

Ca and Mg isotope systematics in acidified forests from the contrasting monolithologic Czech catchments

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A coupled isotope approach, based on $\delta^{44/40}\text{Ca}$ and $\delta^{26}\text{Mg}$ proxies, was used to better understand the sources and biogeochemical pathways of two major base cations, Ca^{2+} and Mg^{2+} , in acidified forest ecosystems in central Europe, Czech Republic. Specifically, we analyzed $\delta^{44/40}\text{Ca}$ and $\delta^{26}\text{Mg}$ in different ecosystem pools and reservoirs (i.e., bedrock, soils, biomass, streams, soil waters, and precipitation) from small catchments with geochemically contrasting lithologies including: granite (Ca-Mg poor), amphibolite (Ca-Mg rich) and serpentinite (Ca poor and Mg-rich) bedrocks [1]. Overall, our results confirmed that Ca and Mg isotopes behave differently during the biological uptake from soil waters into a biomass (i.e., fine roots of Norway spruce), where the latter preferentially takes up lighter isotopes of Ca, but heavier Mg, which was observed for all the studied lithologies. As a consequence, the soil-water pools tend to evolve to heavier $\delta^{44/40}\text{Ca}$, and lighter $\delta^{26}\text{Mg}$, and such isotope fractionation effect is most pronounced in the base-poor catchments and less pronounced, or negligible, at the Ca and Mg rich sites. Importantly, the atmospheric deposition at all sites yielded common $\delta^{44/40}\text{Ca}$ and $\delta^{26}\text{Mg}$, which are however distinct from other sources. This, in turn, allows us to determine and quantify from what ecosystem pools are Ca^{2+} and Mg^{2+} ions being exported into the streams, as a consequence of the previous acid deposition [1]. Our results indicate that for the base-poor sites the majority of Ca in streams originates from the atmospheric deposition, while Mg is derived also from the soil-water pools. This illustrates the contrasting behavior of Ca^{2+} and Mg^{2+} ions in the Critical Zone (CZ), where Ca^{2+} has a tendency to be held more tightly at the soil exchange sites, while Mg^{2+} is more prone to leaching and export from soils into the streams. Finally, $\delta^{44/40}\text{Ca}$ and $\delta^{26}\text{Mg}$ data from our seasonal sampling (every 3 months) will be also discussed in terms of the changing Ca and Mg dynamics in the CZ during the annual forest growth cycle.

[1] Krám *et al.*, 2012, *Appl. Geoch.*, **27**, 1854-1863.