

## Role of peatlands on trace metal cycles in mountains watersheds: fluxes and speciation

Rôle des tourbières dans les cycles des éléments trace métalliques dans les bassins versants de montagne. Flux, spéciation.

### French Summary:

Dans les montagnes européennes, les minerais métalliques ont été exploités depuis l'Age du bronze, induisant leur dispersion dans l'atmosphère. Dans certaines régions, la dispersion d'Eléments Traces Métalliques (ETM) au cours des activités minières médiévales a dépassé celle mesurée après la révolution industrielle. Dans les Pyrénées, il a été démontré que 85% de l'accumulation de Pb dans les tourbières s'est produite avant l'an 1800, soulignant l'importance de l'héritage minier dans les stocks des ETM (Hansson et al., 2017). Les bassins versants de montagne sont par ailleurs particulièrement touchés par la pollution atmosphérique à longue distance du fait de dépôt accru en altitude par des mécanismes orographiques. Par ailleurs, les tourbières, écosystèmes fréquents dans les environnements montagneux et réservoirs de matière organique, ont la capacité de retenir les métaux traces et les radionucléides. Dans les bassins versants de montagne, les tourbières sont donc des «points chauds» d'accumulation de carbone et d'ETM. La zone critique de montagne est très sensible aux changements environnementaux actuels, du fait du changement climatique et des activités humaines locales (exploitation minière et forestière, écobuage...). Dans ce contexte, la stabilité de ces stocks de carbone et d'ETM est remise en cause, notamment du fait que les bassins versants des montagnes sont caractérisés par des phénomènes hydrologiques extrêmes, qui contrôlent fortement les cycles biogéochimiques. Dans le cas du transfert de carbone organique dans les eaux de surface, il a été démontré qu'environ la moitié des flux de carbone organique dissous se produisent pendant moins de 10% du temps, lors des crues (Rosset et al., 2017). Des études préliminaires montrent que les pics de carbone organique dissous lors des crues sont associés à des pics de métaux traces. Cela a conduit à l'hypothèse d'exportations fortement dynamiques des ETM des tourbières, caractérisées par des «moments chauds» de libération des ETM, associés au carbone. Les exportations de métaux-traces et leur impact potentiel sur les milieux aquatiques dépendent de leur spéciation dans l'eau, principalement contrôlée par le pH, le statut redox, ainsi que l'interaction avec la matière organique dissoute et les hydroxydes d'aluminium et de fer. Dans les bassins versants de montagne, ces paramètres présentent une dynamique très rapide en lien avec les conditions hydrologiques et la présence des tourbières.

Dans ce contexte, ce projet doctoral vise à répondre aux questions suivantes:

- Les tourbières sont-elles actuellement des sources ou des puits d'ETM dans les bassins versants de montagne?
- Les ETM exportés des tourbières proviennent-ils d'un ancien héritage minier ou de dépôts atmosphériques contemporains?
- Quelle est l'influence des tourbières sur la spéciation des ETM après leur exportation vers le réseau fluvial?

### Keywords

Trace metals, atmospheric deposition,, Organic matter, Pb isotopes, colloids, C isotopes

### Main scientific fields

Contaminant Fate in the Mountain Critical Zone  
Isotope Biogeochemistry, Organic matter geochemistry

### Profile and skills required

master degree in biogeochemistry, geochemistry, hydrology, Environmental Sciences.

### Project

*The mountain critical zone* is highly sensitive to current environmental changes, in relation to human activities (e.g. mining, peat stubble burning, forest cutting) and climate change. This rapidly evolving context questions the fate of these carbon and Trace Metal stocks. In relation to their sharp topography and harsh climate, mountain watersheds are characterized by extreme hydrological events, which strongly control biogeochemical cycles. In the case of organic carbon transfer to surface waters, it has been shown that about half of the dissolved organic carbon fluxes occur during less than 10 % of the time, during storm events (Rosset et al., 2017). Preliminary studies show that peaks of dissolved organic carbon during storm events to the fluvial networks are paired with trace metal peaks. This lead to the hypothesis of strongly dynamic exports of TM from peatland, characterized by 'hot moments' of TM release to the fluvial network. Trace metal exports, and their potential impact on biota depend on their speciation in water, which is mainly controlled by pH, redox status, as well as interaction with dissolved organic matter (DOM) and aluminum and iron hydroxides. In mountain watersheds, these parameters are strongly influenced by peatlands and sharply evolve during storm events. The complex dynamic of TM in mountain watersheds is poorly constrained.

### Objectives

This doctoral project aims at answering the following questions:

- Are peatlands currently sources or sinks of Trace Metals in mountain watersheds?
- Do trace metal exported from peatlands originate from ancient mining legacy or from recent pollutions?
- What is the influence of peatlands on trace metal speciation after their export to the fluvial network?



In European mountains, valuable metallic ores have been mined since the Bronze Age, inducing metallic dispersion in the atmosphere. In some areas, the intensity of the dispersion of trace metal (TM) during medieval mining activities even exceeded the one measured after the industrial revolution. In addition to local inputs from mining activities, mountain watersheds are specifically impacted by long range transboundary air pollution. Atmospheric deposition of TM can be increased compared to neighboring valleys. Higher precipitation occurs on hills and mountains due to several orographic effects like the feeder-seeder effect or canopy interception of low altitude clouds and fogs. Peatlands are common ecosystems in mountainous environments and act as reservoirs of organic matter. Peat has the ability to retain trace metals and radionuclides and peatlands are considered to have accumulated contaminants since the beginning of metallurgy. Indeed in the Pyrenees, it has been shown that 85% of Pb accumulation in peatlands occurred before AD 1800, highlighting the importance of the ancient mining activity legacy in TM stocks (Hansson et al., 2017). In mountain watersheds, peatlands are then 'hotspots' of both carbon and TM accumulation.

### Methods

In order to establish TM budgets, data gathered on instrumented sites will be compiled. Trace metal fluxes will be modeled using in situ high temporal resolution of discharge and DOC concentrations. The amount of dry deposition as well as the contribution of occult deposition will be assessed using specific collecting devices deployed during the PhD project (fog collector, wet and dry collector). Current TM fluxes and budgets will be compared to established historical fluxes. A coupled isotopic approach ( $^{210}\text{Pb}$ , stable Pb isotopes,  $^{14}\text{C}$ -DOM) will be developed to estimate the origin (recent vs historical deposition) of exported TM. The speciation of TM will be assessed in relation with hydrological conditions combining physical fractionation (dissolved, colloidal and particulate), chemical analysis (focusing on TM interaction with DOM and hydroxides) and geochemical modelling approaches.

### Expected Results

This doctoral project will contribute to significant improvements in the understanding of the role of peatlands in the critical zone biogeochemical cycles. Trace Metal budgets in remote ecosystems, and speciation studies in the context of low contamination are extremely rare. It will use and develop innovative geochemical tools to further investigate TM speciation and the complex link between organic and trace metal cycles.

### Framework

The project will be conducted in the Pyrenees. The main study sites (peatlands) are located within the [OHM \(Observatoire Homme Milieu\) Haut Vicdessos-Vallée des Gaves](#). The sites present contrasted mining history and are influenced by representative practices, including peat stubble burning. The Bernadouze peatland has been instrumented since 2012 (meteorological, hydrological and geochemical in situ sensing). Trace Metal deposition have been recorded since 2012. Additional sites in the Pyrenees, as well as international sites close to active mines (Andes) will be investigated in order to consider a wide range of physicochemical conditions and contamination ranges. The doctoral project is part of the ANR TRAM (Trace Metal Legacy in Mountain Environment). It will benefit from the analytical environment of the EcoLab Laboratory and OMP (ETV, ICP OES, ICP MS, HR-ICPMS...). It will benefit from regional collaboration within the Observatoire Midi Pyrenees, and from the international collaboration within the REPLIM network (a Pyrenean network of research labs working on lakes and peatlands in the Pyrenees).

### Contact:

Dr. Laure Gandois ([laure.gandois@ensat.fr](mailto:laure.gandois@ensat.fr)) & Gaël Le Roux ([gael.leroux@ensat.fr](mailto:gael.leroux@ensat.fr))  
<http://summits.cnrs.fr/>

### References

- T Rosset, L Gandois, JM Antoine, R Teisserenc, S Binet. 2017. Hydrological controls on dissolved organic carbon exports from a-French Pyrenean-mountainous peatland. EGU Confence, Vienna.
- Hansson, S., Claustres A., Probst A., Vleeschouwer F., Baron S., Galop D., Mazier F., Le Roux G. (2017). Atmospheric and terrigenous metal accumulation over 3000 years in a French mountain catchment: Local vs distal influences. *Anthropocene*. 19. . 10.1016/j.ancene.2017.09.002.
- Le Roux, Gaël and Hansson, Sophia V. and Claustres, Adrien: Inorganic Chemistry in the Mountain Critical Zone : Are the mountain water towers of contemporary society under threat by trace contaminants ? (2016) In: Mountain Ice and Water - Investigations of the Hydrologic Cycle in Alpine Environments. (Developments in Earth Surface Processes). Elsevier, p. 131-154. ISBN 978 0 444 63787 1

