The Lithological Metabolic Switch:

How Sandstone Storage and Alluvial Attenuation Control the Fate of Urban Nitrogen in a Tropical Aquifer

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Rapid urbanization imposes massive nitrogen (N) loads to aquifers, yet the relationship between surface inputs and groundwater quality remains poorly constrained. This study reconstructs a century-scale (1910–2025) N mass balance for a catchment overlying the Bauru Aquifer System (Brazil), quantifying the role of lithological heterogeneity on contaminant fate. A cumulative effective load of ~2,403 t was estimated using historical urbanization metrics and Monte Carlo simulation (n=150,000). Modelled loads were validated against high-resolution soil core inventories (TKN) and hydrochemical tracers (NO_3^-, DO, DOC, Cl^-, $\delta^{18}O$-H_2O).

Results reveal a massive subsurface nitrogen legacy: 73% of the cumulative effective load (~1,756 t) remains stored within the catchment. Specifically, 56.6% (~1,361 t) is sequestered in the deep vadose zone (soil stock), while 16.4% (~395 t) is dissolved in the saturated zone (aquifer stock). Sensitivity analysis (Spearman Rank) identifies denitrification ($r = -0.65$) and sewer leakage ($r = 0.41$) as the primary drivers of groundwater N mass. To date, active removal via denitrification has eliminated only 13.4% of the total input.

Hydrochemical and isotopic indicators suggest that N removal is driven by a "lithological metabolic switch." The oxidized sandstone matrix acts as a long-term storage reactor (chemical time lag), whereas effective attenuation is restricted to organic-rich alluvial sediments in valley bottoms. This spatial decoupling between storage and removal explains the observed persistence of nitrate in the aquifer.

In conclusion, aquifer resilience relies on a fragile balance where the vadose zone delays contamination while riparian zones provide the sole active removal pathway. Monte Carlo forecasts indicate that even under a Zero Leakage Mitigation scenario, groundwater concentrations will peak in 2033, with full recovery (< 3 mg/L) requiring 100 years (by 2125). In a broader uncertainty context (90% confidence), recovery timescales range from 51 to 186 years, rendering standard short-term management policies insufficient for urban groundwater security in tropical regions.

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