Controls on $^{26}Mg/^{24}Mg$, $^{44}Ca/^{40}Ca$ and $^{87}Sr/^{86}Sr$ isotope variability in two industrially polluted forested catchments in Central Europe: Insights into nutrient imbalances

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For the past 28 years, monthly hydrochemical monitoring has been performed in 14 headwater catchments of the GEOMON network located throughout the Czech Republic. Input–output mass balances show dramatic decreases in sulfur deposition and retention following the 1980s peak pollution, and decreasing net runoff export of basic cations. We used stable isotope ratios of Mg, Ca, and Sr at two high-elevation GEOMON sites as tracers of nutrient inputs into catchment reservoirs, mixing history between solutes, secondary mineral formation, plant–mineral interactions, and recycling of atmospheric and lithogenic inputs by vegetation. The Cervik catchment is situated on base-poor flysch sediments near the Czech–Polish border, while Jezeri, situated close to the Czech–German border, is underlain by base-poor orthogneiss. Spruce is the dominant vegetation at Cervik, beech covers the lower segments of Jezeri, while spruce stands mostly died back. These two sites belong to the steepest catchments of the network. Jezeri was limed during the acid deposition period. Because ecosystem processes are known to fractionate Mg and Ca isotopes, we expected different isotope ratios of these nutrients in runoff in comparison with isotope ratios of bedrock and atmosphere as the ultimate mixing endmembers. Previously described isotope fractionations include preferential assimilation of isotopically light Ca and isotopically heavy Mg by plants, and adsorption of isotopically heavy Mg by phyllosilicates. Surprisingly, in four out of six cases, we found nearly identical average isotope signature of atmospheric deposition (rainfall and throughfall) and runoff. These cases included Ca at both Cervik and Jezeri, Mg at Cervik, and Sr at Cervik. Strontium isotope ratios in Jezeri runoff were also relatively close to deposition. In all these cases, isotope signature of bedrock differed from atmospheric input and runoff. Magnesium at Jezeri represented the only opposite pattern: Mg isotope ratios in Jezeri bedrock and runoff were nearly identical while being different from local atmospheric input. Jezeri was characterized by hydrological export of mostly geogenic Mg. On the other hand, interpretation of the common deposition–runoff similarity (Mg/Ca/Sr at Cervik, and Ca/Sr at Jezeri) is not straightforward: Annual export of individual base cations is up to 15 times higher than their annual atmospheric input. Non-isotope data *per-se* would thus indicate geogenic rather than atmospheric origin of Mg, Ca and Sr in runoff. The interpretation is additionally complicated by contrasting isotope composition of Mg/Ca/Sr in individual bedrock minerals with contrasting dissolution rates. Funded by the Czech Science Foundation (21-27420S).