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STRONTIUM IN GROUNDWATER AS AN INDICATOR OF DEEP AQUIFER MIXING

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Abstract: Strontium (Sr) is a naturally present trace element in groundwater, and its concentration can vary widely depending on geology, hydrochemistry, and climate. This study integrates the geochemical behaviour of Sr in groundwater environment, emphasizing its sources, mobility, and potential as a tracer of deep groundwater mixing. Sr usually originates from the dissolution of carbonate, sulphate, and silicate minerals, with carbonate aquifers often contributing the highest concentrations. Its mobility is governed by pH, competing ions, ionic strength, and residence time, while redox conditions exert only indirect effects through mineral solubility. Typical concentrations range from <1 mg/L in shallow fresh recharge zones to >10 mg/L in deep, mineralized, or saline systems. High Sr levels in shallow aquifers may indicate deep groundwater input, particularly when accompanied by elevated total dissolved solids or other tracers. The research highlights Sr’s utility as a conservative tracer when a significant geological difference exists between shallow and deep aquifers. Understanding the concentration data requires considering local geochemical processes, co-precipitation and evaporation. When used in combination with other hydrochemical indicators, Sr concentration can present a valuable tool for identifying groundwater mixing and tracing water-rock interactions over varying spatial and temporal scales.

Key words: groundwater mixing, strontium, tracer

INTRODUCTION

Sr is an alkaline earth metal (Group 2) that commonly occurs as a trace element in rocks, soils, and natural waters [1]. Strontium is a widespread constituent in groundwater, as evidenced by a comprehensive survey of U.S. aquifers that detected its presence in 99.8% of analysed samples [1]. It is typically present as the divalent cation Sr^{2+} in solution, and its concentration depends on water-rock interactions. The primary sources of Sr in groundwater are the dissolution of minerals that contain Sr either as a constituent or by isomorphic substitution. The most studied Sr-bearing minerals include carbonates, sulphates, and silicates. In carbonate minerals such as calcite and dolomite, strontium commonly substitutes for calcium, leading to elevated Sr concentrations in groundwater from carbonate aquifers [2]. Among sulphate minerals, celestite ($SrSO_4$) directly contributes strontium, while gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite often contain Sr as an impurity. Silicate minerals, including feldspars ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) and clays, may also release Sr during the weathering of aluminosilicate rocks. This process is typically slower and yields lower concentrations of Sr compared to carbonates [3]. Under natural conditions, typical Sr concentrations in fresh groundwater are on the order of tenths to a few mg/L. A global survey of freshwater indicates background Sr levels around 0.5 - 1.5 mg/L [2]. In many young, shallow aquifers with limited mineral contact, Sr remains <1 mg/L (for example, the median Sr in above 4,800 U.S. groundwater samples was 0.225 mg/L) [1]. Groundwater in carbonate-rich aquifers typically contains the highest strontium concentrations, due to mineral dissolution processes. Similarly, aquifers in arid regions can exhibit elevated Sr levels as a result of evaporative concentration [1]. While low Sr is common in dilute recharge, values of several mg/L or more may occur where geology and climate favour Sr enrichment.

MATERIAL AND METHODS

This study synthesizes current geochemical understanding of Sr behaviour in groundwater environment by integrating hydrochemical data from global case studies and previously published datasets, primarily from the U.S. Geological Survey (USGS), peer-reviewed literature, and regional hydrogeological surveys. Strontium concentrations and associated hydrochemical parameters were examined across various aquifer settings, including carbonate-rich, arid, and saline environments. Special attention was given to aquifer depth, residence time, mineral composition, redox conditions, and evaporative influences as controlling factors for Sr mobility and distribution.

RESULTS AND DISCUSSION

Strontium concentrations in groundwater exhibit systematic variations across different aquifer types and hydrogeological settings. Analysis of published data reveals a clear trend of increasing Sr levels with longer residence time, higher mineralization, and the influence of saline or evaporative processes.

In shallow, fresh recharge zones, typically in humid climates and karstic terrains, Sr concentrations are generally low, ranging from 0.1 to 0.5 mg/L. These systems exhibit minimal water-rock interaction and limited dissolution of Sr-bearing minerals. In contrast, shallow aquifers located in arid or semi-arid environments show significantly higher concentrations, between 1 and 5 mg/L, primarily due to evapoconcentration, irrigation return flow, and longer groundwater residence time.

Deep, confined aquifers in carbonate or evaporite-rich formations often contain Sr concentrations exceeding 4 mg/L, with typical values between 1 and 10 mg/L. This is attributed to prolonged contact with Sr-bearing carbonates and sulphates. The highest concentrations, often ranging from 5 to over 20 mg/L, are observed in deep saline or fossil groundwater, particularly in areas affected by upwelling brines or ancient seawater intrusion.

An overview of these patterns is shown in Table 1, which lists typical Sr concentrations and the corresponding geochemical conditions for each aquifer type.

Table 1. *Representative strontium concentrations across different aquifer settings*

Aquifer Setting	Typical Sr Concentration	Geochemical Context and Source Description
Shallow, fresh recharge (humid climate, short flow path; e.g., karst springs)	≈0.1–0.5 mg/L (typically <1 mg/L)	Limited water-rock interaction leads to low Sr mobilization. Sr concentrations reflect the geochemistry of shallow, young groundwater. [1]; [4]
Shallow, arid or evaporative (unconfined aquifers, high evapotranspiration or irrigation)	≈1–5 mg/L	Increased residence time and evapoconcentration enhance Sr levels, often along with higher total dissolved solids (TDS), Cl^-, and Na^+. [1]
Deep, long-residence freshwater (confined carbonate or evaporite aquifers)	≈1–10 mg/L (often >4 mg/L)	Prolonged contact with Sr-bearing minerals such as carbonates and sulphates leads to higher Sr concentrations. [1]; [4]

Deep, saline or fossil groundwater (brine or paleo-seawater mixing)	5–20 mg/L	High Sr reflects mixing with ancient marine-derived waters or upwelling brines. Modern seawater contains ~8 mg/L Sr. [1]

Sr Mobility and Controlling Hydrochemical Factors

Once released from minerals, Sr^{2+} behaves geochemically similarly to Ca^{2+} in groundwater. Its mobility and concentration are influenced by several the most influential hydrochemical parameters. Groundwater pH controls and significantly impacts the dissolution and precipitation of carbonate minerals. Under neutral to moderately acidic conditions, calcite and dolomite dissolve, releasing Sr^{2+} alongside Ca^{2+}. Sr mobility peaks during early water-rock interactions. As calcite saturation is reached, Sr may co-precipitate or become incorporated into carbonate minerals, particularly in systems with high carbonate alkalinity. In high-pH environments, strontianite ($SrCO_3$) or mixed Ca-Sr carbonates may form, decreasing Sr concentrations in solution.

Elevated Ca^{2+} can induce common ion effects and promote calcite precipitation, which also removes Sr. Due to its larger ionic radius, Sr^{2+} is less readily incorporated into calcite, often remaining longer in solution. Sr/Ca ratios in groundwater can reveal selective incorporation patterns. Strontium can also be temporarily retained through ion exchange with clays and freshly formed minerals, but once those exchange sites become saturated, Sr tends to remain in solution [3].

Sr remains in the +2 oxidation state and is largely redox-independent. However, redox can influence cooccurring elements such as sulphate. In reducing environments, sulphate reduction may dissolve Sr-bearing sulphate minerals. In contrast, under oxidizing conditions, precipitation of celestite ($SrSO_4$) may occur if sulphate and Sr concentrations are high [5].

There is significant positive correlation between TDS and elevated Sr levels. Saline environments, whether from marine intrusion, evaporation, or brines, maintain Sr in solution due to complexation and suppressed mineral precipitation [1]. Marine-derived groundwater or paleoseawater often contributes significantly to increase of Sr concentrations, with ocean water containing ~8 mg/L Sr.

Prolonged water-rock interaction enhances Sr mobilization in water solution. While carbonates rapidly release Sr, silicate minerals contribute more gradually. Older, deeper groundwater typically shows higher Sr due to cumulative dissolution over time.

High Sr levels in shallow aquifers often serve as a geochemical indicator of mixing with deeper groundwater. Deep carbonate systems often exceed 4 mg/L Sr due to extended interaction with Sr-bearing lithologies. If such indications are found in overlying shallow wells, upward leakage may be occurring. In semi-arid regions, evaporation concentrates Sr and other solutes in shallow aquifers. These elevated levels may mimic deep water inputs but can be distinguished through isotopic analysis and simultaneous determination of chloride, sulphate, and TDS [2], [6]. The most distinct source of high Sr is up-coning of deep, saline groundwater. These waters are enriched in Sr due to ancient seawater origins and extensive geochemical aging.

Strontium Isotopes (^87Sr/^86Sr) as Tracers of Aquifer Mixing

Strontium has four stable isotopes, of which ^{87}Sr is radiogenic and formed through the decay of ^{87}Rb. Because the $^{87}Sr/^{86}Sr$ ratio varies depending on lithology and geological age, it can be used as a powerful natural tracer for groundwater source and mixing processes identification. Groundwater receives its isotopic signature through water-rock interaction, and variations in $^{87}Sr/^{86}Sr$ reflect differences in mineralogy and rock age across aquifer systems. For example, studies in the Yucatan Peninsula demonstrated that $^{87}Sr/^{86}Sr$ ratios can clearly distinguish between freshwater recharge and mixing with seawater or older marine-derived waters [7]. In fractured granite aquifers in Korea, Sr isotopic ratios revealed limited mixing between deep geothermal and shallow meteoric waters, indicating slow exchange and long residence times [8].

Strontium isotopes are especially valuable for distinguishing deep from shallow groundwater origin in systems where the results of conventional tracers may be ambiguous. In the Eastern Snake River Plain (Idaho), combining $^{87}Sr/^{86}Sr$ ratios with uranium isotopes enabled quantification of mixing between distinct aquifer zones [9]. Likewise, in Taiwan's Choushui River alluvial fan, $^{87}Sr/^{86}Sr$ ratios differentiated paleo-seawater contributions from recent recharge, highlighting their utility in coastal aquifers [10].

In areas influenced by salinity or brines, the $^{87}Sr/^{86}Sr$ ratio often shifts away from modern seawater values (≈0.7092), pointing to older marine inputs or long-term geochemical evolution. These variations can help distinguish whether elevated Sr comes from ancient seawater mixing, evaporation, or the dissolution of local minerals [7], [10].

CONCLUSION

Sr exhibits several geochemical characteristics that support its use as a tracer for detecting deep groundwater contributions to shallow aquifers. Its solubility, conservative behaviour under most redox and biological conditions, and typically distinct concentration gradient between shallow and deep groundwater make it a useful indicator of mixing processes. In systems where deep, mineralized groundwater with elevated Sr concentrations enter shallow zones with low Sr background, even small mixing inputs can produce detectable shifts in concentration.

Although elevated Sr levels can suggest a deep source, they may also result from local processes such as evaporation or lithological release, making it difficult to distinguish. Shallow aquifers in arid regions or carbonate-rich regions may naturally contain elevated Sr, making it difficult to distinguish deeper inflow impacts from local influences. Under specific geochemical conditions, such as sulphate-rich or carbonate-saturated environments, Sr may precipitate as celestite ($SrSO_4$) or co-precipitate with calcite, reducing its dissolved concentration and affecting its tracer behaviour.

Despite these limitations, Sr remains a valuable component in a multi-tracer framework. When there is a complementary interpretation with other indicators like Cl^-, Br^-, Li^+, or isotopic ratios (e.g., $^{87}Sr/^{86}Sr$), Sr concentrations can provide robust evidence for identifying deep groundwater mixing. Elevated Sr in shallow aquifers, particularly when accompanied by increased total dissolved solids, specific ions, or isotopic signatures, strongly suggests influence from older, deeper, or more mineralized groundwater sources.

Strontium proves to be a feasible and effective tracer for identifying deep groundwater contributions, particularly when interpreted within a broader hydrogeochemical context.

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