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Tracing Mixings and Water-Rock Interactions in the Loire River Basin (France): $\delta^{18}O$-$\delta^{2}H$ and $^{87}Sr/^{86}Sr$

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Abstract

The Loire River drains more than 1/5[th]of the French territory and flows into the Atlantic Ocean through plutonic and volcanic rocks in the upper and lower parts and a large sedimentary basin. Through sampling of the Loire River along its main course and its main tributaries during 2 snapshot campaigns at the basin scale (one during a flood event and the other during the following low flow period), the behavior of the stable and Sr isotopes during water mixing and water/rock interactions at the scale of a large river basin having various lithologies is reported. This study highlighted the complex functioning of the river system and the key issue of the relation between surface and groundwater that must be more investigated, especially regarding water resources management.

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Keywords: Loire River Basin; Stable isotopes; Sr isotopes; Mixing; Water-Rock Interactions.

1. Introduction

The Loire River is the longest French River (1012 km) and drains more than 1/5[th] (117 000 km²) of the French territory. The upper parts of the Loire River and Allier River (main upstream tributary of the Loire) drain the French Massif Central. The bedrock of the upper basin encompasses old plutonic rocks (granite, gneiss and micaschists, 500-300 My) superimposed by a volcanic area. The middle part of the basin belongs to the Paris Basin, the Loire drains sedimentary series from 200 to 6 My, and includes the Cher, the Indre and the Vienne tributaries from the Loire-Allier confluence to the Maine confluence. The lower Loire that includes the Maine River to the estuary drains the granite basement of the Massif Armoricain (Figure 1).

The mean annual discharge in Orléans (median part of the basin; sampling point 5) is 341 m^3/s (calculated since

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1964), with a maximum in February (mean W = 599 m^3/s) and minimum in August (mean W = 99 m^3/s). The mean daily discharge of a 50-year return flood is about 3500 m^3/s.

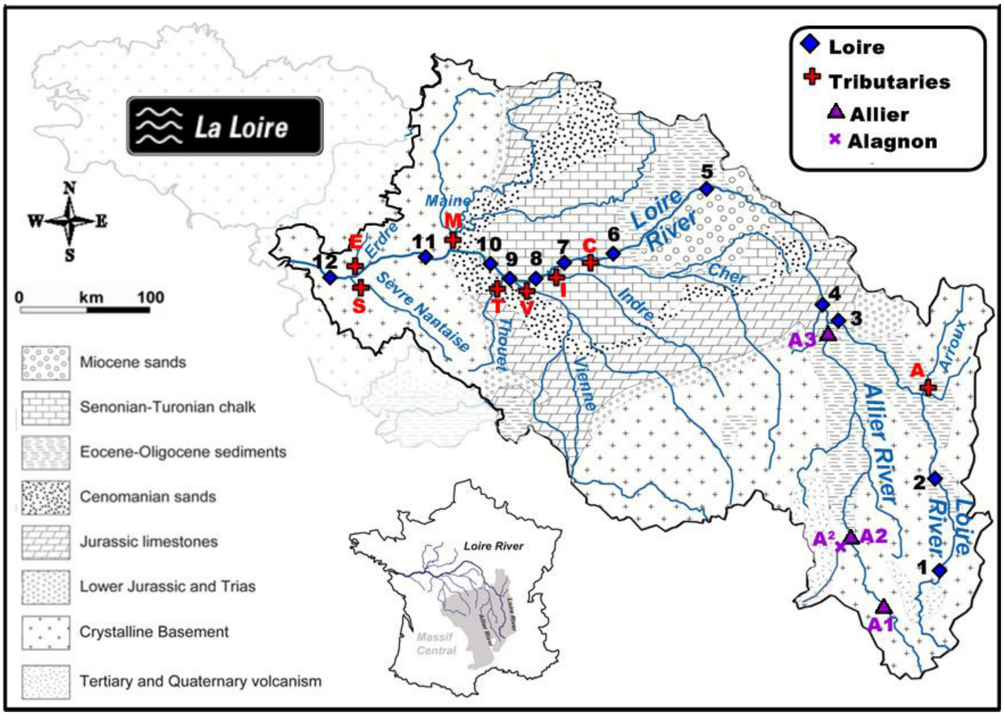

Fig. 1: Location of the Loire basin in France, the main river was sampled upstream and downstream (1 to 12) between the confluences of the main tributaries sampled just upstream of their confluence with the Loire (red symbols).

In this study, we report data from 2 snapshot campaigns at the basin scale; all samplings were preformed within a 2-days period. The first campaign took place during a flood event, a typical 2-year return flood (~1700 m^3/s in Orléans). The second one took place in the following low flow period (~75m^3/s in Orléans). Through $\delta^{18}O$-δ^2H and strontium isotopes ($^{87}Sr/^{86}Sr$), we intend to trace mixings and water-rock interactions at the catchment scale. This study, with two pictures of the whole basin in contrasted hydrological situations, complements previous investigations on the Loire using geochemical tracers (major and trace elements, isotopes)[1,2].

2. Stable isotopes of the water molecule: tracer of the water origin

Stables isotopes of the water molecule can be considered as conservative tracers when two water bodies are mixed at a given time. Mixings can be evidenced if the two water bodies have clearly distinct signatures; in a $\delta^{18}O$ *vs.* δ^2H diagram, the mixings plot on a straight line between the two end-members. At the Loire River basin scale, $\delta^{18}O$ range from -9.2 to -5.6 ‰ during the flood event and between -7.9 and -2.6‰ during low flow (Figure 2). In the upper part of the basin in the Massif Central, the Loire (1-2) and the Allier samples have the typical signature of the rain water inputs ($\delta^{18}O$ ~ -9‰) characterized in the Massif Central[3], reflecting both the continental and altitudinal effects, plot along the Massif Central Local Meteoric water line. Conversely, the tributaries close to the Atlantic Ocean (e.g. Erdre and Sèvre) present typical signatures of coastal rainwaters[3] ($\delta^{18}O$ ~ -5.5‰). Note that during the low flow period, most of the samples downstream of the Massif Central present typical evaporated signatures (slope ~5.5). The Loire River signatures up- to downstream are supposed to result from successive binary mixings (Loire upstream + Tributary = Loire downstream). Figure 2 points out some significant anomalies, i.e. during the flood, the Loire River presents a shift towards enriched values between sampling points 5 and 6 with no significant contribution from tributaries. Then, between sampling points 6 and 7, the contribution of the Cher (C) is not marked as point 7 signature moves back towards depleted values. In the same way, Loire point 10 after the confluence of the Thouet (T) presents a heavily depleted signature compared to point 9 which is inconsistent with the T signature. During the low flow period, the Loire between points 4 and 5 presents a heavy isotopes enrichment without significant contributions from tributaries, note that this enrichment doesn't seem to be related to evaporation as the Cl dissolved content decreases between these two sampling points. As for the flood period, the C confluence into the Loire is not marked during low flow. We highlighted that stable isotopes, as intrinsic tracers of the water molecule, evidenced well the complex hydrological behavior of the Loire River system in agreement with the results of previous local studies[1,2].

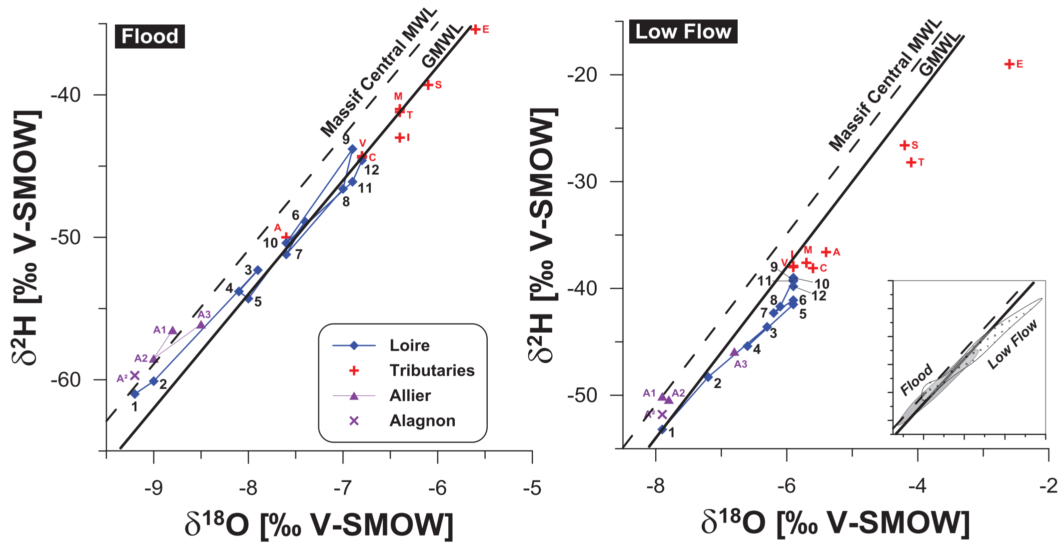

Fig. 2: Stable isotopes of the water molecule in the Loire River and its tributaries during a low flow period (right) and a flood (left)

3. Strontium isotopes : tracer of mixing and water-rock interactions

Surface water Sr isotopic compositions of the various tributaries of the Loire River are assumed to be constrained by the signature of the drained lithologies in each subcatchment. Strontium isotopic ratio $^{87}Sr/^{86}Sr$ varies according to the Rb/Sr ratio and the age of the drained material. Moreover, since natural processes such as dissolution/precipitation do not fractionate Sr isotopes, the measured differences in $^{87}Sr/^{86}Sr$ ratios are the result of mixing of Sr from different sources with different isotopic compositions. The sources of Sr that might control the Sr isotopic composition can be constrained by the relationships between the $^{87}Sr/^{86}Sr$ and Sr concentration or X/Sr ratios. Figure 3a illustrates the relationship in a $^{87}Sr/^{86}Sr$ *vs.* Ca/Sr graph for the tributaries and the Loire main stream. In the upper part of the basin, water samples are partly marked by the drainage of volcanic rocks (A^2, and Loire 1), $^{87}Sr/^{86}Sr$ signatures then increase rapidly through water-rock interaction with crystalline basement (Loire 2 and A2). The confluence with the Arroux (A) is clearly visible in low flow but during the flood, the $^{87}Sr/^{86}Sr$ decrease after the confluence and Ca/Sr increase, that would suggest the contribution of a carbonated component possibly through the contribution of the alluvial aquifer. From sampling 4 to 6 along the Loire River, and without significant inputs from tributaries, the variation of the $^{87}Sr/^{86}Sr$ and Ca/Sr plaid in favor of carbonate drainage (Figure1). The contributions of C and I tributaries are clearly visible during the flood period whereas this is not the case during low flow period. Downstream, the Loire (9) is clearly impacted by the Vienne (V) confluence both in low flow and flood. Towards the outlet into the Atlantic Ocean (from point 10), the contributions of the tributaries are erratic possibly due to the relatively low discharges of the tributaries compared to the Loire main stream. As an example, the E and S tributaries with typical signature of water-rock interaction with crystalline basement do not have any influence on the Loire signature (sampling points 11 to 12).

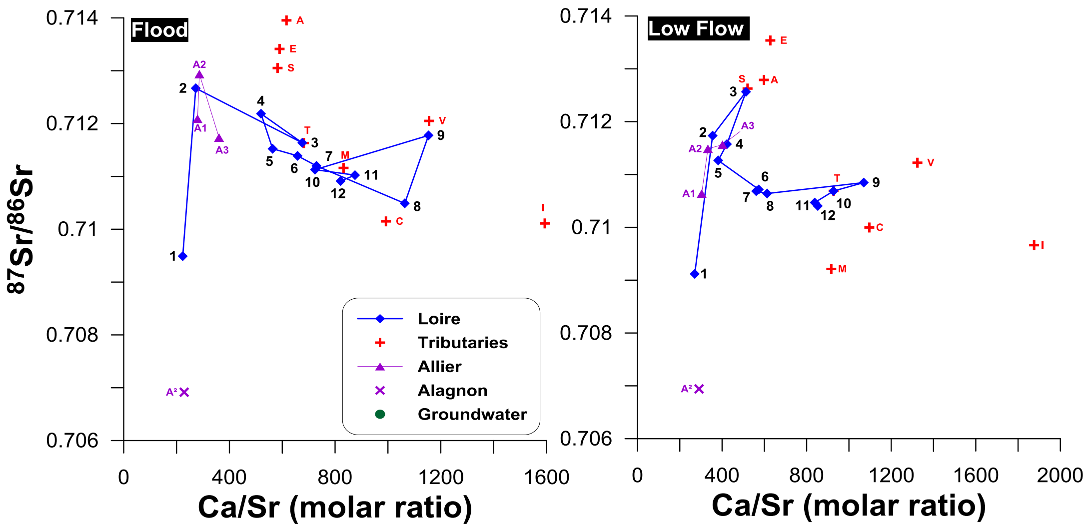

Fig. 3: Strontium isotopes versus Ca/Sr molar ratios in the Loire River and its tributaries during a low flow period (right) and a flood (left)

4. Strontium versus stable isotopes

Stable and Sr isotopes are good tracers of water mixings at the Loire basin scale in most of the cases. Nevertheless, several anomalies are pointed out and two extreme situations can be described. First, close to the outlet (points 11 & 12 along the Loire and tributaries E & S), the tributaries discharges only represent 1/30 (annual mean) of that of the Loire and thus no influence can be seen on both isotopic systematics. In spite of the contrasted $^{87}Sr/^{86}Sr$ between the Loire and these tributaries, the water mass balance precludes any detectable isotopic variation. Secondly, the discharge of the Cher (C) tributary representing about $1/3^{rd}$ of that of the Loire, should notably impact the Loire signatures after its confluence. However, regarding stable isotopes, the variation in the Loire River before and after the confluence (6 and 7) is on the opposite of C signature, in both low flow and flood. Regarding Sr isotopes there is no C influence during low flow on the Loire signature, while mixing is well traced during flood. Indeed, the ~30% of the water balance are confirmed by mixing calculation in figure 3a. The lack of fitting especially during low flow could be attributed to the impact of groundwater, such influence requiring additional specific investigations in both surface and groundwater compartments to evidence surface- groundwater connections.

5. Conclusion

Using the combination of stable isotopes of the water molecule and Sr isotopes at the catchment scale during two contrasted hydrological periods, this study confirms the very complex hydrological functioning of the Loire River system. The relation between surface and groundwater is probably a key issue for the Loire river system, especially regarding water resources management, and additional investigation being paramount in a near future.

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