

Key Parameters Controlling the Seasonal and Inter-annual Variations of pCO₂, Chemical Composition and Carbonate Equilibrium in Stream Water from a Mountainous Karstic Catchment (Pyrenees, France)

Francesco Ulloa Cedamano¹, Jean-Luc Probst¹, Stéphane Binet², Thierry Camboulive¹, Virginie Payre Suc¹, Corinne Pautot¹, Michel Bakalowicz³, and Anne Probst¹

¹EcoLab, Université de Toulouse, CNRS

²Institut des Sciences de la Terre d'Orléans (ISTO), Université d'Orléans, CNRS

³HSM, Université de Montpellier, CNRS

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Abstract

The carbonate dissolution plays a major role in the atmospheric CO₂ sink and in the riverine transfer of dissolved inorganic carbon from the atmosphere to the critical zone and to the oceans. In this context, the Baget watershed (13.25 km², altitude 950 m), essentially forested and weakly exposed to local anthropogenic pollution, drains a karst area in the Pyrenees mountains. It has been monitored for more than 40 years to better understand the impact of global changes on carbonate dissolution and hydro-chemistry of streamwaters. The mean annual precipitation exceeds 1500 mm and the air temperature average is 12°C. Calcareous dominates the lithology (around 2/3 of the area), with some flysch and schists. This experimental catchment belongs to the French Karst Network, to the French (OZCAR) and European (LTER) Research Infrastructures. Based on the hydrochemistry survey since 1978, the results focus on carbonate dissolution, stream water chemistry (mainly Ca, Mg and alkalinity) and calcite saturation index (SI) in relation with pCO₂, temperature (T) and river discharge (Q). We analysed the long term trends of the instantaneous values but also of the inter-annual fluctuations of the mean monthly values. The long-term hydrochemical survey allows to evidence a net increasing trend in [Ca²⁺+Mg²⁺] and [HCO₃⁻] that could be related to an increase in air temperature and a decrease in pCO₂ and discharge. Indeed, changes in vegetation cover over the period might have been another controlling factor that is currently investigated. Furthermore, mean monthly values based on the long-term trends allow to understand the dynamic of carbonate dissolution and to identify the main key controlling factors such as the water amount (discharge) and the air temperature, which influences pCO₂ production. Lastly, the influence of the drainage relative to minor lithology could be evidenced particularly during low water period by an increased proportion of [SO₄²⁻] to [HCO₃⁻] in stream water, due to the relative substitution of [H₂CO₃] by [H₂SO₄] from pyrite oxydation.

Key parameters controlling the seasonal and inter-annual variations of pCO₂, chemical composition and carbonate equilibrium in stream water from a mountainous karstic catchment (Pyrenees, France)



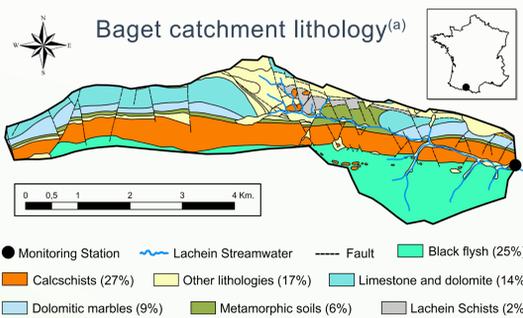
F. Ulloa-Cedamano¹, J.-L. Probst¹, S. Binet^{1,2}, T. Camboulive¹, V. Payre-Suc¹, C. Pautot¹, M. Bakalowicz³, A. Probst¹



¹ EcoLab, Université de Toulouse, CNRS, Toulouse, France. ² ISTO, Université d'Orléans, CNRS, Orléans, France. ³ HSM, Université de Montpellier, CNRS, Montpellier, France.

Baget catchment

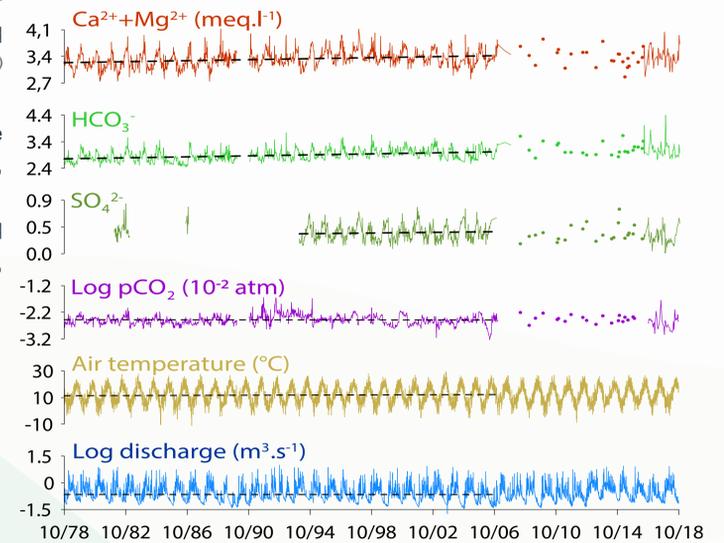
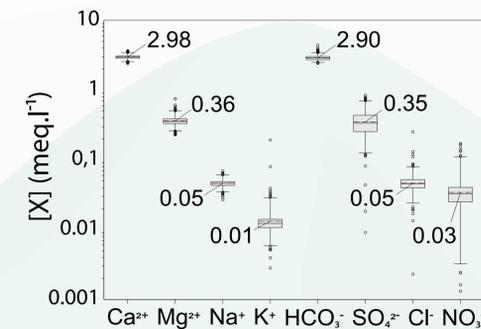
The small Baget catchment (13.2 km²) which drains a karst area in the French Pyrenees mountains, has been monitored for more than 40 years to better understand the impact of global changes on streamwater chemistry. The Baget catchment, essentially forested and weakly exposed to local anthropogenic, lies on limestones and dolomites but also on flysch and some pyrite-rich schists.



This experimental catchment "quasi pristine" belongs to the French Karst Observatory Network^(b) and to the French Critical Zone Network (OZCAR)^(c), now part of European Research Infrastructures (eLTER).

Hydrochemical monitoring: Long term trends

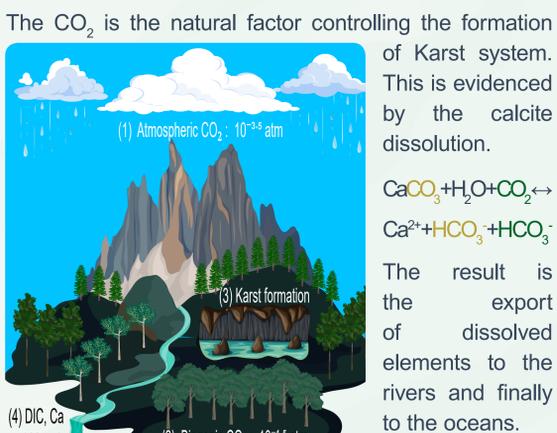
The stream water is mainly composed of Ca²⁺+Mg²⁺ and HCO₃⁻ originating carbonate dissolution and secondary by sulfate from atmospheric deposition^(d) and pyrite oxidation^(e). Trends on instantaneous data evaluated over the period 1978 to 2006 show an increase of T°, pCO₂, Ca²⁺+Mg²⁺, HCO₃⁻, meanwhile the Q decreased. Over the restricted period 1994 to 2006, the T° and SO₄²⁻ exhibited increasing trends while the Q, pCO₂, Ca²⁺+Mg²⁺, HCO₃⁻ trends decreased.



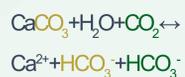
Dryer and warmer conditions may promote the production of CO₂ and the carbonate dissolution. However, the sulfuric acid seems to play an important role in the dissolution of carbonates at Baget catchment.

Scientific background

The carbonate dissolution plays a major role in the riverine transfer of dissolved inorganic carbon from the atmosphere to the critical zone and to the oceans.

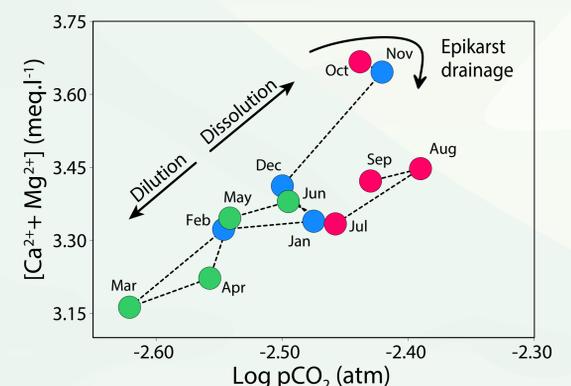
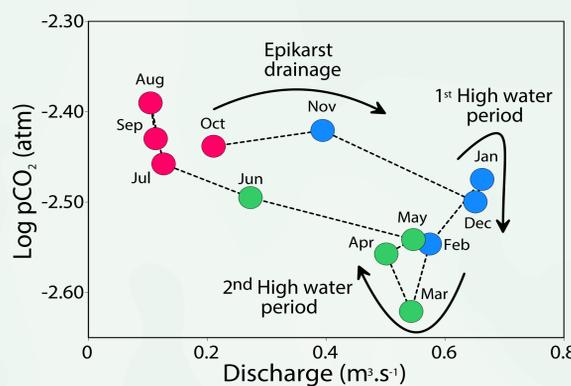


This is evidenced by the calcite dissolution.

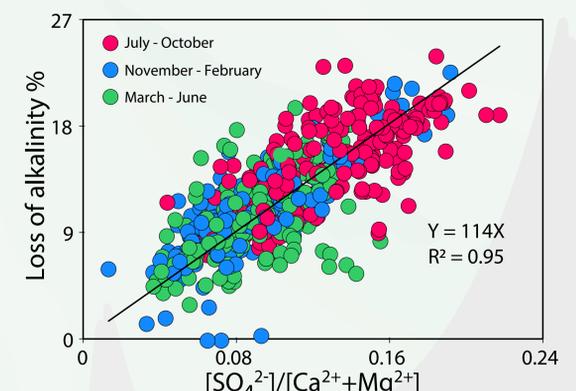
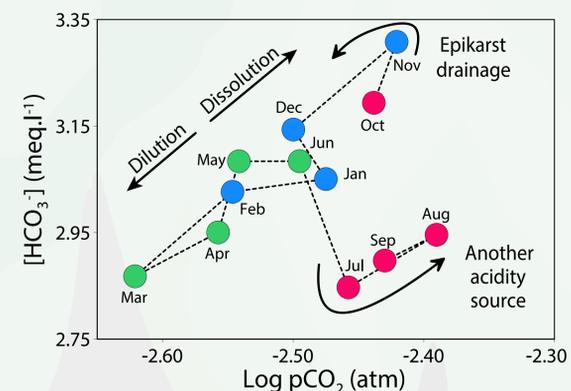


The result is the export of dissolved elements to the rivers and finally to the oceans.

Interannual fluctuations of the mean monthly values (1994-2006)



The pCO₂-Q relationship exhibits a net pCO₂ decrease from end-summer (reddish points) to winter (bluish points) due to dilution effect and T° decrease. The lowest pCO₂ values may be also related to a lower residence time. After this period, pCO₂ increases again with T° until August. The [Ca²⁺+Mg²⁺]-pCO₂ relationship exhibits a positive trend. The highest [Ca²⁺+Mg²⁺] values occur during epikarst drainage when the discharge begins to increase (oct-dec).



The [HCO₃⁻]-pCO₂ relationship also exhibits a positive trend with the highest [HCO₃⁻] values occurring during epikarst drainage. The drop in [HCO₃⁻] (jul-aug) would indicate a relative substitution of [HCO₃⁻] by [SO₄²⁻] from other acidity sources, relatively more influent during low waters. This substitution is also evidenced by the positive trend between the loss of alkalinity and SO₄²⁻/[Ca²⁺+Mg²⁺], reaching the highest values during the low water period (reddish points).

Conclusions

In this work, the hydrochemical survey carried out since 1978 allows to evidence a net increasing trend in [Ca²⁺+Mg²⁺] and [HCO₃⁻] that could be related to the increase in temperature and pCO₂ or also to the decrease in discharge.

Long-term trends of interannual fluctuations of the mean monthly values show the dynamic of carbonate dissolution controlled by: (i) water amount (Q) (ii) epikarst drainage and (iii) air T° which influences pCO₂ production.

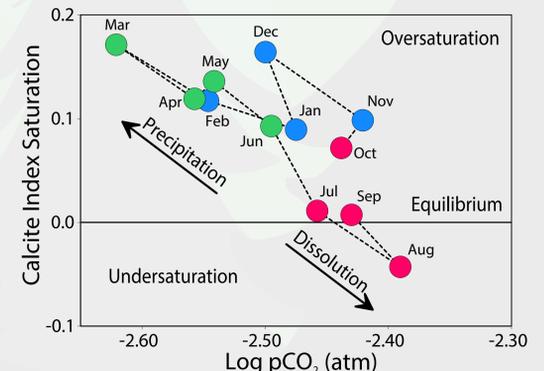
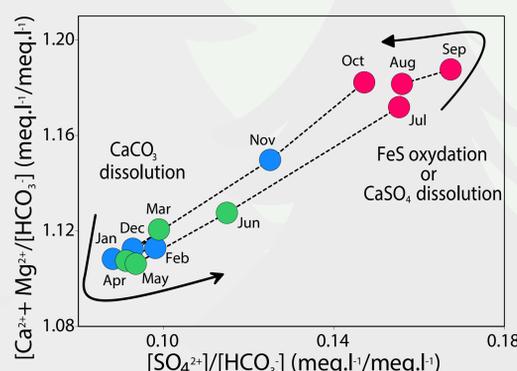
In addition, the increased relative proportion of [SO₄²⁻] to [HCO₃⁻] during low water period could be due to relative substitution of [H₂CO₃] by [H₂SO₄] from pyrite oxydation.

Literature cited

- (a) E.-J. Debroas. Toulouse : Association Strata, 2009.
- (b) H. Jourde, et al. Vadose Zone Journal, 17, 1. 2018.
- (c) J. Gaillardet, et al. Vadose Zone Journal, 17, 1. 2018.
- (d) S. Binet et al. Geochim. Cosmo. Acta (in press)
- (e) F. Ulloa-Cedamano, et al. Submitted to Water.

Acknowledgements

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The SO₄²⁻-[Ca²⁺+Mg²⁺] relationship shows a clear increase of sulphate over the low water period. Its origin would come from the relative influence of upstream source draining schist formations containing pyrite. Finally, the Baget streamwater is oversaturated with regard to calcite, except in august, when high pCO₂ corresponds to calcite undersaturation.

