Calcium, magnesium and strontium isotope dynamics in Central European headwater catchments along lithological and pollution gradients: Atmospheric *vs.* geogenic sources for runoff

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During pedogenesis, the sources of nutrients change. As soils develop on freshly exposed bedrock, geogenic elements are gradually lost. When the rates of hydrological export of geogenic nutrients are higher than the rates of mineral dissolution, atmospheric inputs gradually replace rock-derived nutrient sources and help to sustain productivity of forests. This process was documented for highly weathered soils in humid warm regions, but also inland ecosystems in temperate climatic zones have been shown to store substantial amounts of atmospheric nutrients. Nutrient imbalances negatively affect the health status of forests exposed to multiple stress factors, including drought, and, in Central Europe currently also a bark beetle calamity. We present a combined Ca–Mg isotope and mass-balance study of 7 small forested catchments near the borders between the Czech Republic, Poland, Germany and Austria. Due to acid rain, part of this area suffered from massive spruce die-back 30-60 years ago. Atmospheric deposition of alkaline earth elements increased after 1950 as a result of dust emissions from Soviet-style thermal power plants. Due to technological upgrades, replenishment of base cations in ecosystems *via* deposition decreased after 1990. Our main objective was to constrain the provenance of Ca and Mg in surface runoff. Study sites included base-poor bedrock (granite, orthogneiss, paragneiss, and flysch turbidites; ~1 % of CaO and MgO, respectively) and base-rich rock types (amphibolite and serpentinite; over 10 % of at least one base cation). Throughfall Ca fluxes at individual sites were between 60 and 2.0 kg ha^{-1} yr^{-1}, those of Mg varied between 13 and 1.0 kg ha^{-1} yr^{-1}. Ca, Mg and Sr isotope signatures were determined for 10 ecosystem compartments, including whole rock, bulk soil, lysimeter solutions, rainfall, spruce throughfall, roots, needles, xylem, bark, and runoff. At some sites, up to 7 rock-forming and accessory minerals were separated from ground rock and analyzed for Ca, Mg and Sr isotopes. Strontium was used as a Ca analogue. Isotope ratios were compared with hydrochemical input–output mass balances constructed for the past 28 years. Intuitively, large net Ca/Mg/Sr export *via* runoff should be accompanied by geogenic isotope signatures. The data, however, revealed a much more complicated pattern. Even though bedrock minerals exhibited large isotope variability, one Ca/ Mg/Sr-rich, easily dissolvable mineral was usually responsible for the geogenic input to runoff. Calcium and Mg in runoff were also affected by isotope fractionations accompanying assimilation and adsorption/desorption. Funded by the Czech Science Foundation (Grant 21-27420S).