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Hydrol. Earth Syst. Sci., 4, 439-449, 2000

www.hydrol-earth-syst-sci.net/4/439/2000/

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Hydrological characterisation of stalagmite dripwaters at Grotte de Villars, Dordogne, by the analysis of inorganic species and luminescent organic matter

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Abstract. Five stalagmite drip-waters in the Grotte de Villars, Dordogne, have been monitored from early 1997 to early 1998, for variations in discharge, major inorganic species and dissolved luminescent organic matter. When compared to surface precipitation, each drip-water has a subtly different response, both in terms of discharge variability and lag time between surface precipitation and drip rate response. Calculated water excess is shown to be important in determining drip-water discharge; during periods of soil moisture deficit, drip-waters either show no response to surface precipitation, or in the case of one sample station, respond only to high intensity and/or high quantity precipitation events. All drip-waters have a large storage component to their flow. Four sample stations have a similar hydrochemical and luminescence response, although the precise timing and magnitude of the responses may vary between drip sources that are <5 m apart. Drip-water luminescence intensity increases in winter and spring, and increases in discharge lag by 2 – 3 months, suggesting that the water in the rising limb and peak of the winter discharge comes from the stored groundwater component rather than a soil source. Drip-water strontium anti-correlates with luminescence and exhibits a strong ($\pm 100\%$) seasonal variation, with high-strontium waters derived from stored groundwater and is inferred to originate in localised Sr-rich primary components in the limestone. Drip-water conductivity reflects Ca-HCO₃ variations and falls during late summer to autumn, which is inferred to result from increased calcite precipitation above the cave with enhanced degassing related to progressive drying of the aquifer. Drip-water magnesium (following removal of the marine aerosol component) is just above detection limits and does not show strong seasonal variations. Variations in solution Pco₂ occur, with a particularly strong increase in early 1997. The various chemical trends are observed at a number of different sites despite a pronounced variation between them in terms of total Ca-HCO₃ mineralisation and Pco₂. One sampling station of the five investigated had a different response to surface precipitation; drip discharge was more variable, with evidence of non-linear responses, and luminescence intensity exhibited a dilution

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response to drip rate. For this site, flow switching occurred at times of high rainfall, with a rapid discharge response less than 24 hours after rainfall. Luminescence intensity, inorganic chemistry, and discharge characteristics at the site are compared with results published from other cave systems; significant inter-site variability depends on the geology, depth of sample sites and extent of karstification. This suggests that the interpretation of stalagmite luminescence, and variations in Sr, Ca and Mg must be considered on a site by site basis.

Keywords: stalagmite; dripwaters; luminescence; discharge; major ion chemistry

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Citation: Baker, A., Genty, D., and Fairchild, I. J.: Hydrological characterisation of stalagmite dripwaters at Grotte de Villars, Dordogne, by the analysis of inorganic species and luminescent organic matter, *Hydrol. Earth Syst. Sci.*, 4, 439-449, 2000. ▣ [Bibtex](#) ▣ [EndNote](#) [Reference Manager](#)