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Water Rock Interaction [WRI 14]

Carbon sources and water-rock interactions in the Allier River, France

K. Rivé<sup>a\*</sup>, S.Rad<sup>b</sup>, N. Assayag<sup>c</sup>

<sup>a</sup>CEGEO, 159 Allée Chardin, 59491 Villeneuve d'Ascq, France

<sup>b</sup>BRGM, 3 avenue Claude-Guillemain 45060 Orléans Cedex 02, France

<sup>c</sup>IPGP, 1 Rue Jussieu, 75238 Paris Cedex 05, France

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**Abstract**

The Allier River is an important tributary of the Loire River, one of the major rivers in France. The Allier River presents both a natural environment upstream and a zone deeply impacted by mines and human activities. The  $\delta^{13}\text{C}$  and  $\delta^7\text{Li}$  combination show that the Allier River DIC is due to mixing of carbon from organic decay produced in a natural environment upstream, progressively enriched in DIC of anthropogenic origin downstream, and magmatic carbon inputs often associated with hydrothermal contributions.

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*Keywords:* DIC, isotopes, carbon, lithium, water rock interactions, hydrothermalism, Allier.

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**1. Introduction**

The Allier River (France), known as to be one wild river in Europe crossed by high anthropogenic impacts (agriculture, urban zones, mining exploitation). With the aim to better constrain the carbon cycle of the surface waters of the catchment, DIC (dissolved inorganic carbon) and isotopic compositions of carbon and lithium were measured on water sampled all along the river downward.

The Allier River is a tributary of the Loire River, which has been the object of comprehensive geochemical characterization [1 - 3]. The Allier River offers particular features due to the geological diversity of the Massif Central. From metamorphic and volcanic in the south of the catchment, the Allier River drains sedimentary basins to the north. With a course of 425 km long, the Allier River shows a very active dynamic. The relief and land cover are contrasted: steep and with few agricultural environments in the upstream part of the basin, and the downstream part of the catchment is occupied by the plain of intensive agriculture. Exchanges between the alluvial aquifer and the river are complex; schematically the water flows downstream, feeding the Allier River in summer and recharging during winter time [4].

Sampling has been done from downstream up to the confluence with the Loire River in September 2010 and 2011. The DIC and  $\delta^{13}\text{C}$  have been measured with an AP2003 He-CFMS according to the protocol

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\* Corresponding author. Tel.: +33663052444

E-mail address: [karine.rive@cegeo-environnement.com](mailto:karine.rive@cegeo-environnement.com)

described by Assayag et al. [5], and  $\delta^7\text{Li}$  with a MC-ICPMS Neptune according to the protocol described by Millot et al. [6]. Errors are respectively of less than 10 ‰, 0.3 ‰ and 0.1 ‰ for these measurements.

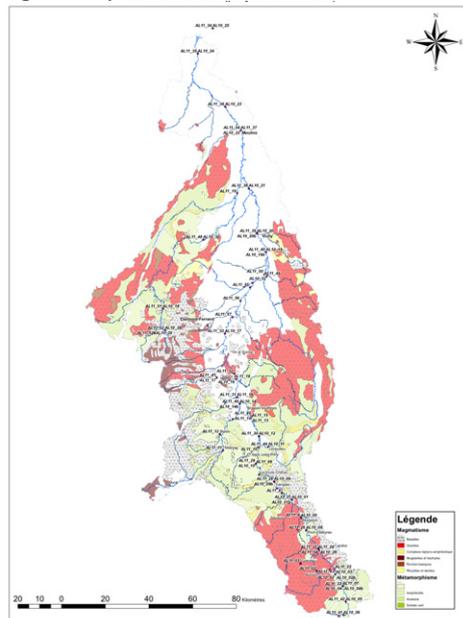


Figure 1: Geological map of Allier catchment (France).

## 2. Results

The DIC concentrations vary from 50 to 2840  $\mu\text{M}$ . The  $\delta^{13}\text{C}$  of the DIC varies from -19.0 to -3.5 ‰. The  $\delta^7\text{Li}$  range from 3.3 to 30.3 ‰. We observe a continuous variation of the DIC and  $\delta^7\text{Li}$  from upstream to downstream (not shown). The  $\delta^{13}\text{C}$  values also globally increases from upstream to downstream but this trend is less clear than for DIC, as discussed hereafter.

## 3. Discussion

### 3.1. Carbon sources.

The Figure 2 displays the Allier River samples in the diagram of  $\delta^{13}\text{C}$  versus DIC, which suggests 4 different carbon end-members. The two first end-members have an organic origin. One with a depleted carbon isotopic composition ( $\delta^{13}\text{C}$  (-19.0‰) and low concentrations in DIC (50  $\mu\text{M}$ ) may correspond to organic decay and respiration processes in soils of woodland areas (C3 photosynthesis, e.g. [7]); whereas the second one, with higher  $\delta^{13}\text{C}$  (-10.7‰) and very high DIC (3280  $\mu\text{M}$ ), reflects organic matter decay and respiration processes in intensive cultivation areas (mainly C4 plants as starch and cereals; e.g. [7, 8]). The third end-member, enriched in  $^{13}\text{C}$  (-3.5‰) and presenting high DIC (3260  $\mu\text{M}$ ), suggests contribution of magmatic carbon via the tributary Couze Pavin, this river being located in a volcanic and deeply faulted area where magmatic  $\text{CO}_2$  ( $\delta^{13}\text{C}$  at -3.5 ‰) contributions to DIC budgets of Couze Pavin have been demonstrated [9 and references therein]. The fourth end-member, with a medium  $\delta^{13}\text{C}$  (-9.6 ‰) and low DIC (34  $\mu\text{M}$ ), corresponds to water re-equilibrated with atmospheric  $\text{CO}_2$ , mainly at the surface of lakes (e.g. [9]). The data are not following clear mixing lines between these end-members, suggesting internal river processes affecting DIC (e.g.  $\text{CO}_2$  equilibration with the atmosphere) and  $\delta^{13}\text{C}$  and/or a three end-member mixing

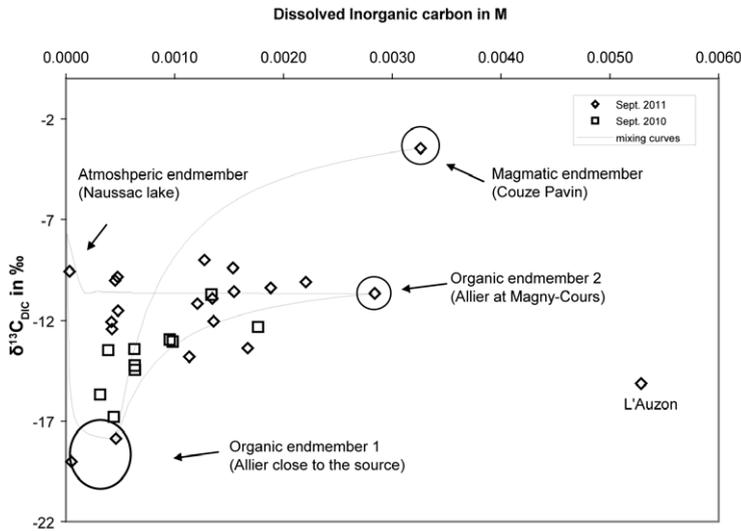


Figure 2:  $\delta^{13}\text{C}$  DIC vs. DIC with different end-members in the Allier basin. Mixing lines were calculated using the values of the end-members described above using two end-member mixing equations.

### 3.2. Lithium isotopes

The combination of  $^{13}\text{C}$  with  $\delta^7\text{Li}$  allows identifying the inputs of waters with dissolved magmatic  $\text{CO}_2$ , for they are often associated with high temperature water rock interactions.  $\delta^7\text{Li}$  is a conservative tracer that depends on water rock temperature and contact time [10 - 13].

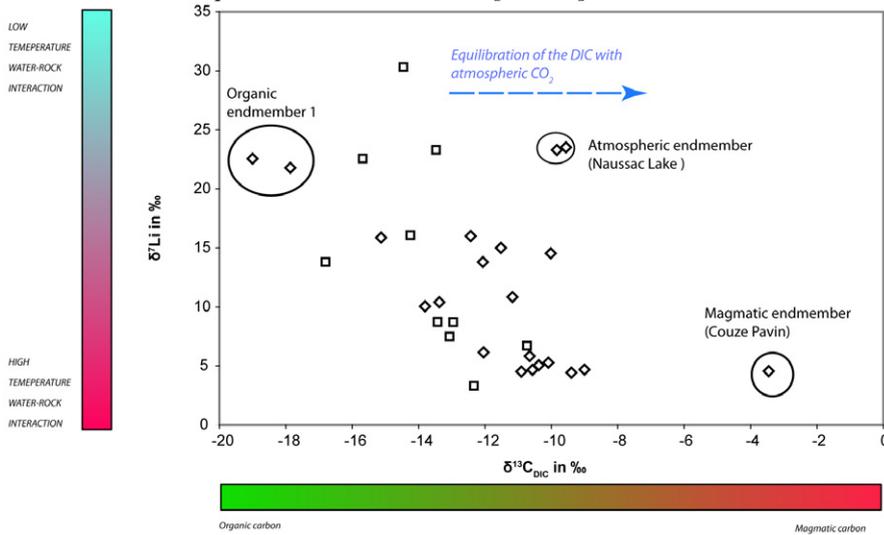


Figure 3. Comparison of carbon and lithium isotopes in the waters of the Allier River, showing the correspondence of water-rock interaction temperature and carbon sources in the Allier River.

Geothermal waters show low  $\delta^7\text{Li}$  in the Allier River between 2.4 and 6.9 ‰ [13], and magmatic  $\text{CO}_2$  is  $\delta^{13}\text{C}$  around -3.5 ‰. The figure 3 displays samples with low  $\delta^7\text{Li}$  and high  $\delta^{13}\text{C}$ , which confirms hydrothermal associated with magmatic  $\text{CO}_2$  inputs into the river. For some samples, the trend is tilted to higher  $\delta^{13}\text{C}$  values due to inputs of water equilibrated with atmospheric  $\text{CO}_2$  at -7 ‰ such as lakes. These waters show  $\delta^{13}\text{C}$  higher than pure organic carbon and a high  $\delta^7\text{Li}$  relevant with low-temperature water-rock interaction and organic carbon end-member. The figure suggests that the majority of the water samples collected along the Allier River follow a mixing between a “cold” water rock interaction where the carbon is mainly of organic origin (upstream) and hydrothermal inputs where carbon originates

mainly from a magmatic source. Some waters as lake samples could be interpreted as the result of cold water-rock interaction and organic end-member, where a re-equilibration with atmospheric CO<sub>2</sub> has occurred (light carbon is preferentially released to the atmosphere).

#### 4. Conclusion

This study proposes to describe water-rock interactions in the Allier river basin using isotopes of C and Li. The results show high temperature water-rocks interactions where the carbonic acid originates mainly from magmatic CO<sub>2</sub>. These river samples with hydrothermal waters signatures are associated with high DIC. A second type of water-rock interaction has been identified in the Allier River as low-temperature water rock interaction, where the carbonic acid is mainly of organic origin. These results suggest that the dissolved load of the Allier rivers waters is mainly the product of these two water-rock interaction modes, depending on the contribution of the deep waters to surface water. A perspective of this study would be the focus on the aquifers-rivers interactions systems through time and meteorological events.

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