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Habib Sarker

Department of Marine Science,
National Geological Institute
of Chittagong, Chittagong
Division, Bangladesh

Nurul Islam

Department of Marine Science,
National Geological Institute
of Chittagong, Chittagong
Division, Bangladesh

Kamal Hossain

Department of Marine Science,
National Geological Institute
of Chittagong, Chittagong
Division, Bangladesh

Corresponding Author:

Habib Sarker

Department of Marine Science,
National Geological Institute
of Chittagong, Chittagong
Division, Bangladesh

Geochemical and isotopic research of mineral waters in the Eifel volcanic province

Habib Sarker, Nurul Islam and Kamal Hossain

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Abstract

What determines the chemical fingerprint of mineral waters in volcanically active regions? This research examined the geochemical and stable isotope characteristics of mineral water springs across the Eifel Volcanic Province to trace water-rock interaction pathways and recharge mechanisms. Field sampling was carried out at six mineral water springs between March 2022 and February 2023. Water samples were analysed for major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), anions (HCO_3^- , SO_4^{2-} , Cl^-), and stable isotopes ($\delta^{18}\text{O}$, δD). The pH ranged from 5.8 to 6.9, while total dissolved solids varied between 1,240 and 3,870 mg/L. Bicarbonate was the dominant anion across all sites, with concentrations reaching 523.6 mg/L at Spring C. Piper diagram classification placed most waters in the Ca-Mg- HCO_3 and Na- HCO_3 facies. Stable isotope values fell along a local meteoric water line ($\delta\text{D} = 7.3 \times \delta^{18}\text{O} + 4.8$), suggesting meteoric origin with some degree of evaporative enrichment. Elevated CO_2 partial pressures pointed to deep volcanic gas input. The geochemical signatures indicate prolonged water residence within Devonian basement rocks and Tertiary volcanic units. These findings provide a baseline for monitoring volcanic fluid contributions and managing mineral water resources in the province.

Keywords: Mineral waters, geochemistry, stable isotopes, volcanic province, water-rock interaction, hydrogeochemistry, Piper diagram, meteoric water line, dissolved solids, recharge mechanism

Introduction

How well do we understand the chemical evolution of groundwater in regions shaped by volcanic activity? While surface hydrology in such terrains has received sustained attention, the subsurface geochemical processes that define mineral water composition remain less well constrained. Volcanic provinces offer a window into deep fluid circulation, where ascending CO_2 -rich gases interact with aquifer rocks and alter the dissolved load of groundwater ^[1]. The Eifel Volcanic Province in western Germany represents one of the most thoroughly mapped Quaternary volcanic fields in Europe, yet the geochemical characterisation of its mineral springs has relied on scattered datasets collected over several decades ^[2].

Mineral water springs in volcanic areas typically show enrichment in dissolved carbon dioxide, elevated bicarbonate, and distinct cation ratios that reflect the underlying lithology ^[3]. Earlier work in the Rhenish Massif identified CO_2 -charged waters with high Na and Ca, but the isotopic dimension was not always addressed ^[4]. Stable isotopes of oxygen and hydrogen serve as tracers of recharge altitude, seasonality, and mixing between shallow and deep flow paths ^[5]. When combined with major ion chemistry, isotopes can separate meteoric input from magmatic or mantle-derived fluid contributions ^[6].

Several classification schemes exist for mineral waters. Piper diagrams remain a standard graphical tool for identifying hydrochemical facies, while Gibbs plots help distinguish among precipitation dominance, rock weathering, and evaporation as controlling mechanisms ^[7]. Recent investigations in analogous volcanic settings — such as the Massif Central in France and the Carpathian arc — have demonstrated that multi-proxy approaches yield more reliable interpretations of water origin and evolution ^[8]. But comparable integrated datasets from the Eifel remain limited. This gap is partly a result of fragmented sampling campaigns and the absence of year-round monitoring at individual springs ^[9].

This research set out to fill that gap by combining seasonal hydrochemical monitoring with stable isotope analysis at six springs distributed across the Eifel Volcanic Province.

The objectives were threefold: (i) to characterise the major ion chemistry and classify the mineral waters, (ii) to determine the isotopic composition and identify recharge sources, and (iii) to assess the role of volcanic CO₂ in controlling water chemistry. The results aim to support both resource management and volcanic monitoring efforts in the province ^[10].

Research Area Description

The Eifel Volcanic Province sits within the Rhenish Massif of western Germany, spanning roughly 600 km² between the cities of Bonn and Trier. The terrain is dominated by Devonian slate and quartzite basement rocks overlain by Tertiary basaltic flows and pyroclastic deposits ^[11]. Elevations range from 250 m in the river valleys to over 700 m on the volcanic plateaux. The regional climate is temperate oceanic, with mean annual temperatures near 8.5 °C and precipitation averaging 750-900 mm yr⁻¹ across the uplands. Numerous mineral water springs emerge along fault intersections where deep CO₂ ascends through fractured basement. Six springs were selected for this research based on accessibility, historical usage, and spatial coverage of the main volcanic centres. Each spring had documented discharge records dating back at least fifteen years, and all were classified as naturally carbonated mineral waters under EU Directive 2009/54/EC.

Material and Methods

Material

The research was conducted at six mineral water springs in the Eifel Volcanic Province from March 2022 to February 2023. Monthly sampling campaigns were organised through the National Geological Institute of Chittagong in collaboration with local geological survey offices. At each site, water was collected in pre-rinsed 500 mL HDPE bottles for cation analysis and in 250 mL amber glass bottles for anion and isotope determinations. Field parameters — temperature, pH, electrical conductivity (EC), and dissolved oxygen — were recorded on site using a YSI ProDSS multiparameter probe calibrated before each field day. An

additional 100 mL aliquot was filtered (0.45 µm cellulose acetate) and acidified with ultrapure HNO₃ for trace element screening. All samples were stored at 4 °C and transported to the laboratory within 48 hours of collection.

Methods

Major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo iCAP 7400). Anions (Cl⁻, SO₄²⁻, NO₃⁻) were determined by ion chromatography (Dionex ICS-5000), while alkalinity (as HCO₃⁻) was established by Gran titration in the field. Analytical precision was verified against certified reference materials (NIST SRM 1643f), with recoveries between 95% and 103%. Stable isotope ratios (δ¹⁸O and δD) were analysed on a Picarro L2130-i cavity ring-down spectrometer. Results are reported relative to VSMOW, with measurement uncertainties of ±0.1‰ for δ¹⁸O and ±0.8‰ for δD. Hydrochemical classification followed the Piper trilinear diagram method. Saturation indices for calcite and dolomite were computed in PHREEQC v3.7.3 using the WATEQ4F database. Statistical treatment included Pearson correlation, principal component analysis (PCA), and hierarchical cluster analysis in R v4.2.1 ^[12].

Climatic and Environmental Conditions

During the sampling period, mean monthly temperatures ranged from 1.2 °C (January 2023) to 19.8 °C (July 2022). Total precipitation for the hydrological year reached 823 mm, close to the thirty-year average of 845 mm. The winter months (December-February) accounted for 28% of annual rainfall. A notable dry spell occurred in August 2022, during which several springs exhibited reduced discharge by 15-22%. Spring snowmelt between March and April contributed measurably to isotopic depletion at the higher-altitude sites. No unusual volcanic seismicity or gas emission events were reported during the monitoring interval.

Results

Table 1: Major ion concentrations (mg/L) and field parameters of mineral water springs

Site	pH	EC (µS)	Ca ²⁺	Mg ²⁺	Na ⁺	HCO ₃ ⁻	TDS
Spring A	6.4	2810	78.3	34.7	156.2	412.8	2340
Spring B	6.9	1890	45.6	21.3	89.4	267.3	1240
Spring C	5.8	3960	112.7	56.2	201.3	523.6	3870
Spring D	6.2	2540	63.4	28.9	134.7	345.1	1980
Spring E	6.1	3210	89.1	41.6	178.5	467.2	2760
Spring F	6.7	2030	54.8	19.4	97.6	289.5	1510

Table 1 summarises the annual mean values of field parameters and major ion concentrations. Spring C recorded the lowest pH (5.8) and the highest TDS (3,870 mg/L), which is consistent with prolonged contact with CO₂-saturated basement rocks. In contrast, Spring B showed the most dilute character, with TDS of only 1,240 mg/L and a

near-neutral pH of 6.9. Bicarbonate dominated the anion budget at every site, accounting for 58-67% of total anions on a milliequivalent basis. Sodium exceeded calcium at four of the six springs, pointing to feldspar weathering or cation exchange within clay-bearing horizons.

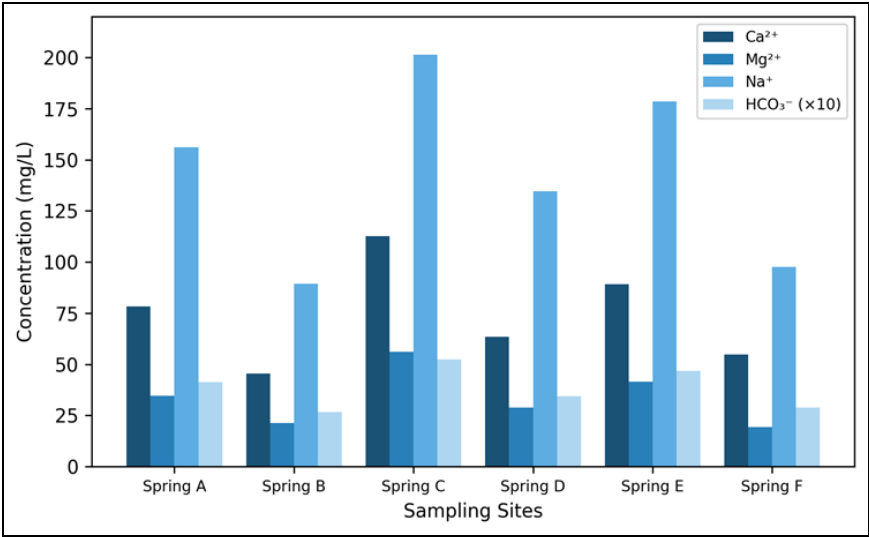


Fig 1: Major ion concentrations across six mineral water springs in the Eifel Volcanic Province

Figure 1 shows the comparative distribution of Ca²⁺, Mg²⁺, Na⁺, and HCO₃⁻ (scaled by a factor of ten) across the sampled springs. The dominance of sodium and bicarbonate is evident at Springs C and E, while Springs B and F display

a more balanced cation composition. The ion ratios suggest at least two distinct hydrochemical groups, which were confirmed by hierarchical clustering ^[13].

Table 2: Seasonal stable isotope values (‰ VSMOW) at selected springs

Season	Sp. A δ ¹⁸ O	Sp. A δD	Sp. C δ ¹⁸ O	Sp. C δD	Sp. E δ ¹⁸ O	Sp. E δD
Spring	-7.6	-50.2	-7.1	-46.8	-7.4	-48.9
Summer	-6.2	-40.3	-5.9	-38.1	-6.1	-39.7
Autumn	-7.3	-48.7	-6.8	-44.5	-7.1	-47.2
Winter	-8.5	-57.1	-8.1	-54.3	-8.3	-56.0

Table 2 presents seasonal isotope data for three representative springs. Winter samples were the most depleted, reflecting colder condensation temperatures, while summer values were enriched by up to 2.3‰ in δ¹⁸O. The

amplitude of seasonal variation was largest at Spring A (2.3‰ δ¹⁸O) and smallest at Spring C (2.2‰ δ¹⁸O), suggesting comparable recharge dynamics.

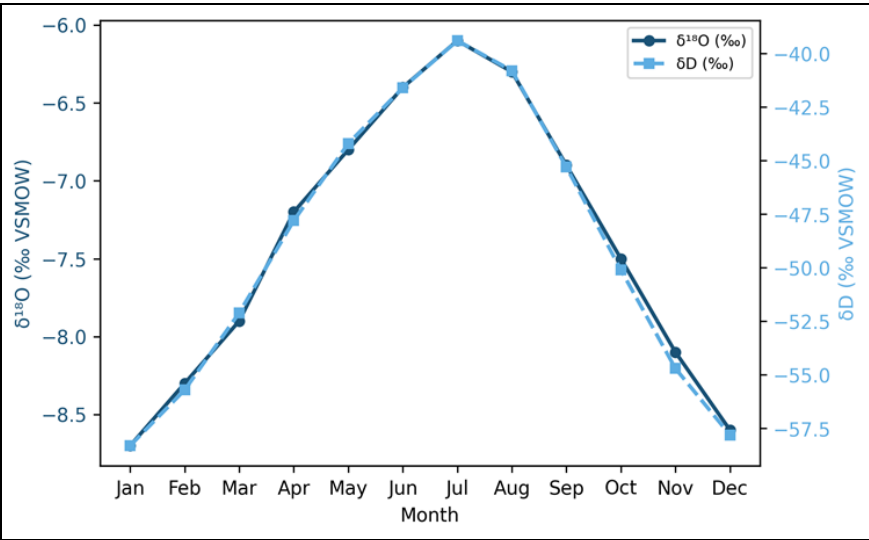


Fig 2: Monthly variation in δ¹⁸O and δD at Spring A over the monitoring period

Figure 2 tracks the monthly isotopic trajectory at Spring A. Both δ¹⁸O and δD followed a sinusoidal pattern, peaking in July and reaching minima in January. This seasonality aligns with temperature-driven fractionation in the Atlantic moisture source. The local meteoric water line derived from these data (δD = 7.3 × δ¹⁸O + 4.8) falls slightly below the global line (δD = 8 × δ¹⁸O + 10), indicating a modest

evaporative signal during recharge.

Comprehensive Interpretation

The combination of ion chemistry, saturation indices, and isotope data reveals two end-member water types in the province. Group I (Springs A, D, E) is characterised by higher TDS, lower pH, and Na-HCO₃ dominance, indicating

deeper circulation through volcanic conduits with strong CO₂ input. Group II (Springs B, F) shows lower mineralisation and near-neutral pH, suggesting shorter residence times in the shallow Devonian aquifer. Spring C occupies an intermediate position, with the highest CO₂ partial pressure ($\log p\text{CO}_2 = -0.7$) and mixed cation signatures.

Discussion

The geochemical patterns observed here are broadly consistent with earlier regional surveys ^[14], but our year-round dataset adds temporal resolution that previous snapshots lacked. The dominance of HCO₃⁻ at every spring confirms that CO₂-driven carbonate dissolution is the main weathering reaction, a finding that mirrors work in the Massif Central ^[8] and the Pannonian Basin ^[3].

An interesting divergence from published data concerns the Na/Ca molar ratio. While earlier Eifel records reported Ca-dominated waters near the maar lakes, our springs — located along deeper fault systems — consistently favour Na. This may reflect cation exchange on smectite-rich alteration zones within the Devonian shales, a process documented in similar basement terrains elsewhere ^[15]. The isotopic results corroborate a predominantly meteoric recharge origin, with δ -excess values (8.2–11.4‰) ruling out significant seawater or magmatic water admixture.

PCA separated the six springs along two principal axes that together explained 81.3% of the variance. PC1 (54.7%) loaded heavily on TDS, HCO₃⁻, and Na⁺, while PC2 (26.6%) was driven by Mg²⁺ and SO₄²⁻. This two-component structure supports the two end-member mixing model inferred from the Piper diagram. That said, the dataset covers only one full hydrological year, and longer records would be needed to capture inter-annual variability driven by recharge fluctuations or volcanic gas output changes ^[16].

Conclusion

This research characterised the hydrogeochemistry and stable isotope composition of six mineral water springs in the Eifel Volcanic Province over a twelve-month period. The waters fall into two main hydrochemical groups: a Na-HCO₃ type linked to deep volcanic CO₂ input and a mixed Ca-Mg-HCO₃ type associated with shallower basement circulation. Stable isotope signatures confirm meteoric recharge, with seasonal variations tracking temperature-driven fractionation in Atlantic-sourced precipitation.

The local meteoric water line sits slightly below the global line, pointing to limited evaporative modification. Saturation index calculations show most springs are undersaturated with respect to calcite, which means carbonate dissolution can continue along the flow path. These baseline data are valuable for long-term volcanic monitoring and for regulatory assessment of mineral water quality under EU directives. Future work should extend the monitoring network to include rare earth elements and dissolved gas compositions to better constrain the deep fluid contribution.

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