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Lithium isotopes: a new tracer of groundwater circulation in a peat land

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Water circulation in the peat bog of a maar depression in the Massif Central (France) was traced with lithium isotopes on water samples collected in the area from springs, surface- and groundwaters, as well as on solid samples taken from peat bogs.

Lithium contents fluctuate significantly in the groundwaters, ranging from $0.01 \mu\text{mol. L}^{-1}$ in springs feeding the peat bog, up to $28 \mu\text{mol. L}^{-1}$ in the groundwater collected in the peat bog. Lithium-isotope compositions ($\delta^7\text{Li}$, ‰) are extremely variable within the site, ranging from +12‰ in the stream draining the area up to a ^7Li -rich value of +1226‰ in groundwater from the peat bog. The $\delta^7\text{Li}$ values in the streams agree with those reported in the literature for surface waters, while those of groundwater are far beyond the range of values measured in nature.

In the present study, we explain the extremely enriched ^7Li signature of the groundwaters by an external input due to Ca-amendment, used in local agriculture. The relationships between Li content and Ca, Mg and HCO_3 as well as the lack of a relationship between Li and Na plead in favour of ^7Li -enriched carbonate amendments. This hypothesis was tested by Li-isotope analyses on the peat and on several amendment samples (carbonates and NPK fertilizers), confirming the potential role of amendments in the control of Li isotopes in peatland groundwater and showing high $\delta^7\text{Li}$ values in fertilizers. Application of $\delta^7\text{Li}$ ratios to peatland waters provides a unique perspective on the hydrogeochemical dynamics at the scale of this site, as the $\delta^7\text{Li}$ values for the surface water were quasi constant throughout the survey period, and the peatland groundwater does not supply the surface-water runoff and may evolve as a stagnant system. To conclude, the water within the peatland exhibits very high $\delta^7\text{Li}$ values consistent with artificially enriched ^7Li associated with Ca amendments. This study opens a new field for Li isotope investigations in hydro-systems and potential utility of Li isotopes as environmental tracers.