

Inversion of river geochemical mass balances for provenancing dissolved species

Julien Bouchez, CNRS, IPG Paris
Éric Lewin, CNRS, ISTERre Grenoble
Éric Gayer, Université Paris Diderot, IPG Paris
Jérôme Gaillardet, IPG Paris
Pascale Louvat, CNRS, IPGP Paris

Key words: rivers, solutes, sources, geochemistry, inversion

River dissolved loads as a mixture of different weathering pathways

Chemical interactions at the Earth surface between water and various types of minerals lead to the release of solutes in soil and ground water. Although the style and extent of these reactions can be spatially heterogeneous, the study of the geochemical composition of rivers offers an integrated view of these chemical weathering processes, be it in terms of the rates of these processes, their fluxes, or of their underlying mechanisms. In this scope, large rivers draining continental surfaces of several thousands of km², provide the most geologically relevant insight into the functioning of the Earth system. However, rivers transport dissolved species collected throughout their catchments, and that can be derived from a variety of chemical weathering pathways. For example, even in a small river catchment, vertical variability in the subsurface in terms of mineralogy (*e.g.*, soils vs. rock) and water flow velocity will result in different dissolved chemical compositions of water pathways. In larger, heterogeneous catchments, different rock types can be present such that various, rock-specific weathering pathways exist, thereby producing distinct dissolved chemical compositions which are then mixed in the large river. In addition, at all scales, atmospheric wet and dry deposition over the catchment might also influence the dissolved budget of the river. Finally, different acids can fuel chemical weathering reactions, from atmospheric CO₂ to pyrite-derived or anthropogenic H₂SO₄.

Finding where river solutes are sourced from, through the inversion of geochemical mass balances

Different methods have been suggested by geochemists to tease apart the contribution of different solute sources to the dissolved load of rivers, which all rely on building a set of elemental and/or isotope mass balance equations, but differ in the way the solution to this system of equations is found. The so-called “Bayesian” inversion has been shown to be a particularly powerful approach to better constrain these numbers. In this approach, the *a priori* knowledge available on the parameters of the model (*i.e.*, the set of mass balance equations) is used to narrow down the space of most likely parameter values and to converge towards a unique solution. Theoretical frameworks [1] allow for solving such inverse problems, even if they include non-linear equations (*e.g.*, radioactive decay, Rayleigh fractionation...) taking into account the *a priori* knowledge on parameters, and providing as output parameters the most likely parameter values together with their uncertainties (*a posteriori* parameters). Although a very usual method in geophysics, applications of Bayesian inversion in the field of geochemistry are less common but have proven powerful to provide constrain on important questions in Earth Science such as the structure of Earth mantle [2] or the amount of CO₂ consumed by chemical weathering at a global scale [3].

Addressing the current limitations of inversion of river geochemical mass balances

In this contribution we wish to explore the limitations of the applications of these inverse methods in the field of geochemistry hitherto.

Applications of Bayesian inversion have been particularly successful at determining the source of cations to rivers in terms of lithologies (*e.g.*, silicate *vs.* carbonate rocks, [3]), which is in many cases equivalent to determining the source of alkalinity to rivers (atmospheric CO₂ *vs.* carbonates). However, there is a growing interest in the knowledge of the source of acidity fuelling weathering reactions, in particular at disentangling the relative roles of atmospheric CO₂ *vs.* H₂SO₄ formed during oxidative weathering of sulfide minerals [4] - which bears some consequences on the long-term influence of weathering reactions on atmospheric CO₂ levels [6], and hence on climate. In the present contribution, we use a large dataset of rivers draining the Andean region of the Amazon, and spanning a large range of chemical compositions, to explore how Bayesian inversion - and other methods, such as the "forward method" - can be efficient at sourcing river solutes and identifying suppliers of protons to weathering reactions.

First, we suggest a novel way of writing such sets of mass balance equations, which includes charge balance equations and therefore explicitly accounts for the formation of sulfate. This allows for simultaneously determining the relative contributions of different rocks to the cationic load of rivers and the relative contributions of CO₂ *vs.* H₂SO₄ to the acidity needed for these weathering reactions to happen. We also show how this source apportionment routine might fail for some *a priori* values for the composition of the rock end-members, which can occur in specific geological contexts.

Another, more fundamental limitation of the existing framework is the fact that it relies on the assumption that all parameters have a normal distribution. However, the two main types of parameters used in the geochemical mass balances, namely isotope/element ratios (always positive) and relative contributions of end-members (limited to the range [0,1]), cannot take any real values, as is required for a normally distributed variable. Using a series of numerical experiments based on the same dataset as above, we show in which conditions this theoretical issue can be deemed as negligible in practice, and in which conditions it can be considered as a severe limitation. We also suggest substitutions of variables that allow for partially circumventing this problem.

Finally, the results of Bayesian inversion are compared with different, more widespread techniques for solving river geochemical mass balance, such as the so-called "forward method" or solving an exactly determined system of equations, each combined with Monte Carlo experiments to estimate *a posteriori* uncertainties on the inferred parameters.

References

- [1] Tarantola A. and Valette B.: Generalized nonlinear inverse problems solved using the least squares criterion. *Rev. Geophys. Space Phys.*, **20**(2):219-232, 1982.
- [2] Allègre C.J. and Lewin É.: Chemical structure and history of the Earth: evidence from global non-linear inversion of isotopic data in a three-box model. *Earth Planet. Sci. Lett.* **96**:61-88, 1989.
- [3] Gaillardet J., Dupré B., Louvat P. and Lewin É.: Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* **159**:3-30, 1999.
- [4] Calmels D., Gaillardet J., Brenot A. and France-Lanord C.: Sustained sulfide oxidation by physical erosion in the Mackenzie River basin: climatic perspectives. *Geology* **35**(11):1003-1006, 2007.
- [5] Torres M.A., West A.J., Clark K.E., Paris G., Bouchez J., Ponton C., Feakins S.J., Galy V. and Atkins J.F.: The acid and alkalinity budgets of weathering in the Andes–Amazon system: insights into the erosional control of global biogeochemical cycles. *Earth Planet. Sci. Lett.* **450**:381-391, 2016.