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Using a high-resolution cave drip water dataset to clarify the link between trace element concentrations in stalagmite calcite and climate

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A thirteen-month long daily-scale record of cave drip water major and trace element concentrations reveals that drip water chemistry responds seasonally to recharge and vegetation conditions. Drip water was collected continuously at Ballynamintra Cave, Ireland, using an automatic water collector, and concentrations of Mg, Na, Ca, Sr, Ba, P, Cu, Zn, Rb, Y, Cs, U, Th, and Pb in the collected water were subsequently measured. In the late summer, alkali and alkali earth element concentrations decreased with decreasing drip rate, coinciding with an increase in concentrations of colloidally-associated trace elements. This supports the hypothesis that the seasonal increase in colloidally-associated elements observed in some published stalagmite samples results from the influx of colloidal organic material in the late summer or early autumn at sites where vegetation begins to dieback at this time. Alkali and alkali earth element concentrations are instead controlled by interactions with the soil, bedrock, and by prior precipitation of calcite or another mineral phase; at our site a summer water deficit resulted in lower drip rates and reductions in alkali and alkali earth element concentrations. The seasonal distribution of elements in the drip water record closely resembles the distribution found in some high resolution stalagmite trace element records. This research suggests that these possible controls on alkali and alkali earth elements and colloidally-associated elements (groundwater residence time and colloidal flux, respectively) are independent but occur contemporaneously in many parts of the world. Therefore the shifting in-and-out of phase of some annual trace element cycles (e.g., Sr and P cycles) may represent shifts in the relative timing of the season of lowest recharge and that of greatest release of colloidal material from the soil, which do not necessarily need to occur simultaneously. This research provides high-resolution monitoring data that further clarifies the link between trace elements in stalagmite calcite and climate.