Key parameters controlling the seasonal and inter-annual variations of pCO_2, chemical composition and carbonate equilibrium in stream water from a mountainous karstic catchment (Pyrenees, France)

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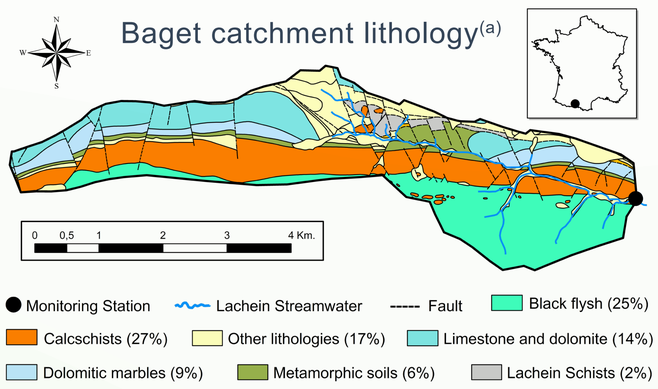
Baget catchment

The small Baget catchment (13.2 km^2) 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 flysh and some pyrite-rich schists.

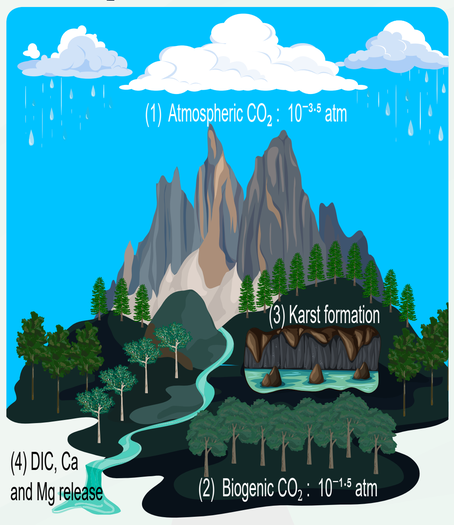


This experimental catchment "quasi pristine" belongs to the French Karst Observatory Network(b) and to the French Critical Zone Network (OZCAR)(c), now part of European Research Infrastructures (eLTER).

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.

The CO_2 is the natural factor controlling the formation of Karst system. This is evidenced by the calcite dissolution.



$CaCO_3+H_2O+CO_2 \leftrightarrow Ca^{2+}+HCO_3^-+HCO_3^-$

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

Conclusions

In this work, the hydrochemical survey carried out since 1978 allows to evidence a net increasing trend in $[Ca^{2+}+Mg^{2+}]$ and $[HCO_3^-]$ that could be related to the increase in temperature and pCO_2 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 pCO_2 production.

In addition, the increased relative proportion of $[SO_4^{2-}]$ to $[HCO_3^-]$ during low water period could be due to relative substitution of $[H_2CO_3]$ by $[H_2SO_4]$ 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-Cedamanos, et al. Submitted to Water.

Acknowledgements

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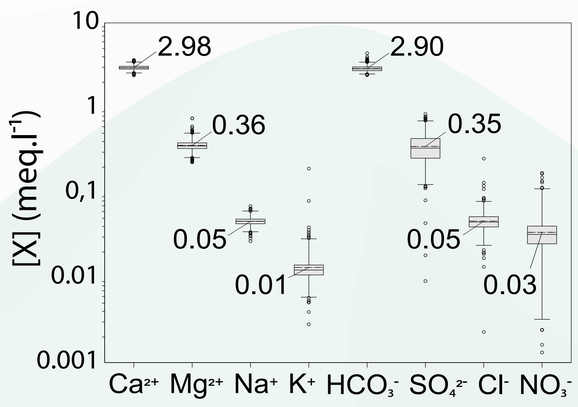
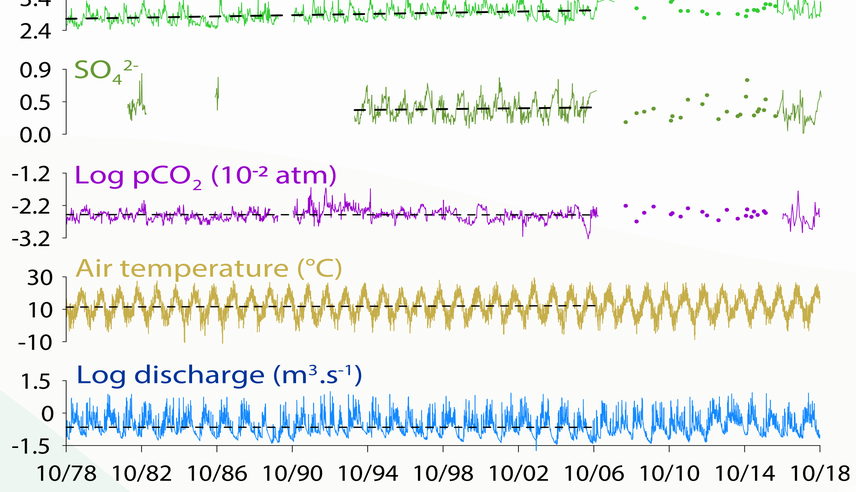
Hydrochemical monitoring: Long term trends

The stream water is mainly composed of $Ca^{2+}+Mg^{2+}$ and HCO_3^- 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°, pCO_2, $Ca^{2+}+Mg^{2+}$, HCO_3^-, meanwhile the Q decreased.

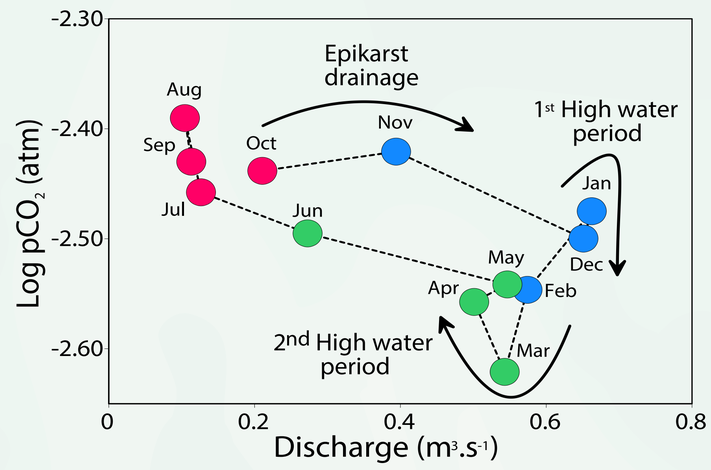
Over the restricted period 1994 to 2006, the T° and SO_4^{2-} exhibited increasing trends while the Q, pCO_2, $Ca^{2+}+Mg^{2+}$, HCO_3^- trends decreased.

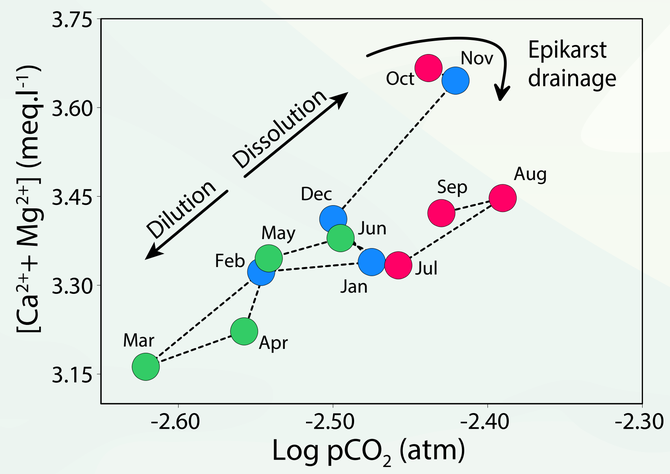




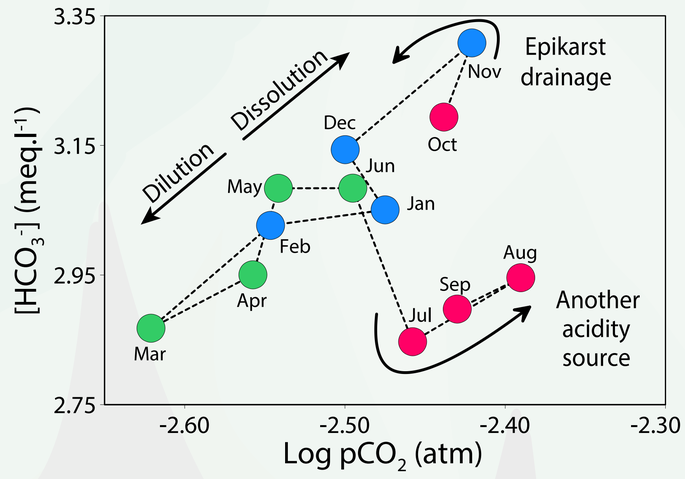
Dryer and warmer conditions may promote the production of CO_2 and the carbonate dissolution. However, the sulfuric acid seems to play an important role in the dissolution of carbonates at Baget catchment.

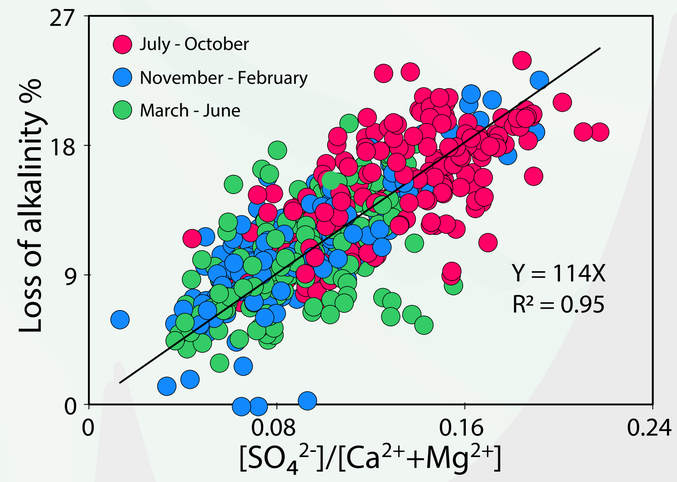
Interannual fluctuations of the mean monthly values (1994-2006)



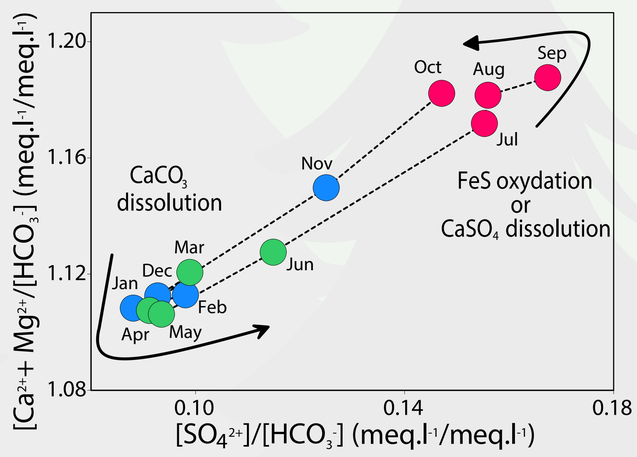


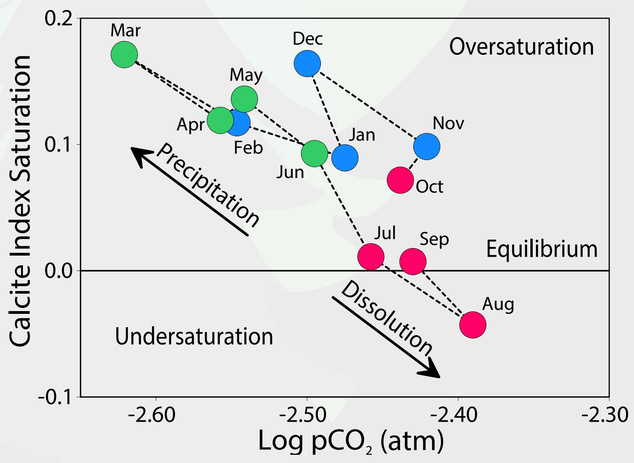
The pCO_2-Q relationship exhibits a net pCO_2 decrease from end-summer (reddish points) to winter (bluish points) due to dilution effect and T° decrease. The lowest pCO_2 values may be also related to a lower residence time. After this period, pCO_2 increases again with T° until August.The $[Ca^{2+}+Mg^{2+}]$-pCO_2 relationship exhibits a positive trend. The highest $[Ca^{2+}+Mg^{2+}]$ values occur during epikarst drainage when the discharge begins to increase (oct-dec).





The $[HCO_3^-]$- pCO_2 relationship also exhibits a positive trend with the highest $[HCO_3^-]$ values occuring during epikarst drainage. The drop in $[HCO_3^-]$ (jul-aug) would indicate a relative substitution of $[HCO_3^-]$ by $[SO_4^-]$ 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 $SO_4^{2-}/[Ca^{2+}+Mg^{2+}]$, reaching the highest values during the low water period (reddish points).





The SO_4^{2-}-$[Ca^{2+}+Mg^{2+}]$ 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 pCO_2 corresponds to calcite undersaturation.