Long- *vs.* short-term trends of Ca, Mg, nitrates and alkalinity in a small agricultural catchment (Auradé, SW France): influence of N-fertilizer on carbonate dissolution

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In cultivated area, the Critical Zone (CZ) is under the pressure of agricultural practices. Particularly N-fertilizer spreading leads to soil acidification by nitric acid and carbonate dissolution increase [1, 2].

In this context a long-term hydrological and chemical monitoring was performed since 30 years for nitrates and discharge, and for 10 years for major elements at the stream outlet of a small agricultural carbonated catchment (Auradé site). This catchment is part of the French Research Infrastructure OZCAR and since 1992 it is an experimental site for improving water quality by adapting sustainable agricultural practices.

The long-term and middle-term hydrochemical trends indicated an increase in alkalinity, COD, F and K concentrations and a decreasing in Ca, Mg, Na, Cl, NO_3 and SO_4. These trends can be related to the evolution of agricultural practices (fertilizers inputs, vegetative buffer strip etc…) and inter-annual and seasonal hydroclimatological fluctuations.

The decreasing impact of N-fertilizer can be evidenced by the decreasing trend of the loss of alkalinity (Δ Alk) over the period. This negative trend is fairly well correlated to the Ca+Mg decrease indicating a reduction of carbonate dissolution rate and/or soil base cations desaturation, due to less nitric acid inputs.

Short-term fluctuations (dry and wet periods, winter and spring flood events etc...) show dilution *vs.* concentration patterns of the elements according to their origin (anthropogenic *vs.* natural) and their transfer pathways (surface and sub-surface runoffs *vs.* groundwater). Δ Alk variation shows a similar pattern during the flood event as observed for the long-term trends. But it is also controlled by the discharge variation according to the contribution of the different storm flow components.

[1] Perrin *et al.* (2008) *Geochim. Cosmochim. Acta* 72, 3105-3123.

[2] Raymond and Cole (2003) *Science* 301, 88-91.