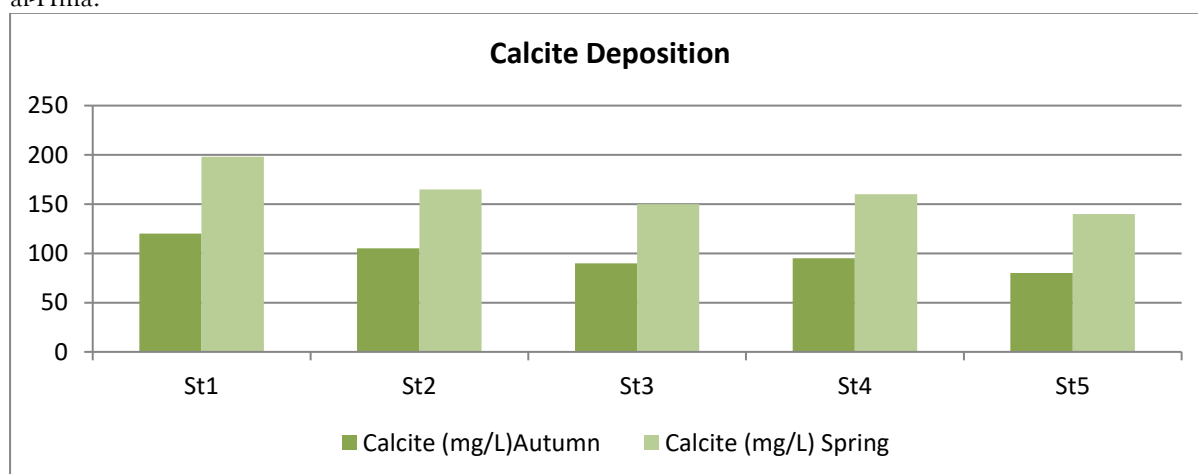


Figure 6: Shows calcite concentrations during the fall of 2024 and spring of 2025 in the waters of Shatt al-Hilla.



DISCUSSION

The study results revealed a notable increase of approximately 66% in the amount of precipitated calcite between the autumn and spring seasons, reflecting a clear seasonal variation in the dynamics of chemical hardness. This increase is attributed to the elevated pH levels observed in the spring of 2025 compared to autumn 2024, coinciding with a rise in calcium ion (Ca^{2+}) concentrations. These conditions created a carbonate-saturated aquatic environment that promoted the precipitation of larger quantities of calcite. Linear correlation analysis ($r = 0.92$) indicated a strong relationship between the hardness balance ($\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio) and the amount of precipitated calcite, particularly in hydraulically calm areas where low flow velocities enhance the stability of sediment deposition. This supports the study's central hypothesis regarding the role of chemical hardness in stimulating the formation of consolidated calcareous layers.

Geomorphologically, field observations during the autumn season revealed a Plane Bed channel pattern, with a thin clay layer at station St3 and the emergence of calcite-sand riffles at station St4, while laminated layers were entirely absent. In contrast, the spring season exhibited a transition toward a more complex Riffle-Pool pattern, coinciding with increased chemical activity leading to calcite precipitation.

Laminated (Armored) Layers ranging from 4 to 6 cm in thickness were documented at stations St1 and St4, indicating that chemical precipitation influenced not only the environmental context but also the geomorphological characteristics of the river channel by stabilizing the bed and enhancing resistance to erosion.

UNCERTAINTY ANALYSIS

An uncertainty analysis was conducted to estimate the impact of field and laboratory measurement errors on the accuracy of the calculated hydraulic indicators, specifically bed shear stress (τ_b) and friction velocity (u_*).

1. Friction Velocity (u_*):

The uncertainty associated with u_* was calculated as a direct result of inaccuracies in field measurements of flow depth and channel slope. The margin of error in these measurements was found to be approximately ± 0.02 m/s, representing nearly 2% of the recorded value.

2. Bed Shear Stress (τ_b):

The estimation of uncertainty in τ_b values was based on the precision limits of the instruments used to measure slope and depth. The cumulative error for this indicator was estimated at around $\pm 10\%$, attributed to the interdependence of the measurement variables in the final calculation.

This analysis indicates that, although the study relies on field-based measurements, the results fall within acceptable error margins for hydrological studies, thereby reinforcing the reliability of the research conclusions and the accuracy of the models employed.

CONCLUSIONS

This study concluded that calcite precipitation in the Shatt Al-Hillah channel is directly influenced by chemical factors associated with water hardness, particularly calcium ion concentration and pH levels. Laboratory and field analyses revealed a significant increase—approximately 66%—in calcite deposition during the spring season compared to autumn, a statistically meaningful rise that supports the hypothesis that elevated pH and increased Ca^{2+} concentrations create a carbonate-saturated environment conducive to chemical precipitation.

The study also demonstrated a very strong correlation ($r = 0.92$) between the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio and calcite precipitation, indicating that the imbalance of this ionic ratio serves as a sensitive indicator of chemical precipitation activity. This finding is of substantial importance in the context of water quality monitoring and river channel management.

From a geomorphological perspective, field observations showed that increased calcite deposition was accompanied by a morphological transition of the channel from a Plane Bed pattern in autumn to a more complex Riffle–Pool structure in spring. Additionally, the formation of laminated (Armored) Layers with thicknesses ranging between 4–6 cm at certain stations reflects the interplay between chemical changes and morphological transformations.

Collectively, these findings highlight the importance of integrating chemical and hydraulic indicators in evaluating river channel stability, particularly in agricultural regions subject to pronounced seasonal variations. They also underscore the need for continuous monitoring of the factors influencing calcite precipitation within the broader framework of sustainable water resource management.

RECOMMENDATIONS

Based on the findings of this study, the following recommendations are proposed for water resource and environmental management authorities:

1. Addressing Chemical Hardness at Water Entry Points:

It is recommended to mitigate chemical hardness at irrigation system entry points, particularly at stations St3 and St4, due to the elevated concentrations of calcium and magnesium, which may negatively affect soil efficiency and alter flow behavior within the channel.

2. Utilization of Naturally Formed Armored Layers:

The naturally occurring armored layers can be leveraged to enhance protection of the channel bed against erosion and scouring, especially in areas with low bed shear stress. These layers may be further reinforced using riprap techniques in stations with higher flow rates.

3. Monitoring Phosphate Concentrations in Autumn:

Regular monitoring of phosphate concentrations during the autumn season is advised to limit eutrophication, which could disrupt the ecological balance of the aquatic system.

4. Implementation of Localized Water Treatment Units:

The application of localized treatment units, such as ion exchange systems or chelating agents, with an operational capacity of 100 m³/h and an estimated cost ranging between \$500–800, is recommended to reduce water hardness and improve water quality before its entry into channels or agricultural fields.

5. Integration of Chemical Hardness into River Channel Evolution Models:

It is essential to incorporate the effects of chemical hardness into models of river channel evolution, linking chemical and hydromorphological characteristics of the stream. This integration would support the development of future scenarios that promote sustainable environmental management and enhance the resilience of hydrological systems to seasonal changes.

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