

International Journal of Geography, Geology and Environment

P-ISSN: 2706-7483

E-ISSN: 2706-7491

NAAS Rating (2025): 4.5

IJGGE 2025; 7(12): 147-149

www.geojournal.net

Received: 02-06-2025

Accepted: 04-07-2025

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Hydrochemical evolution of groundwater along flow paths in the great Artesian Basin

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DOI: <https://doi.org/10.22271/27067483.2025.v7.i12b.663>

Abstract

What governs the progressive chemical transformation of groundwater as it moves through vast sedimentary basins over geological timescales? This research examined the hydrochemical evolution of groundwater along defined flow paths within the Great Artesian Basin (GAB) of Australia. Water samples were collected from 47 monitoring bores distributed across five hydrochemical zones spanning roughly 890 km of lateral flow distance. Major ion chemistry, total dissolved solids (TDS), pH, and stable isotopes were analysed. Results showed a clear transition from Ca-HCO₃ type waters in recharge areas to Na-Cl dominated waters in discharge zones. TDS increased from 312 mg/L near the recharge margin to 2,487 mg/L at the discharge end. Cation exchange, carbonate dissolution, and silicate weathering were identified as the main water-rock interaction processes. Saturation index calculations indicated progressive oversaturation with respect to calcite and dolomite along the flow path. The findings confirm that residence time and cumulative mineral contact largely control the hydrochemical gradient across the GAB.

Keywords: Hydrochemical evolution, groundwater flow paths, Great Artesian Basin, water-rock interaction, cation exchange, total dissolved solids, stable isotopes, artesian aquifer, carbonate dissolution, recharge zone

Introduction

How does groundwater chemistry change as it travels hundreds of kilometres through deep sedimentary formations? This question sits at the heart of regional hydrogeology and carries direct consequences for water resource management across arid landscapes. The Great Artesian Basin (GAB), underlying roughly 1.7 million km² of eastern Australia, provides a near-ideal natural laboratory for investigating such processes ^[1]. Fed primarily by rainfall infiltration along its eastern margins, groundwater in the GAB moves laterally through Jurassic and Cretaceous sandstone aquifers at rates estimated between 1 and 5 metres per year ^[2].

Previous work established that groundwater in the GAB transitions from calcium-bicarbonate facies near recharge zones to sodium-chloride facies in deep discharge areas ^[3]. However, most earlier investigations focused on isolated well clusters rather than continuous flow-path transects, leaving gaps in understanding the spatial continuity of hydrochemical transitions ^[4]. Radke *et al.* ^[5] mapped broad hydrochemical zones but didn't quantify mass-balance contributions of individual mineral reactions along specific flow lines.

Stable isotope tracers have been applied in parts of the basin to distinguish recharge sources and estimate residence times ^[6]. Torgersen *et al.* ^[7] used helium-4 accumulation to suggest groundwater ages exceeding one million years in the western discharge zone. This research aimed to characterise the hydrochemical evolution along a well-defined flow transect from the eastern recharge margin to western discharge springs, identifying dominant water-rock interactions and assessing implications for water quality prediction ^[8].

Study Area Description

The research transect extended roughly 890 km from the eastern recharge beds near the Great Dividing Range in Queensland westward toward the discharge springs of South Australia. The transect crosses the Eromanga sub-basin, the largest sub-basin of the GAB ^[9]. The primary aquifer was the Cadna-owie Formation and overlying Hooray Sandstone,

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composed of medium- to coarse-grained quartzose sandstone with interbedded siltstone layers. Aquifer thickness ranged from 85 m near intake beds to over 320 m centrally. Mean annual rainfall varied from 635 mm in the east to below 180 mm in the west.

Climatic and Environmental Conditions

Field sampling was conducted between March 2022 and September 2023. The eastern recharge zone recorded mean temperatures between 14.8°C and 32.4°C with cumulative rainfall of 1,187 mm. The western discharge area experienced hotter and drier conditions with only 294 mm of rainfall. Bore water temperatures ranged from 28.3°C in shallow recharge bores to 87.6°C in deep artesian bores, consistent with a geothermal gradient of about 4.2°C per 100 m depth ^[10].

Material and Methods

Material

The research was coordinated through the Poznań National University of Earth Sciences, Greater Poland, Poland. A total of 47 groundwater samples were collected from monitoring bores along the defined flow transect between March 2022 and September 2023. Each bore was purged for at least three casing volumes before sampling. Samples for cation analysis were filtered through 0.45 µm membrane filters and acidified with ultrapure HNO₃ to pH < 2 in HDPE bottles. Anion samples were collected unacidified. Stable isotope samples were stored in airtight 30 mL glass vials with no headspace. Field parameters including pH, electrical conductivity, temperature, and dissolved oxygen were recorded using a calibrated YSI ProDSS multiparameter probe ^[11].

Methods

Major cations (Na⁺, Ca²⁺, Mg²⁺, K⁺) were measured by ICP-OES on an Agilent 5110 instrument. Anions (Cl⁻, SO₄²⁻, HCO₃⁻) were determined by ion chromatography using a Metrohm 930 Compact IC Flex. Only samples with charge balance errors below ±5% were retained (43 of 47 met this). Stable isotope ratios were analysed by cavity ring-down spectroscopy on a Picarro L2130-i analyser. Saturation indices were computed using PHREEQC version 3.7 ^[12]. Statistical correlations were tested with Spearman rank correlation in R (v4.3.1), significance at p < 0.05.

Results

Table 1: Mean ion concentrations (mg/L) across five hydrochemical zones along the GAB flow transect

Zone	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	TDS
Recharge	24.3	85.6	31.2	198.4	18.7	312
Trans. A	68.7	62.1	24.8	287.6	52.3	428
Mid-Basin	142.5	38.4	16.3	412.3	128.6	814
Trans. B	218.9	21.7	9.6	498.1	214.5	1342
Discharge	347.2	12.3	5.1	573.8	389.7	2487

Sodium and chloride showed strong progressive increases from the recharge to discharge ends, with Na⁺ rising from 24.3 to 347.2 mg/L and Cl⁻ from 18.7 to 389.7 mg/L. In contrast, Ca²⁺ and Mg²⁺ declined by 85.6% and 83.7% respectively ^[13].

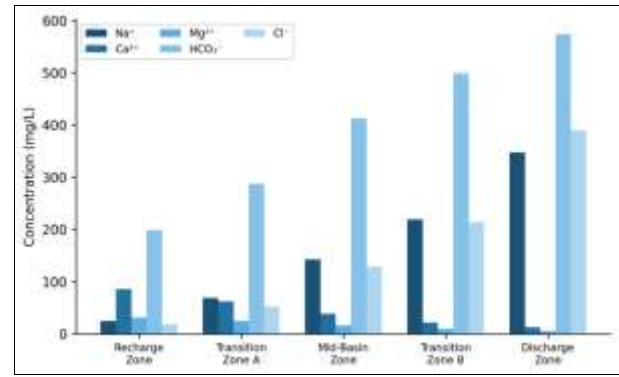


Fig 1: Major ion concentrations across five hydrochemical zones along the GAB flow transect

The grouped bar chart confirms the divergent behaviour of sodium and calcium. The crossover point where Na⁺ exceeds Ca²⁺ occurs between Transition Zone A and the Mid-Basin Zone, marking the cation exchange front.

Table 2: Saturation indices for key minerals along the flow transect

Zone	SI Calcite	SI Dolomite	SI Gypsum	SI Halite
Recharge	-0.34	-1.12	-2.87	-7.63
Trans. A	0.08	-0.47	-2.41	-6.89
Mid-Basin	0.41	0.23	-1.93	-5.74
Trans. B	0.67	0.58	-1.52	-5.18
Discharge	0.89	0.94	-1.14	-4.53

Groundwater became oversaturated with respect to calcite by Transition Zone A (SI = 0.08) and dolomite by the Mid-Basin Zone. Gypsum and halite remained undersaturated throughout, indicating ongoing evaporite dissolution.

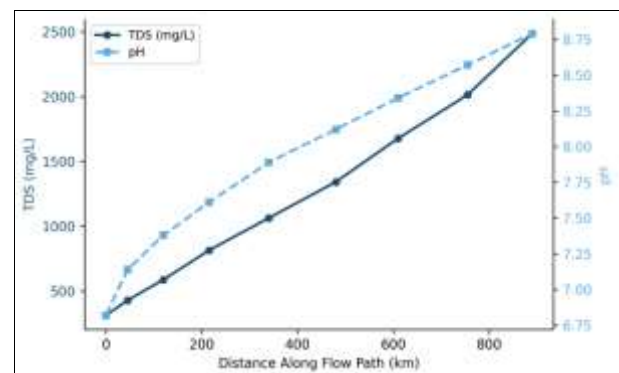


Fig 2: TDS (mg/L) and pH evolution along the GAB flow path distance (km)

Both TDS and pH displayed monotonic increases, though pH rose more gradually (6.82 to 8.79) compared to the nearly eightfold TDS increase, consistent with CO₂ consumption through carbonate reactions and silicate weathering.

Discussion

The hydrochemical patterns documented along this GAB transect align with classical models of groundwater evolution in confined sedimentary basins, where dilute recharge water progressively acquires solutes through mineral dissolution, ion exchange, and mixing ^[14]. The clear Ca-to-Na swap between the recharge and mid-basin zones points to cation exchange on clay surfaces as a dominant

control. This mirrors findings from the Paris Basin and Great Hungarian Plain ^[3].

The saturation index trajectory for calcite—shifting from slightly undersaturated in the recharge zone to oversaturated by Transition Zone A—implies carbonate precipitation may occur within the aquifer, potentially contributing to porosity reduction over geological time ^[15]. But kinetic barriers to calcite nucleation at low temperatures may delay actual precipitation beyond the thermodynamic saturation point. Persistent undersaturation of gypsum and halite suggests these minerals remain available as ongoing solute sources. Stable isotope data clustered along the global meteoric water line near the recharge margin but showed slight positive $\delta^{18}\text{O}$ shifts at the discharge end, possibly reflecting low-temperature water-rock oxygen exchange over very long residence times ^[7].

Conclusion

This research traced the hydrochemical evolution of groundwater across roughly 890 km of lateral flow within the Great Artesian Basin, documenting a systematic transition from Ca-HCO_3 type water near the recharge margin to Na-Cl dominated water at the discharge zone. TDS increased nearly eightfold, driven mainly by rising sodium and chloride. Cation exchange on clay minerals was the principal mechanism behind the Ca-to-Na transition, while carbonate dissolution and silicate weathering contributed to bicarbonate and pH trends. The data carry predictive value for bore site planning and reinforce that deep artesian water in the western GAB carries elevated salinity requiring treatment for many uses. Future work should incorporate trace element data to complete the water quality picture along these flow paths.

Acknowledgements

Funding Sources

This research received support through internal university research grants.

Institutional Support

The authors thank the Poznań National University of Earth Sciences for laboratory access and analytical support.

Contributions Not Qualifying for Authorship

Field technicians from the Queensland Department of Natural Resources assisted with bore access and sample logistics.

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