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It's all about the baseline - geochemical perturbations in hydrochronology

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At surface recharge, atmospheric-equilibrated groundwater contains multiple geochemical components at trace levels, including short-lived isotopes (e.g. ^{3}H, ^{14}C, ^{81}Kr) produced via a combination of anthropogenic and natural processes. The initial concentrations of these 'tracers' are highly dependent on the environmental and geographic setting at the point of recharge. Once isolated from the surface, concentrations of these tracers progressively decrease over time through radioactive decay. Consequently, it is possible to constrain the last time surface-recharged groundwater was in contact with the atmosphere through precise measuring of the absolute and relative abundances of these degradative tracers compared to initial concentrations and stable isotope signatures. However, subsurface processes such as mixing, dissolution, and precipitation, can produce groundwaters with multiple components of different provenance. This can result in apparent temporal discrepancies between tracers which need to be considered when applying this kind of hydrochronologic modelling approach. One complex set of processes less commonly considered arises due to *in situ* subsurface production through naturally occurring nucleogenic reactions involving U and Th decay. Specifically, neutron capture reactions are known to produce ^{3}H, ^{14}C, ^{36}Cl, ^{39}Ar, and ^{81}Kr, in the host matrix as well as in any associated fluids[e.g.1-3]. Remarkably, to date, the dependence of geochemistry, host rocks and geologic settings and impact on such tracer production and alteration of “baseline” assumptions remains poorly constrained.

This study investigates how the geochemistry of the host rock and fluids control *in situ* production of tracers via neutron capture of parent elements. The rates and production routes of ^{3}H, ^{14}C, ^{36}Cl ^{39}Ar, and ^{81}Kr are modelled for a variety of host rock lithologies and fluids to evaluate the impact baseline fluid production may have on apparent residence times. This approach demonstrates how the combination of high radioelement concentration in host rocks, coupled with multiple parent elements in the fluids, may result in non-negligible effects for ^{36}Cl, ^{39}Ar, (and potentially ^{14}C)-derived residence times, while ^{3}H and ^{81}Kr remain principally related to surficial recharge.

[1]Andrews et al. (1989) GCA 53, 1803–1815.

[2]Lehmann et al. (1993) WRR 29, 2027–2040.

[3]Purtschert et al. (2021) GCA 295, 65–79.