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From Recharge to Rivers: Integrating Geochemical Tracers and Mixing Models to Assess Hydrosystem Vulnerability in an Agricultural Region (Montérégie, Québec, Canada)

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Understanding water and solute transfer dynamics within hydrological systems is essential for assessing water resource vulnerability. However, most vulnerability frameworks remain aquifer-focused and insufficiently integrate the role of the unsaturated zone (UZ) and groundwater-surface water exchanges [1,2].

This study applies isotopic ($\delta^{18}O$, $\delta^{2}H$) and geochemical (major ions) tracers within a mixing-model framework to quantify vulnerability along the transfer continuum from recharge to streams in an intensively agricultural region of southern Québec (Montérégie, Canada).

28 soil profiles (363 samples) were collected from the UZ and analyzed using a controlled leaching protocol to determine pore-water anion concentrations (Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) [3]. Chloride was used as a conservative tracer of evaporative enrichment, supported by line-conditioned-excess calculations derived from δ18O'-H2O' and $\delta^{2}H$'-H_2O' measurements. In parallel, weekly to fortnightly river sampling was conducted in four watersheds. Stable water isotopes ($\delta^{18}O$, $\delta^{2}H$) and major ions were used as tracers in a hydrograph deconvolution framework to quantify groundwater contributions relative to surface runoff [4,5].

Results show that solute dynamics in the UZ are primarily controlled by near-surface hydrological processes, with no systematic relationship between pore-water chemistry and mapped soil texture classes. Strong chloride enrichment within the upper 20 cm reflects evaporation-driven concentration. In contrast, nitrate does not scale proportionally with chloride as expected under purely evaporative conditions. Both excesses and deficits relative to conservative behaviour indicate coupled biogeochemical processes, including nitrification, denitrification, biological uptake, and agricultural inputs.

These processes define recharge chemistry and the groundwater endmember involved in streamflow mixing. Across the four watersheds, dissolved silica (SiO_2) emerged as a robust tracer of groundwater input, enriched during low-flow conditions and associated with isotope-derived baseflow contributions. Groundwater influence varied between catchments, reflecting differences in hydrological dynamics and vulnerability. Catchments with higher groundwater proportions exhibited more stable geochemical signatures and reduced sensitivity to recent surface inputs, whereas event-dominated systems showed greater short-term variability and higher vulnerability to surface-derived solutes.

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[5] Picard et al. (2026), J. Hydrol. 664, 134529.