Fingerprinting dissolved organic compounds: A potential tool for identifying the surface infiltration environments of meteoric groundwaters

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Current methods for tracing the surface infiltration of meteoric groundwaters rely on isotope geochemistry and dye tracers, which can be used to determine groundwater age and altitude at the point of infiltration. Temporal and spatial variability in atmospheric conditions, and water-rock interactions, can make the interpretation of isotopes uncertain. Low tracer recovery and long residence times often make dye tracers impractical. Here, we propose a new method of groundwater tracing based on fingerprinting of natural dissolved organics (derived from local flora and fauna). We validate our method at the Grimsel Test and Mont Terri underground rock laboratories in Switzerland, located within fractured crystalline rock (granite) and sedimentary systems, respectively. Based on a non-targeted approach using two-dimensional gas chromatography, we derive detailed organic fingerprints for groundwater, surface soils, and lakewater and river water samples from each location. These organic fingerprints are then compared to determine the near-surface infiltration environments feeding individual groundwater samples. Using principal component analysis, we show that individual groundwater samples can be identified as having derived from identifiable surface sources. Our research demonstrates that dissolved natural organic molecules, and their relative abundance, are sufficiently well-preserved in groundwater over timescales of several decades, that they can be used to discriminate the near-surface environment(s) through which meteoric groundwater has infiltrated. Organic fingerprinting could prove a powerful tool for an improved understanding of groundwater flow systems, particularly when used in combination with other complimentary tracing techniques.