Subject offered for a contract starting October 2023

**SUBJECT TITTLE:**

**Chloride as a tracer for human activities in rivers: coupling big data of high frequency with isotopic constrains.**

Advisor: **Gaillardet Jérôme, Professeur.**

Second Advisor/ Supervisor : Pierre Agrinier

Host lab/ Team: *please fill in and leave out meaningless information*

**G2E and GIS teams, IPGP**

**Collaboration network:**

The project associates two teams of IPGP. It will use the facilities of the national infrastructure OZCAR, a multidisciplinary research community and in particular the River Lab instrumentation, and of the PARI analytical platform of IPGP. The project will be conducted in collaboration with Pr. Jennifer Druhan, Illinois University, USA.

Available funds : European eLTER project. Application to EC2CO program at CNRS

Financing: Doctoral contract with or without teaching assignment

*For more information go to* [*http://ed560.ipgp.fr*](http://ed560.ipgp.fr)*, section: Offres de these (PhD offer), You must apply on the Doctoral School website*

Presentation of the subject: (1 or 2 pages)

Human activities are affecting the composition of river and ground water in an unprecedented way. Application of fertilizers, irrigation, atmospheric emissions, urban wastes, and climate change are some of the processes whose imprint is already affecting water resources. Maintaining river quality is without any doubts one of the main challenges humanity is faced with for the following decades.

From a scientific point of view, there is a clear need to better understand the whole chain of processes that controls the chemical composition of rivers, as well as the routing of water through the critical zone (orCZ, that is the Earth’s planetary layer “between the rock and the sky”, hosting life and civilization) from the rainfall to discharge into the oceans.

In this PhD, we will concentrate on the behavior of the element chlorine (Cl) in the CZ. Chlorine is an element that traces human activities. Due to its lack of toxicity when in its ionic form, and due its high natural abundance (ocean), chlorine is widely used for different industrial activities: water treatment plants, deicing, bleaching agent, or associated to organic compounds for example in plastics. Chlorine speciation is variable, with significant in redox state, and ranging from gaseous forms to organochlorides.

Rivers collect chlorine from various sources in their watershed. Historically, chloride in rivers has been used to estimate how much of the river dissolved load is derived from the atmosphere, where Cl exists as sea-derived aerosols. River geochemists have postulated that chloride (the Cl- ion), which is poorly involved in biological activity, is conservative, i.e. that once introduced to the watershed by rain input or any other source, it does not react and passively traces the movement of water masses. For example, many studies have used the fact that rain, surface, and subsurface waters have different chloride concentrations to "decompose" stream flood events into various water inputs. However, significant uncertainty still exists as to whether (1) chlorine is derived solely from atmospheric inputs, especially in regions heavily impacted by industrial, agricultural, or domestic activity; (2) can indeed be used as a conservative tracer, given the possibility for chlorine to associate with organic compounds.

These knowledge gaps can now be addressed thanks to two recent major technological advances:

* The first is the ability to measure stream chlorine concentrations at a high frequency by avoiding manual sampling. The River Lab is a "lab-on-field" type of instrument that was developed at IPGP and INRAE Antony to automatically measure river chemistry every 30 minutes (Floury et al., 2017). Three river labs have been developed and deployed in France through the Equipex CRITEX.
* The second is the possibility of measuring the isotopic ratio of chloride in water. Chlorine has two stable, naturally-occurring isotopes (35Cl and 37Cl), with the light isotope representing about 1/3 of chloride atoms in nature. Preliminary data (Agrinier et al., 2021) indicate that a range of processes fractionate chlorine isotopes in nature, (such as diffusion, ionic filtration or changes in redox state). Although poorly involved in biological activity, chlorine isotopes are strongly fractionated by biological processes.

The aim of this PhD project is to couple the high frequency data recorded by the River Labs in three catchments of the OZCAR (the French Critical Zone observatory network) national infrastructure to isotopic measurement to identify both the sources and mechanisms that affect chloride. These catchments are characterized by contrasted lithologies and agricultural use. Relevant available constraints for this project at these catchments include low-frequency (~monthly), long-term (more than 30 years) chronicles of discharge data, and previous hydrological investigation using a variety of models.

The River Lab data will be investigated by developing automated routines for multivariate analysis (*e.g.*, principal component analysis, PCA) and inversion techniques allowing us to trace water mixing at the catchment scale, and to quantitatively determine the contribution of each endmember. PCA will be applied to the whole set of dissolved concentrations measured by the River Lab. Mixing models deduced from the analysis of this big data set will be then further constrained by sparser chlorine isotope data (supplemented by water and strontium isotopes). Analytical improvement of the chlorine isotopic measurement technique will be necessary to increase its sensitivity and reduce the required sample size for rainwater in particular.

The PhD candidate will benefit from the recent expertise acquired on the River Labs at the G2E team of IPGP, in particular through the involvement of the start-up company Extralab, as well as through the collaboration with Pr. Jennifer Druhan (U. of Illinois), who holds a position of Associate Researcher at IPGP, who is operating a River Lab in the US. The candidate will benefit from the recent developments of reactive transport models and inversion algorithms in G2E (Julien Bouchez, Eric Gayer) and from the analytical expertise of the PARI platform. He/she will collaborate with the multidisciplinary scientific community of the OZCAR national research infrastructure.

The applicant should have a general background in Earth Sciences and biogeochemistry, good skills and interest in applying automated workflow to big data series, as well as a strong interest for isotope geochemistry within the Critical Zone (rivers, soils, vegetation, weathering and transport processes). The candidate should be interested in working on the impact of human activities on water quality and on the related socio-ecological implications.