



# Tracing surface water mixing and groundwater inputs using chemical and isotope fingerprints ( $\delta^{18}\text{O}$ - $\delta^2\text{H}$ , $^{87}\text{Sr}/^{86}\text{Sr}$ ) at basin scale: The Loire River (France)



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## ABSTRACT

The spatial and temporal distributions of major elements, stable isotopes of water molecule and strontium isotope ratios were investigated in the surface waters of the Loire River basin. The present study, using a coupled hydrological and geochemical approach, focuses on surface water mixing and the interactions between ground- and surface water. Stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) provide good evidence for the complex hydrological behavior of the Loire River system at the basin scale, and if binary mixing of surface water masses explain the longitudinal evolution of the Loire signature in the upstream part of the basin, groundwater contributions are required to explain locally the Loire signature. The water chemistry in the different zones of the basin shows large variations in major-element contents. The  $\text{NO}_3$  content in the Loire River roughly increases from up-to downstream and is mainly controlled by the input from tributaries. The highest concentrations are observed in the middle part of the Loire basin, in close relation with the diffuse agricultural sources. In terms of water-rock interaction, using Na as the reference element, the Loire Basin data are scattered between the three main end-members representing the major lithologies i.e. basalts, granite/gneiss and carbonate. Strontium-isotope ratios measured in water range from 0.70691 to 0.71395 and plotted vs. the Ca/Na ratios, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios clearly discriminate the three main lithological endmembers. In the Middle Loire section, the Loire flow rate increases without significant inputs of surface water, previous studies attributed this increase to groundwater inputs. The relationship between  $^{87}\text{Sr}/^{86}\text{Sr}$  and the Cl/Sr ratios clearly shows the groundwater inputs from the Beauce carbonate aquifer along a 90 km river profile, between Orléans and Amboise. These conservative tracers can be used to calculate up to 20% groundwater mixing during low flow period.

## 1. Introduction

Surface- and groundwater have been considered as separate water bodies for a long time by hydrologists and also decision makers, so that the relevance of interconnections between groundwater and surface water has frequently been underestimated. Due to a generalized growing water demand combined to increasing uncertainties in water supply in the context of global change, the awareness for the need to manage surface- and ground-waters as a single resource has steadily grown (e.g. Sophocleous, 2002). Since the last decades, rivers and aquifers are no more considered as physically independent entities and are now viewed as integral components of a continuum with strong mutual influences between river, aquifer and the interconnected hyporheic zone (e.g. Winter et al., 1999). This awareness was supported by new legal frameworks such as the European Framework Directive that emphasis to regulate the sustainable use of water resources through an integrated management of ground- and surface water resources and linked ecosystems (WFD, 2000, 2006).

Numerous research approaches were developed to identify and quantify the river-aquifer exchanges that can be in both directions depending on the river profile, the seasonal water levels and hydraulic

gradients (e.g. Winter et al., 1999; Fleckenstein et al., 2010 and references therein). The most developed approaches are probably the hydrological-hydrogeological ones based on the hydraulic gradient calculations and geological structures properties (Flipo et al., 2014 and references therein).

Among the other existing investing methods of surface water and groundwater relations, isotope techniques constitute a powerful approach. Considering stable isotopes,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are the most commonly used as intrinsic “ideal” tracers of the water molecule (e.g. Ladouche et al., 2001; Stewart et al., 2010; Négrel et al., 2011; Mohammed et al., 2014; Duvert et al., 2016). Furthermore, among the isotopes of dissolved elements, strontium isotopes are excellent tracers of water-rock interactions as  $^{87}\text{Sr}/^{86}\text{Sr}$  reflects the signature of the minerals that constitute the drained aquifer lithologies, and thus constitute valuable tracers to identify and, in optimal conditions, to quantify the exchanges between surface- and ground-water bodies (e.g. Négrel et al., 2003, 2004; Négrel and Petelet-Giraud, 2005; Shand et al., 2007; Petelet-Giraud et al., 2007; Petelet-Giraud and Négrel, 2007; Gao et al., 2010; Gourcy and Brenot, 2011; Paces and Wurster, 2014; Petelet-Giraud et al., 2016).

The Loire River Basin (117,480 km<sup>2</sup>) is the largest river basin in

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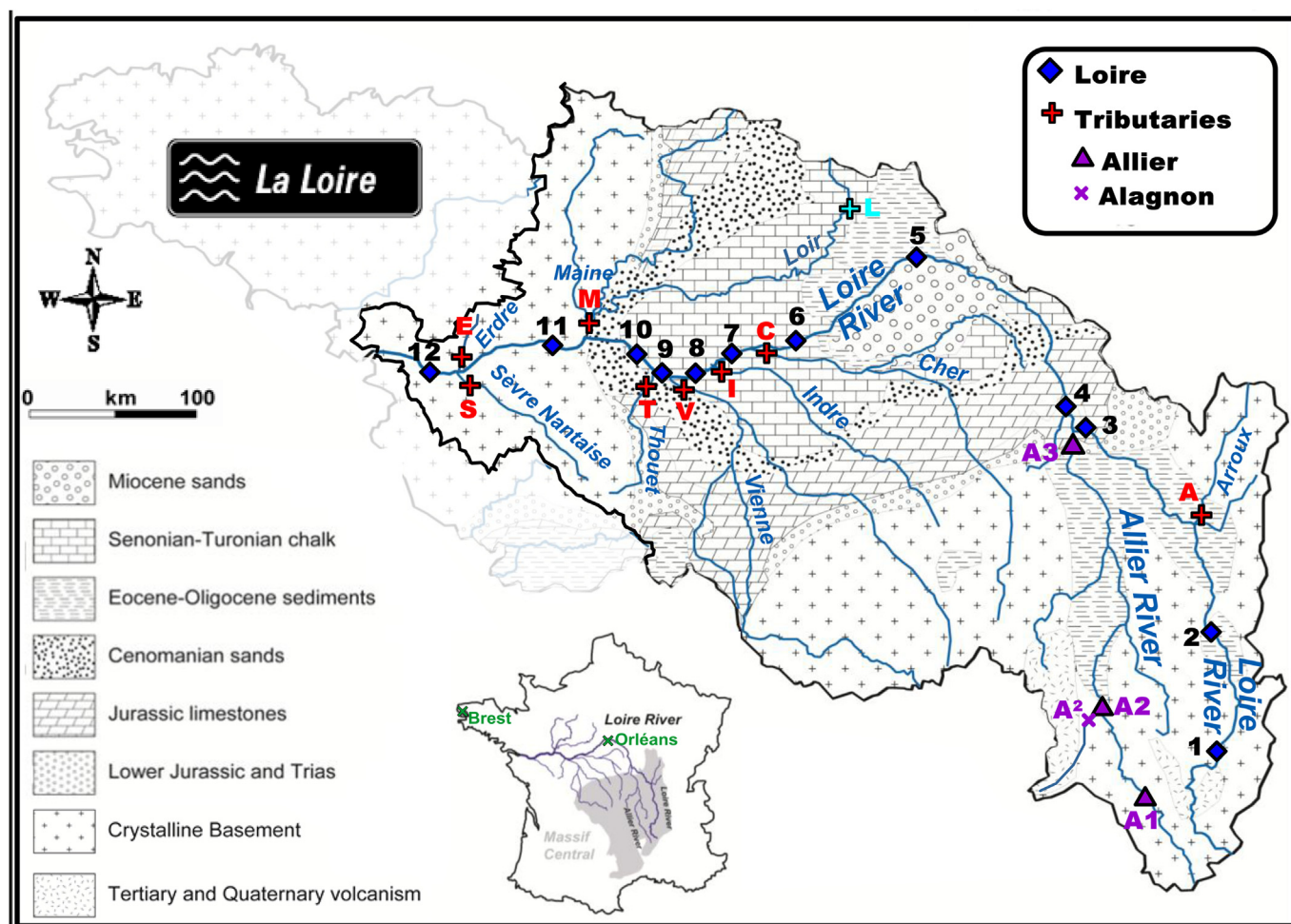


Fig. 1. Location of the Loire basin in France, the Loire main river was sampled upstream to downstream (location 1 to 12) between the confluences of the main tributaries sampled just upstream of their confluence with the Loire (red symbols, for labels see text). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

France covering 1/5th of the metropolitan territory. A total of 11.5 M inhabitants live in this area, including 4 M located along the main river course. The role of groundwater and the exchanges with surface waters have been studied in various areas of the basin for various purposes and through several techniques. Baratelli et al. (2016) have applied an integrated distributed surface-subsurface model to the Loire basin, taking into account the in-stream water level fluctuations with a simplified Manning-Strickler approach. They concluded that the river network mainly drains the aquifer system, the average net exchanged flow being  $2.10^{-2} \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$ , corresponding to 12% of the averaged discharge at the outlet of the basin. In the upper part of the Loire basin, connections between surface and groundwaters have been investigated in restricted area through chemical and isotopic tracers. In that way, Négrel et al. (2003) have pointed out the complex relations between surface and groundwater bodies using stable isotopes of the water molecule and strontium isotopes in secondary anastomosing channels just below the confluence the Allier River with the Loire River main stream, and in two unconnected oxbow lakes along the Loire River about 50 km upstream the Loire – Allier confluence (Fig. 1). They proposed a conceptual scheme of the Loire hydrosystem, based on  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ , to explain the annual variability of the Loire River isotopic signatures in Orléans (station 5 on Fig. 1) based on various contributions of runoff water from the upper part of the watershed and groundwaters. The primary characterization of the dissolved load chemistry in the upper Loire using temporal fluctuations of the major and trace elements (Négrel and Deschamps, 1996; Négrel, 1999;

Grosbois et al., 2000, 2001) has allowed the identification and quantification of geochemical signature from lithologies weathering and to calculate chemical weathering rates and anthropogenic fluxes.

Complementary to these previous approaches, we propose in this study to investigate for the first time the Loire River and its tributaries as a whole through two snapshot sampling campaigns during a low flows and a flood period. We first draw up a large scale evaluation of the Loire River, studying how the tributaries and water-rock interactions control the river geochemical signature (section 4). Secondly, we focus on a restricted river section to evaluate the exchanges between surface and groundwater through selected chemical and isotopic tracers (section 5).

## 2. Analytical methods

The water samples were collected in polyethylene bottles as raw samples for  $\delta^{18}\text{O}$ - $\delta^2\text{H}$  analysis, and filtered through  $0.45 \mu\text{m}$  PVDF filters using a Nalgene filter apparatus for chemical and strontium isotopes analysis. Bottles dedicated to cation and strontium isotopes analysis were acidified with 15N ultrapure  $\text{HNO}_3$  to  $\text{pH} < 2$ . Physicochemical parameters of each sample were measured on site, i.e. the electrical conductivity, standardized to  $25^\circ\text{C}$ , water temperature, pH, dissolved oxygen and redox potential. Samples were stored at  $4^\circ\text{C}$  in the dark prior to analysis. The water samples were analyzed in BRGM Laboratories by ICP-AES (Ca, Na, K, Mg; uncertainty less than 10%), ion chromatography (Cl,  $\text{SO}_4$ ,  $\text{NO}_3$ ; uncertainty less than 10%) and ICP-MS

(Rb, Sr; uncertainty 10–15%) and titration method according to N EN ISO 9963–1 ( $\text{HCO}_3^-$ ;  $\text{CO}_3^{2-}$ , uncertainty 5%). Chemical separation of Sr was done with an ion-exchange column (Sr-Spec), with total blank < 0.5 ng for the entire chemical procedure. After chemical separation, around 150 ng of Sr was loaded onto a tungsten filament and analyzed with a Finnigan MAT262 multiple collector mass spectrometer. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to an  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194. An average internal precision of  $\pm 10 \cdot 10^{-6}$  ( $2\sigma_m$ ) was obtained during this study. The reproducibility of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measurements was tested through replicate analyses of the NBS987 standard for which the mean value obtained was  $0.710233 \pm 24 \cdot 10^{-6}$  ( $2\sigma$ ;  $n = 20$ ) for the campaign of March 2001 and  $0.710227 \pm 13 \cdot 10^{-6}$  ( $2\sigma$ ;  $n = 11$ ) for the campaign of June 2002. Sample ratios were normalized to the certified value of the NBS987 ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.710240$ ). Oxygen and hydrogen isotopes of the water molecule were measured by mass spectrometry (Finnigan MAT252) by the gas equilibration method ( $\text{H}_2$  for hydrogen and  $\text{CO}_2$  for oxygen). Results are expressed as  $\delta$  values in ‰ vs. V-SMOW, associated errors are  $\pm 0.8\text{‰}$  for  $\delta^2\text{H}$  and  $\pm 0.1\text{‰}$  for  $\delta^{18}\text{O}$ .

### 3. The Loire River Basin: description and hydrological conditions

The Loire River is the longest French River (1012 km) and drains more than 1/5th of the French territory (Fig. 1). The upper parts of the Loire River and Allier River (main upstream tributary of the Loire) drain the mountainous area of the French Massif Central (maximum elevation 1500 m). The bedrock of the upper basin encompasses old plutonic rocks (granite, gneiss and micaschists, 500–300 My old) superimposed by tertiary to quaternary volcanic rocks. The middle part of the basin belongs to the sedimentary deposits of the Paris Basin, the Loire River drains sedimentary series mainly composed of carbonates from 200 to 6 My old, and includes the Cher (C), the Indre (I), the Vienne (V) and the Thouet (T) tributaries from the Loire-Allier confluence to the Maine (M) confluence. The lower Loire, that includes the Maine (M), Sèvre Nantaise (S) and Erdre (E) tributaries to the estuary, drains the crystalline basement of the Massif Armoricaïn (Fig. 1).

The Loire constitutes one of the major river inputs to the Atlantic Ocean with a mean annual discharge of  $850 \text{ m}^3/\text{s}$  at the outlet, the maximum mean monthly discharge being  $1630 \text{ m}^3/\text{s}$  in February and the minimum  $257 \text{ m}^3/\text{s}$  in August. The mean daily discharge of a 2-year return flood is about  $3200 \text{ m}^3/\text{s}$ , and  $4400 \text{ m}^3/\text{s}$  for a 5-year return flood (monitoring station M6240010; Banque Hydro, 2018; statistics over the last 50 years, 1967–2017). The Loire River basin receives precipitations originating from four main air-mass trajectories: (1) Predominantly westerly, originating from the Atlantic Ocean, (2) Northeasterly to northwesterly, with a marine origin from the North Atlantic and North Sea, (3) Easterly with a continental origin, and (4) Southeasterly to southwesterly, originating from the Mediterranean Sea, and carrying natural Saharan aerosols.

Data from two snapshot campaigns are reported for the first time at the basin scale. All samplings of each campaign were performed within a 2-days period. The Loire main river was sampled 12 times upstream to downstream (1–12, blue diamond on Fig. 1) between the confluences of the main tributaries (red cross and purple triangle on Fig. 1). The 9 main tributaries were sampled just upstream of their confluence with the Loire River. Note that the Allier tributary (A) was sampled in 3 different locations from upstream to downstream as well as one small contributing river, the Allanche river ( $A^2$ ) draining a small basaltic basin (Négreil and Deschamps, 1996). The first sampling campaign took place in March 2001 during a flood event corresponding to a typical 2-year return flood in Orléans in the middle of the basin ( $\sim 1700 \text{ m}^3/\text{s}$ ), and to a 5-year return flood at the outlet of the basin ( $\sim 4200 \text{ m}^3/\text{s}$ ). The second one took place in June 2002 during a low flow period ( $\sim 75 \text{ m}^3/\text{s}$  in Orléans and  $275 \text{ m}^3/\text{s}$  at the outlet). The Loire River, and its tributaries, discharge profiles of the sampling campaigns are presented in Fig. 2 (river flow rates are from Banque HYDRO, where discharge measurements are not available, they were estimated by

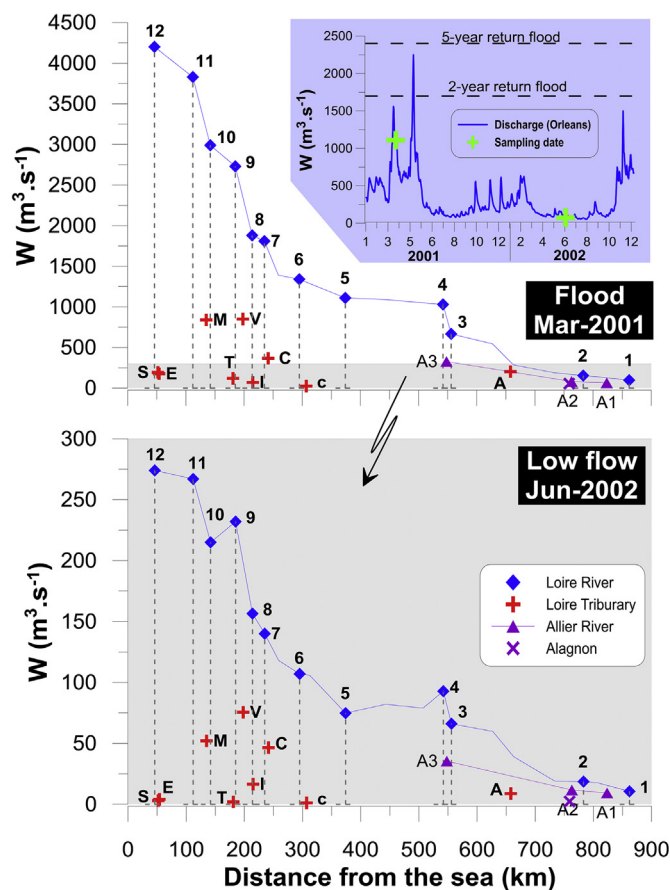


Fig. 2. Discharge ( $W$  in  $\text{m}^3/\text{s}$ ) of the Loire River and its tributaries from upstream to downstream of the Loire Basin during a flood period (March 2001) and a low flow period (June 2002). Sampling periods are replaced in the context of the Loire River discharge in Orleans in the Middle of the Basin (2001–2002).

difference). For comparison, both sampling periods are placed in the general context of the Loire River discharge in Orleans over two years (2001–2002).

Fig. 2 shows that the Loire River discharge increases at the basin scale, from a factor 43 and 26, between stations 1 and 12, during the flood event and the low flows respectively. This increase can be mainly explained by the flow contributions from the tributaries, especially in the upper and lower parts of the basin. We note that the variations of the Loire discharge in the middle of the basin (between stations 4 and 6) are not related to the tributaries and that connections with groundwater are necessary to explain the measured flow rates, this will be address in details in section 5.

### 4. Large scale evaluation of the Loire River: tributaries and water-rock interactions control on the river geochemical signature

#### 4.1. Stable isotope $\delta^{18}\text{O}$ and $\delta^2\text{H}$ , intrinsic tracers water origins

Stables isotopes of the water molecule ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) are suitable tracers of water origins at the Loire basin scale as their natural variations in precipitations mark the continental effect, i.e. air masses trajectories mainly eastwards from the Atlantic coast, as well as the altitude effect (Craig, 1961). Both phenomena being superimposed upstream of the Loire River in the Massif Central. Considering the temperatures encountered in catchment studies, the stable isotope  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signatures are not affected by exchange with soils or rocks, and thus can be considered as conservative tracers when two water bodies are mixed at a given time (e.g. Mook, 2000). In the classical  $\delta^{18}\text{O}$  vs.

$\delta^2\text{H}$  diagram, mixing can be shown if the two water bodies have clearly distinct signatures. The result of a mixing plot on a straight line between the two end-members.

At the Loire River basin scale,  $\delta^{18}\text{O}$  range from  $-9.2$  to  $-5.6\text{‰}$  during the flood event and between  $-7.9$  and  $-2.6\text{‰}$  during low flow (Fig. 2). In the upper part of the basin in the Massif Central, the Loire (locations 1 and 2) and the Allier samples (A1 and A2) have the typical signature of the rain water inputs characterized in the Massif Central ( $\delta^{18}\text{O} \sim -9\text{‰}$ ; Millot et al., 2010), reflecting both the continental and altitudinal effects. Data plot along or close to the Massif Central Regional water line ( $\delta^2\text{H} = 8 \delta^{18}\text{O} + 13.1$ , Fouillac et al., 1991). This line was defined according to 105 analysis of superficial waters: springs, rivers and shallow boreholes, and thus can be less representative than a rainwater monitoring, but considering the few available data for the whole Massif Central, it probably constitutes the best estimated of the water input signal. Some rainwater monitoring in the Massif Central, at lower altitude (420–650 m), define lower d-intercept (Mohammed et al., 2014 and references therein). This can be explained by an increase of evaporation within the air column below the air masses (Clark and Fritz, 1997) and these monitorings probably only represent very local conditions. Downstream, the tributaries close to the Atlantic Ocean (e.g. Erdre and Sèvre) present typical signatures of coastal rainwaters as represented by the precipitation monitoring in Brest represented by the mean weighted values for the years 2001 and 2002 (Millot et al., 2010). Note that during the low flow period, most of the samples downstream of the Massif Central present typical evaporated signatures (slope  $\sim 5.5$  in the  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  diagram).

Previous studies have focused on the temporal variability of the stable isotopic signatures along the hydrological year (Grosbois et al., 2000; Négrel et al., 2003), especially in Orléans station (5) which integrates all the upper part of the basin (Fig. 1). Here, through the two snapshot campaigns, we intend to explain the stable isotopic signatures variations all along the Loire River by successive binary mixing corresponding to the following scheme: Loire upstream the confluence + Tributary (ies) = Loire downstream the confluence. In that way, in the upper part of the Loire Basin, up to the Loire-Allier confluence (Fig. 1), the inputs of the main tributaries (Arroux: A and Allier: A3) explain the signatures observed in the Loire main stream, both in low flows and flood periods. Downstream, during the low flow period,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signatures of the Loire remain relatively stable, especially between Orléans (5) and the outlet of the basin (12). Also, note that the tributaries from the middle part of the basin (Cher, Indre, Vienne as well as the Maine) present similar signatures than the Loire ( $\delta^{18}\text{O} \sim -5.5$  to  $-6\text{‰}$ ) and thus mixing with these tributaries cannot be shown with stable isotopes of the water molecule because of a lack of isotopic contrast. Considering the location of Maine River (M,  $\delta^{18}\text{O} = -5.7\text{‰}$ ,  $\delta^2\text{H} = -37.6\text{‰}$ ) we could expect a signature similar to that of the western tributaries (Thouet, Sèvre and Erdre,  $\delta^{18}\text{O} > -4\text{‰}$ ), i.e. significantly influenced by the enriched inputs from the Atlantic coast (cumulative rain of June 2002 in Brest:  $\delta^{18}\text{O} = -4.55\text{‰}$ ;  $\delta^2\text{H} = -31\text{‰}$ , Millot et al. (2010), not shown in Fig. 3) superimposed with evaporation process (Fig. 3), this point will be further discussed in the following. During the flood episode, the signal remains the same from the Loire-Allier confluence (4) down to Orléans (5) in agreement with the signature of the cumulative rain of March 2001 in Orléans ( $\delta^{18}\text{O} = -8.2\text{‰}$ ;  $\delta^2\text{H} = -53.3\text{‰}$ ; Millot et al. (2010), not shown). Nevertheless, during the low flow period, the Loire River from locations 4 to 5 presents a heavy isotopes enrichment without significant contributions from tributaries. It is worth noting that this enrichment does not seem to be related to evaporation as the Cl dissolved content decreases between these two sampling locations (Négrel et al., 2011). During this period, the river discharge varies between locations 4 and 5 (decreases, increases and decreases again, Fig. 2), reflecting that the river lose water, then gain water and then lose water again. Such an evolution could explain the observed Cl decrease according to the following scheme: part of river recharges the

adjacent aquifer, then there is a dilution from another water source (with low Cl and heavier isotope signature) like groundwater recharged during winter and sustaining locally the river flow in low flow period.

Within this general scheme, Fig. 3 points out some significant anomalies considering binary mixing during the flood event. First, the Loire River presents a shift towards enriched values from sampling locations 5 and 6 with no significant contribution from tributaries, the  $\sim 25\%$  increase of the discharge between these 2 locations should reflect short distance drainage of local rain, but this is inconsistent with the Orléans rainwater signature during this period. Secondly, downstream, between the Loire sampling locations 6 and 7, the contribution of the Cher River (C), representing about 20% of the Loire discharge at location 7, is not marked as location 7 signature is similar (slightly depleted) to that measured at location 6. Lastly, the Loire at location 10, after the confluence of the Thouet (T) estimated to represent less than 10% of the Loire after the confluence, presents a heavily depleted signature compared to location 9, which is inconsistent with the Thouet signature.

The stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , intrinsic tracers of the water molecule, show well the complex hydrological behavior of the Loire River system at the basin scale. Binary mixing of surface water masses allow explaining the longitudinal evolution of the Loire signature especially in the upper part of the basin where isotopic signatures are clearly distinct due to the combination of the altitudinal and the continental effects. Nevertheless, in the lower part of the basin, the evolution of the Loire signature cannot be easily explained by binary mixing with the main tributaries, possibly due to the lack of sensitivity of these tracers when the contribution of the tributaries only represent a few percent of the mixing, or because other water contributions, like groundwater inputs, are required to explain locally the Loire signature. In that way, dissolved chemical and isotopic tracers, potentially more sensitive are tested in the next session.

## 4.2. Water-rock interactions and water mixing at the basin scale

### 4.2.1. Major element chemistry

At the basin scale, the Total Dissolved Solids (TDS, mg/L) significantly increases from up-to downstream of the Loire River with 129–265 mg/L during low flow period in locations 1 and 12 respectively (Table S1, Supplementary Material). During the flood event, the river water is more diluted as TDS values vary from 91 mg/L (location 1) to 201 mg/L (location 12), the maximum TDS being observed in Orléans (location 5) with 229 mg/L. The dissolved inputs to a river result from atmospheric inputs through precipitations, anthropogenic inputs resulting from agricultural, urban and industrial activities, and finally from water-rock interactions (e.g. Meybeck, 1986; Roy et al., 1999).

The dissolved contents of rainwater are mainly controlled by the distance to the sea according the main air masses trajectories (Meybeck, 1986). Négrel et al. (2007) summarized rainwater data from different locations within the Loire basin, precipitations being dominated by Cl and Na. Along the coast the Cl weighted mean value is 245  $\mu\text{mol/L}$ , the dissolved content rapidly decreases eastward, with a Cl weighted mean of 35  $\mu\text{mol/L}$  in Orléans and 18  $\mu\text{mol/L}$  in Clermont-Ferrand (Massif Central). This eastward trend is also clearly marked in the Loire tributaries, with a maximum Cl content observed in the western tributary, the Erdre (E) and the lowest one in the Allier upstream (A1), both in high and low flows (Fig. 4A). Note that all the samples plot below the seawater dilution line (representing the Na/Cl ratio of the sea spray salts present in rainwater, Fig. 4A), samples with a high Na excess result from the drainage of the crystalline basements (e.g. Sèvre Nantaise (S), Arroux (A), Allier (A1 – A3)). The tributaries draining the carbonated basins plot close to the seawater dilution line, reflecting the common origin of Cl and Na from the sea spray salts.

In evaporite free basins, Cl may also originates from anthropogenic inputs (Meybeck, 1983), Fig. 4A shows that none of the samples present

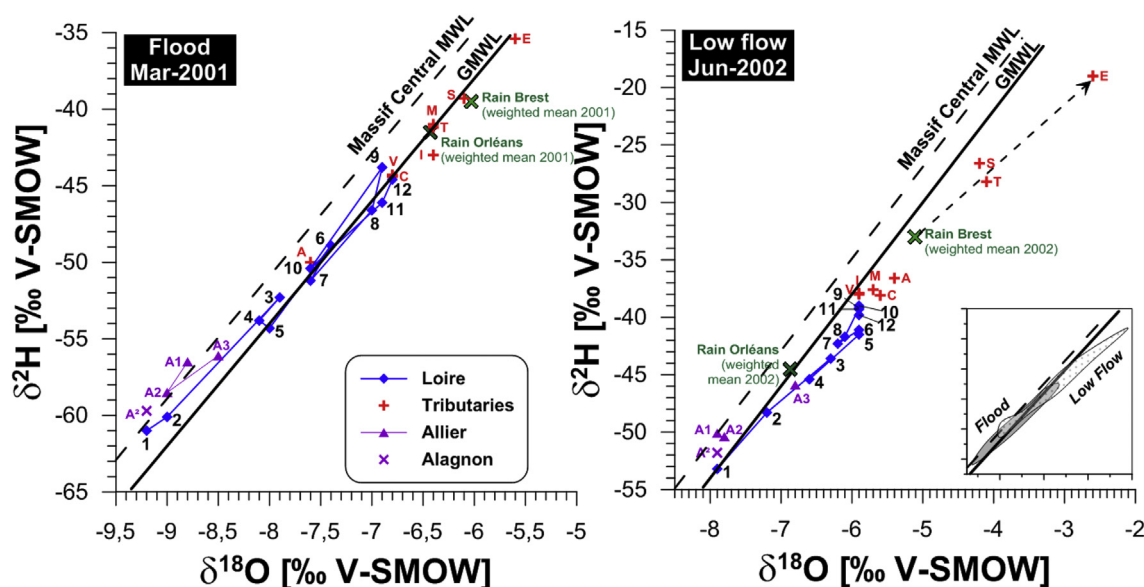


Fig. 3. Stable isotopes of the water molecule ( $\delta^{18}\text{O}$ - $\delta^2\text{H}$ ) in the Loire River and its tributaries during low flow period (right) and a flood episode (left). Rainwater monitoring in Brest and Orléans locations are reported as annual weighted mean values for the years 2001 and 2002 (Millot et al., 2010).

a Cl enrichment compared to Na, meaning a limited Cl inputs from anthropogenic activities. Nitrates ( $\text{NO}_3$ ) is the most dominant N species in the Loire Basin surface water compared to nitrites ( $\text{NO}_2$ ) and ammonium ( $\text{NH}_4$ ), and nitrates is one of the main nutrient degrading the surface water quality and responsible of water eutrophication (Minaudo et al., 2015 and reference therein). There is no correlation between Cl and  $\text{NO}_3$  contents in the Loire tributaries (Fig. 4B and C), the maximum  $\text{NO}_3$  being measured in the Cher River (C) with notably constant values in low flow and flood periods ( $\sim 300 \mu\text{mol/L}$ , i.e.  $\sim 18.5 \text{ mg/L}$ ), together with a moderate Cl content of 355 and  $631 \mu\text{mol/L}$  in flood and low flow respectively. At the opposite, the lower  $\text{NO}_3$  contents are observed in the Arroux (A), and Erdre (E) as well as the Allier upstream, with values below  $80 \mu\text{mol/l}$  corresponding to nitrates contents that can be observed in natural environment. Note that denitrification processes can also lead to  $\text{NO}_3$  depletion while the Cl content remains unaltered, this was shown in the neighboring Seine basin to explain the seasonal nitrate variation in the Seine River (Curie et al., 2011). The data acquired on the main tributaries during this study are replaced in their context using the water quality monitoring (Naiades database available at <http://www.naiades.eaufrance.fr/>) at the outlet of these tributaries over the 2001–2002 period (Fig. 4B). There is no correlation between Cl and  $\text{NO}_3$ , and our data fall within the domains defined by the monitoring data. Nevertheless it is noteworthy that some samples, sampled during the flood event, present more diluted concentration regarding Cl (Thouet (T), Cher (C) and Sèvre Nantaise (S)) but also in  $\text{NO}_3$  (Cher (C) and Thouet (T)), probably due the high river discharges compared to the monthly monitoring. It can be agreed that Cl concentrations can vary greatly between both sampling campaigns with a dilution effect when the river discharge increase, while the  $\text{NO}_3$  concentrations remain more or less constant or increase with increasing river discharges, reflecting the leaching of soils N through rainfall during winter. Within this global scheme, the Loire River itself presents a general increase of nitrates concentrations from upstream to downstream (Fig. 4C), reaching its maximum after the Vienne confluence in low flows and after the Indre confluence during the flood episode. The  $\text{NO}_3$  content in the Loire is mainly controlled by the input from tributaries, with the highest concentration in the middle part of the Loire basin (Cher, Indre and Maine). This is consistent with the strong correlation between nitrates concentration along the Loire longitudinal profile and the percentage of the basin classified as arable land as shown by Minaudo et al. (2015), and thus that nitrates concentrations originate from diffuse

agricultural sources.

As our sampling campaigns represent two instantaneous picture of the basin, and considering the observed variations of both Cl and  $\text{NO}_3$  concentrations in the main tributaries, the Loire main river concentrations should be explained by the successive inputs of the tributaries. During the low flows period, the  $\text{NO}_3$  concentration remain low in the upper part of the basin up to the Loire-Allier Confluence, while Cl increase up to  $550\text{--}600 \mu\text{mol L}^{-1}$ . In the middle of the basin,  $\text{NO}_3$  concentration decreases between locations 4 and 5, as well as Cl ones, which could support the mentioned hypothesis of a groundwater supply with low nitrates contents (naturally or resulting from a denitrification process).

According to the discharge measurements, the Cher tributary (C) contributes to about 30% of the Loire discharge at location 7. Fig. 4C shows that Cl remains constant and  $\text{NO}_3$  slightly decreases in the Loire while the Cher  $\text{NO}_3$  concentration is about  $300 \mu\text{mol/l}$ . The sampling of the Loire (location 7) is located 6.5 km downstream of the Cher confluence on the right bank; here we suspect an incomplete mixing of the Cher within the Loire as shown by Grosbois (1998). The river configuration with several branches and isles do not favor a rapid mixing. Downstream, the confluence of the Indre (I), accounting for 10% of the Loire discharge at location 8, slightly impacts the Loire signature with an increase of nitrates. The Vienne tributary (V) represents about 30% if the Loire discharge in location 9, considering the high nitrates increase and the Cl decrease measured in the Loire, we here again suspect an incomplete mixing between the Loire and the Vienne (meanders and islets), our sampling location favoring the Vienne. Downstream, the Loire River signature evolves slowly, probably because of the limited water inputs from the tributaries. Note that the Maine tributary (M) impact is not marked at location 11 despite a discharge estimated to account for about 20% (difference between Loire discharges at locations 10 and 11). From a general point of view, during the flood period, the scheme is roughly identical, with a more marked impact of the tributaries in the lower part of the basin.

All the samples present a calcium-bicarbonate chemical facies as calcium and bicarbonate are the main dissolved species in the Loire River and its tributaries. Calcium represents between 10% and 20% of the TDS both in the Loire and in the tributaries during the flood and during the low flow period, while bicarbonate represents between 37% and 62% of the TDS. The highest percentages are observed in the Indre River (I) draining almost exclusively carbonates. Considering calcium,

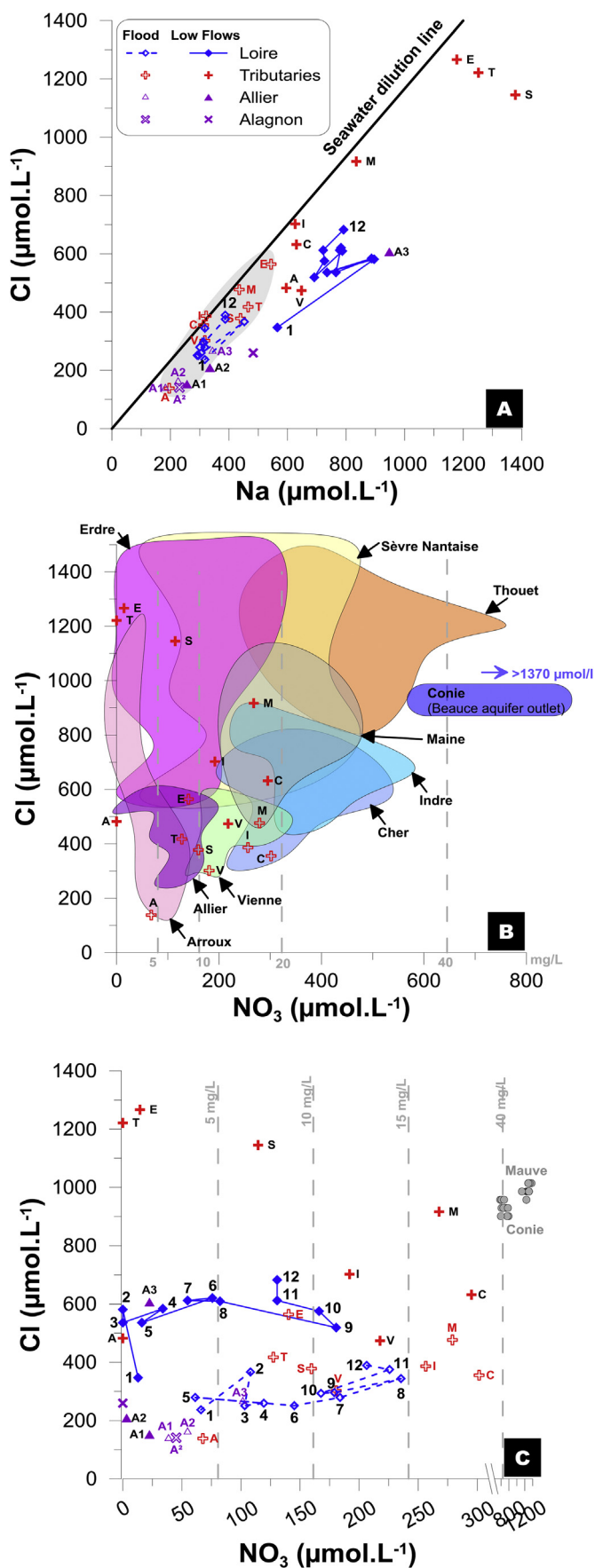


Fig. 4. A: Cl versus Na (µmol.L<sup>-1</sup>) of the Loire River and its tributaries during low flow and flood periods. B: Cl versus NO<sub>3</sub> (µmol.L<sup>-1</sup>) of the tributaries during this study compared to the monitoring of the same location of the years 2001 and 2002 (colored bubbles, Naiades database on surface water quality: <http://www.naiades.eaufrance.fr/>). C: Cl versus NO<sub>3</sub> of the Loire and its tributaries during this study.

the concentrations present low variations between the two sampling campaigns, in agreement with the scheme defined by Grosbois et al. (2000, 2001) during both low and high discharge values. They showed that calcium and bicarbonate concentrations increased up to an intermediate flow rate of 300 m<sup>3</sup>/s and then decrease with increasing discharge, this pattern was attributed to authigenic calcite precipitation in the river during low discharge period in summer, partly controlling the Ca and HCO<sub>3</sub> concentrations in the Loire River. In this study, during the low flow period, the Loire River is oversaturated relative to calcite (IS calcite = 0.89) in Orléans, while it is close to the equilibrium during the flood event (IS calcite = - 0.15). Note that despite the oversaturation concerning calcite, Ca and HCO<sub>3</sub> concentrations continue to increase in the Loire River downstream Orléans (Table S1).

Dissolved concentrations in water can vary deeply for a given type of rock, depending on residence time, water flux, water/rock interaction, and possible dilution-evaporation effects (Gaillardet et al., 1999). To overcome these effects, elemental concentrations are commonly normalized to Na concentrations (Négrell et al., 1993; Gaillardet et al., 1999; Brenot et al., 2014; Petelet-Giraud et al., 2016). On a Mg/Na vs. Ca/Na molar ratios diagram, mixing between two end-members are represented by a straight line as the same element (i.e. Na) is used for normalization. Fig. 5A represents the Loire Basin data during low flows in the Mg/Na vs. Ca/Na diagram, they are scattered between three main end-members that can be defined as follows: (1) the first end-member is characterized by low Mg/Na and Ca/Na ratios and includes three tributaries of the Loire, the Arroux (A), the Thouet (T) and the Sèvre-Nantaise (S), that drain crystalline basements in the eastern and western parts of the basin respectively. This is in agreement with the ratios defined by Meybeck (1986) from French remote rivers draining granite, gneiss and alkaline (+/- calco-alkaline) micaschistes. Data from the Desges River in the French Massif Central, mainly draining granite and gneiss, are also reported (Négrell, 1999; Négrell and Roy, 2002), defining the reference granite/gneiss domain; (2) the second end-member is characterized by a higher molar Mg/Na (> 0.4) and a low Ca/Na ratio, similar the silicate end-member. It is defined by the Allagon tributary (A<sup>2</sup>) draining the volcanic area in the Massif Central. These ratios are in agreement with those reported by Meybeck (1986) for such rock type, as well as with the data from the Allanche, a small tributary of the Alagnon draining 160 km<sup>2</sup> of basalt (Négrell and Deschamps, 1996; Négrell and Roy, 2002). It is noteworthy that the Allier River (location A2, downstream the Alagnon confluence) is clearly imprinted by the high Mg/Na ratio of its tributary; (3) the third end-member is characterized by a medium Mg/Na ratio (intermediate between end-members 1 and 2) and a higher Ca/Na ratio, attributed to a carbonated end-member as represented by the Indre tributary (I) mainly draining the Jurassic limestones and Senonian-Turonian chinks. The Ca/Na ratio (close to 4) is relatively low compared to Meybeck's reference (Meybeck, 1986) for rivers draining pure or dolomitic limestones (Ca/Na ~ 60–80) and chinks (Ca/Na ~ 20), or the source of the Seine river emerging from Jurassic limestones (Ca/Na ~ 30; Roy et al., 1999). Note that this ratio is closer to that we observed in the discharge of the Beauce aquifer (Ca/Na ~ 8 for the Mauve, and Ca/Na ~ 6.5 for the Conie). The difference could be related to the supersaturation with regard to calcite (IS calcite = 1.12) of the Indre river that may control the dissolved calcium content. Within this general scheme, the Cher (C) and Maine (M) tributaries tend towards the carbonates end-member implying that the carbonated part of their basin imprints dominantly their Ca/Na and Mg/Na ratios. The Vienne (V) signature is intermediate

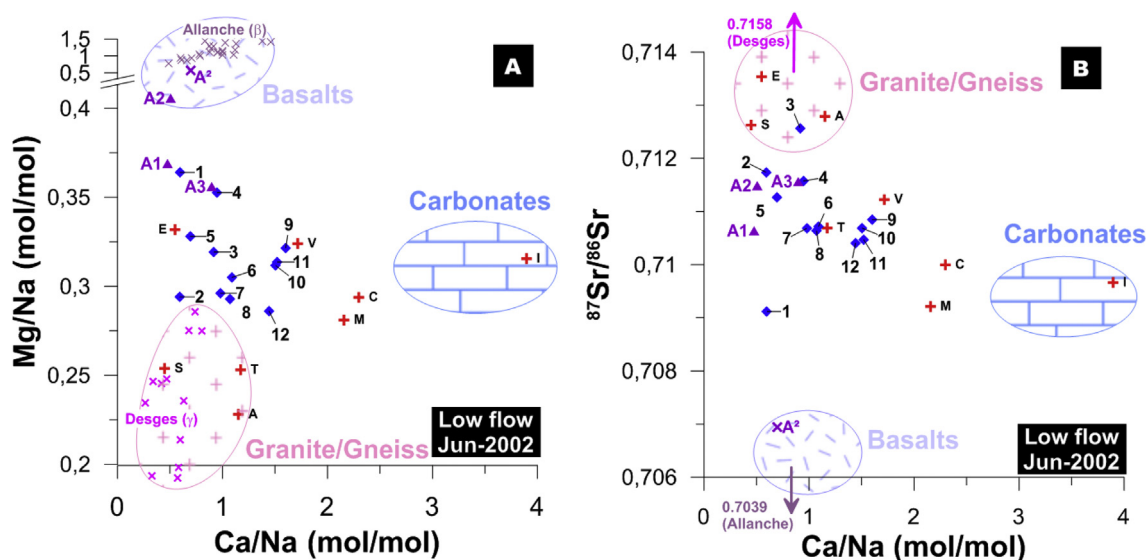


Fig. 5. Mg/Na versus Ca/Na (molar ratios) of the Loire River and its tributaries during low flow period (A) and  $^{87}\text{Sr}/^{86}\text{Sr}$  versus Ca/Na (B). The Desges River draining granites and the Allanche River draining basalts in the Massif Central are also reported (Négrel and Deschamps, 1996; Négrel, 1999; Négrel and Roy, 2002).

between the carbonates and granite/gneiss end-members, reflecting the geology of its drainage area composed of a large part of crystalline rocks upstream. The Erdre (E) presents a higher Mg/Na ratio than the granite/gneiss end-member, potentially related to the more complex geological settings of its basin mainly composed of Brioverian-Ordovician-Devonian sediments with few orthogneiss and granitic rocks. The Allier River is characterized by an intermediate Mg/Na signature reflecting the impact of both crystalline and volcanic rock drainage. The Loire River globally evolves from an intermediate signature between the granite/gneiss and basalts endmembers upstream towards a more pronounced imprint of the carbonated endmember due to the confluence of the main tributaries. Nevertheless, binary mixing are not always well defined in this diagram during low flow period, probably due the oversaturation with regard to calcite and dolomite in the middle Loire section that can partly control the dissolved concentration of Ca and Mg.

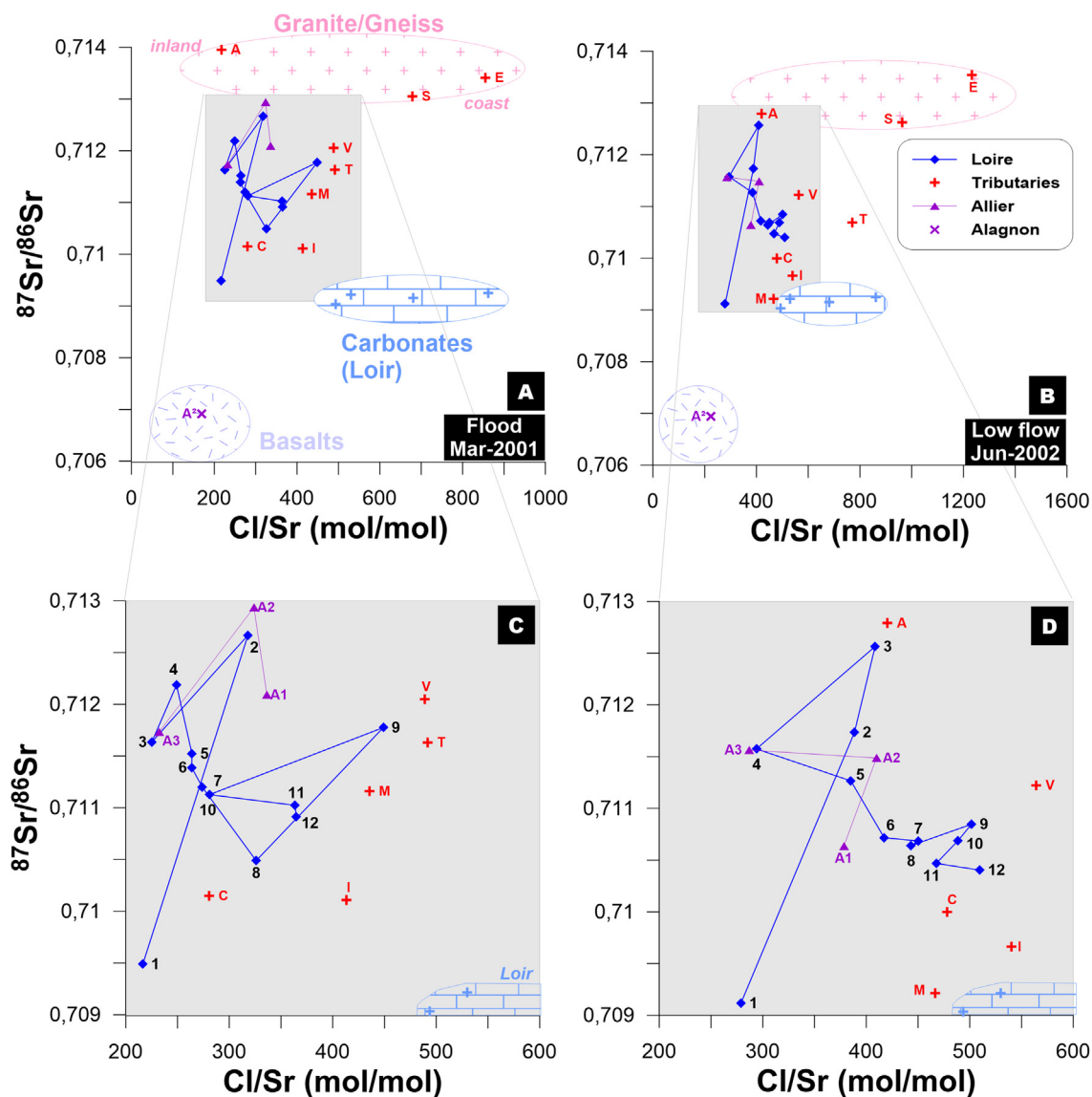
#### 4.2.2. Strontium isotopes

Strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) naturally vary in rocks because one of the strontium isotopes ( $^{87}\text{Sr}$ ) results from the radioactive decay of the naturally occurring rubidium  $^{87}\text{Rb}$  whose initial abundance varies significantly from a rock type to another (Faure, 1986). As the rubidium period is among the longest in naturally occurring radioactive isotopes, the resulting  $^{87}\text{Sr}/^{86}\text{Sr}$  can be used as a conservative tracers of water-rock interactions (e.g. Blum et al., 1994), and thus constitute a powerful tool for understanding water circulation in different reservoirs in a watershed (e.g. Petelet-Giraud et al., 2003a; Petelet-Giraud and Négrel, 2007). The  $^{87}\text{Sr}/^{86}\text{Sr}$  signature of surface water reflects the type of drained rocks, high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are observed in water draining silicates with high Rb and low Sr concentrations, whereas low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios reflect drainage of carbonates with low Rb and high Sr contents whose isotopic compositions are related to the Sr isotopic signature of seawater at the time of deposition (e.g. Koepnick et al., 1990).

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, here we will not distinguish the part of the Sr originating from fertilizers (Négrel, 1999; Petelet-Giraud et al., 2003b). The Loire tributaries present Sr isotopic signatures varying between  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70694$  and  $0.71354$  during the low flow period (Alagnon (A<sup>2</sup>) and Arroux (A) respectively) and between  $0.70691$  and  $0.71395$  during the flood event (Alagon and Erdre respectively). The Loire main stream varies in lower proportions, i.e.

between  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70912$  and  $0.71256$  during the low flow period (locations 1 and 3 respectively) and between  $0.70949$  and  $0.71267$  during the flood event (locations 1 and 2 respectively). Fig. 5B presents the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios versus the Ca/Na ratio discussed above, it allows to clearly discriminate the three main lithological endmembers controlling the water signatures in the Loire Basin. The granite/gneiss end-member is characterized by the highest Sr isotope ratios measured in the Loire basin ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.712$ ), in agreement with the drainage of old granitic and metamorphic rocks basement (Négrel and Roy, 2002). The lowest ratio ( $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.707$ ) is measured in the Alagnon (A<sup>2</sup>) draining the recent volcanic rock, and define the basalts endmember in agreement with that defined by Négrel and Roy (2002) in the Allanche basaltic small basin. The tributaries mainly draining carbonated areas (Indre, Cher and Maine), with  $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.709$ – $0.710$ , define the carbonates endmember. Note that the Loire upstream (location 1) is marked by the interaction with volcanic rocks with a low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio about  $0.70912$ . The Allier Sr isotope signature increases upstream to downstream towards the granite/gneiss endmember, its signature being consistent with previous measurements along its course ( $\sim 0.7110$ – $0.7113$ ) by Négrel et al. (2003, 2004).

Natural processes such as dissolution/precipitation do not fractionate Sr isotopes, implying that  $^{87}\text{Sr}/^{86}\text{Sr}$  can be considered as a conservative tracer when two water bodies are mixed, the resulting signature depending on the amount of dissolved Sr of each endmember (Faure, 1986). It is worth noting that surface waters are not oversaturated with regard to Sr-bearing minerals meaning that the dissolved concentrations are not controlled. The sources of Sr that might control the Sr isotopic composition of the Loire main stream can be constrained by the relationships between the  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration or X/Sr ratios, where binary mixing can be shown through straight lines. In the following, we chose to not use any chemical element whose dissolved concentration can be partly controlled by mineral precipitation. We are thus using Cl as a conservative tracer normalized to Sr (Fig. 6). In this diagram,  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. Cl/Sr, the three identified endmembers are also clearly distinct, because coastal and inland tributaries draining the crystalline basements and having similar radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$ , are discriminated by their Cl/Sr ratios. Considering the low flows period (Fig. 6B and D), the evolution of the Loire  $^{87}\text{Sr}/^{86}\text{Sr}$  signature up to the confluence with the Allier River is consistent with both the evolution of the drained lithology and the confluence of the main tributaries (Arroux (A) and Allier (A3)). The evolution around Orléans (location 5) will be discussed in the next section. As shown in the previous section, the



**Fig. 6.**  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $\text{Cl}/\text{Sr}$  in the Loire River and its tributaries during low flow period (B and D) and a flood episode (A and C). The Loire samples (blue cross) represent the signature of the Beauce groundwater (this study). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

confluence of the Cher (accounting for ~30% of the Loire discharge) does not change the Loire Sr isotopic signature despite the Cher has a clearly lower  $^{87}\text{Sr}/^{86}\text{Sr}$ . This highlights the incomplete water mixing at location 7 where the Loire water is dominant. In the same way downstream, the proportion of the Vienne (V) within the Loire at location 9 is about 70% based on the dissolved element contents and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, whereas according to the flow rates measurement it only accounts for about 30%, here again the mixing appears to be incomplete due to the river configuration. During the flood this phenomenon is amplified, as the Vienne seems to account for 90% of the Loire signature at location 9, when the flow rate measurements indicate about 30%. During the flood event, the Vienne  $^{87}\text{Sr}/^{86}\text{Sr}$  signature increases from 0.71064 to 0.71205 together with a decrease of the Sr concentration from 0.84 to 0.62  $\mu\text{mol}/\text{L}$ , reflecting a water origin from the crystalline upper part of the Vienne basin, while during low flows, the carbonates from the lower part imprint their signature dominantly. During the low flow period, the confluence of the Cher and Indre rivers were not reflected by the Loire signature evolution, this is not the case during the flood where the  $^{87}\text{Sr}/^{86}\text{Sr}$  signature at location 8 decreases down to 0.71048 towards an intermediate signature between the Cher and Indre

tributaries (Fig. 6C).

### 5. Small scale evaluation: focus on the groundwater inputs to the Loire River

Along the Loire River, the middle section in the vicinity of Orléans (upstream and downstream location 5, Fig. 1), is recognized to receive groundwater inputs from the Beauce aquifer and from the leakage-recharge system of the Loire through the Loiret (both surface and groundwater circulation, e.g. Gonzalez, 1991; Gutierrez and Binet, 2010). In their global study of the Loire river system, Baratelli et al. (2016) point out that the maximum exfiltration rate (i.e. groundwater towards surface water) is observed downstream Orléans City (Fig. 7) with a flux up to 1.2  $\text{m}^3 \text{s}^{-1} \text{km}^{-1}$ , corresponding to the Beauce aquifer discharge. The main role of the Beauce aquifer has also been investigated more specifically through heat budget method based on river temperature estimated with satellite thermal infrared images along a 135 km river transect from Gien to Blois (Lalot et al., 2015). They show that the main groundwater discharge is concentrated along a 9 km transect just downstream of Orléans city with a discharge of



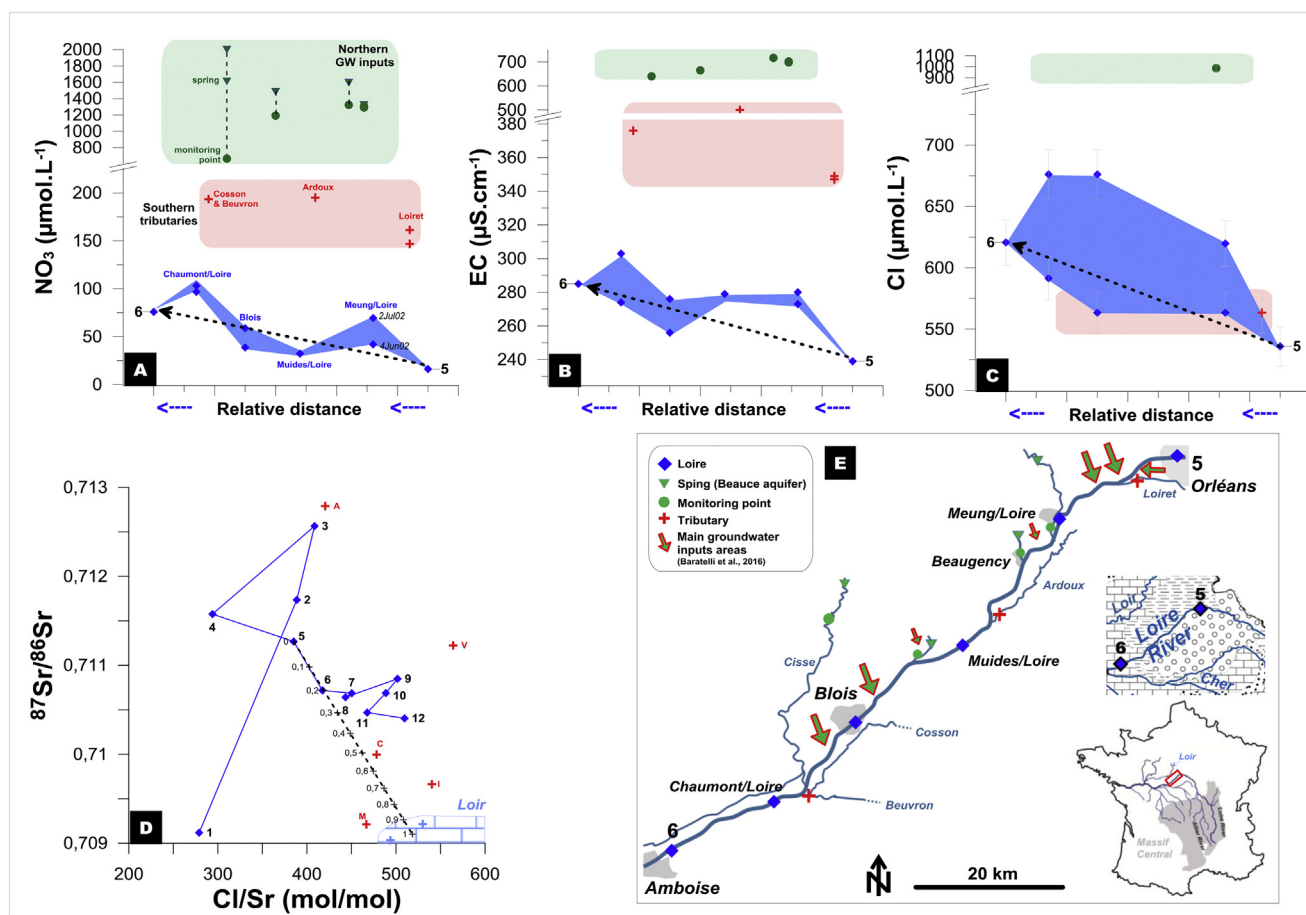


Fig. 7. A:  $\text{NO}_3^-$  profile, B: EC profile, C: Cl profile, D:  $^{87}\text{Sr}/^{86}\text{Sr}$  versus Cl/Sr in the Loire River (zoom of Fig. 6) and its tributaries during low flow period. The Loire samples represent the signature of the Beauce groundwater (blue cross). E: simplified Loire river profile between Orleans and Amboise with the main groundwater inputs. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

$5.3\text{--}13.5\text{ m}^3\text{ s}^{-1}$  during summer and winter respectively. This is roughly in agreement with the previous calculations based on groundwater modeling (calculated groundwater discharge:  $0.6\text{--}0.9\text{ m}^3\text{ s}^{-1}\text{ km}^{-1}$ ), Schomburgk et al. (2012) calculated a slightly lower but still significant groundwater discharge of  $0.5\text{ m}^3\text{ s}^{-1}\text{ km}^{-1}$ .

### 5.1. Impact of the ground-surface water connection on the river water quality

Between Orléans (location 5) and Amboise (location 6), the surface water contributions to the Loire through the tributaries were considered negligible. Indeed, for the heat budget studies (Lalot et al., 2015), the temperature of the tributaries are very close to that of the Loire itself, and more generally, their flow rates are very low (often less than  $1\text{ m}^3\text{ s}^{-1}$  in low flow periods) compared to the Loire. Considering the chemical signature evolution of the Loire between these two locations, we first have to verify the potential impact of these tributaries. In the southern part of the Loire, three tributaries are monitored regarding their quality (Naiades database): Loiret, Ardoux, Cosson and Beuvron that joint just before the confluence with the Loire (Fig. 7E). This quality monitoring mainly focus on the nutrient inputs so that complete major elements analyses (cations and anions) are often not available. N species (highly dominated by nitrates) and the electric conductivity are systematically available. In the same way, the quality of the Loire River is also monitored in 4 locations between Orléans and Amboise on a monthly basis. In Fig. 7 (A to C), we report the available data close to our sampling during low flow, i.e. 26-Jun-2002: The Loire river in Meung/Loire, Blois and Chaumont/Loire were sampled the 4-Jun-2002

and 2-Jul-2002 respectively, as well as the Loiret, Cosson and Beuvron tributaries. The Loire in Muides/Loire and the Ardoux tributary were samples the 24-Jun-2002. Considering the  $\text{NO}_3^-$  concentrations, they increase from 16.13 to  $75.81\text{ }\mu\text{mol/L}$  (factor 4.7) between locations 5 and 6 (Fig. 7A), while the southern tributaries are much more concentrated in  $\text{NO}_3^-$  (around  $150\text{--}200\text{ }\mu\text{mol/L}$ ). Nevertheless, these  $\text{NO}_3^-$  inputs cannot explain the Loire evolution considering the very low discharge of these tributaries. Note that the nitrates increase cannot be explained by the inputs of wastewater effluents only representing a few percent (1–2%) of the river discharge. This  $\text{NO}_3^-$  increase could be related to the groundwater inputs from the calcareous Beauce aquifer as pointed out in this area in previous studies (e.g. Baratelli et al., 2016). The Beauce aquifer is highly impacted by agricultural activities (Schnebelen et al., 1999), it discharges to the south directly into the Loire River and additionally through springs close to the Loire.

Four main springs were identified between Orléans and Blois (Fig. 7C) and their nitrate concentrations are monitored since 2001 (DIREN Centre, 2005). The  $\text{NO}_3^-$  concentrations in these springs vary between  $1300$  and  $2000\text{ }\mu\text{mol/L}$  (i.e. up to  $100\text{ mg/L}$ ) in June 2002, which is significantly higher than the measurements in the brooklets formed by these springs before their confluence into the Loire (Mauve, Ru de Beaugency, Tonne and Cisse):  $665\text{--}1320\text{ }\mu\text{mol/L}$  (Naiades database). This difference can be due to a dilution and/or a denitrification process, but cannot be demonstrated because any conservative parameter is available in the spring measurements.

Considering the flow rate increase between the Loire locations 5 and 6 ( $\sim 32\text{ m}^3\text{ s}^{-1}$ ), and a maximum surface water contribution of  $4\text{ m}^3\text{ s}^{-1}$  along this section, the groundwater contribution can be estimated to be

around 25% of the discharge measured in location 6. This means that  $\text{NO}_3$  concentrations would reach  $300 \mu\text{mol/l}$  at location 6 considering a mean groundwater nitrates of  $1300 \mu\text{mol/L}$  and a conservative binary mixing, this thus reflects a continuous  $\text{NO}_3$  removal (plant/microbial uptake) in this section of the Loire River. This is confirmed by the Loire profile for nitrates (Fig. 7A) that appears to be very reactive to the main groundwater inputs enriched in  $\text{NO}_3$ , followed by a  $\text{NO}_3$  decrease. This is especially true just downstream Orléans (location 5) and Blois, two sectors where groundwater inputs are particularly significant according to Baratelli et al. (2016), with up to  $1 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$  and  $0.4 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$  respectively, as an average based on the simulations between 1990 and 2007. The Cl concentrations are only available for the Mauve brooklet with a value of around  $1000 \mu\text{mol/l}$  (almost constant over the hydrological year), which is about twice that measured in the Loire river in location 5. Considering that about 25% of the Loire discharge in location 6 comes from the inputs from the Beauce aquifer, the measured Cl concentration in location 6 is in agreement with such a mixing.

## 5.2. Towards quantification of groundwater contribution through Sr isotopes

The Sr isotopic signature of the Loire River at location 5 remains relatively radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.71126$ ) reflecting the residual imprint of the crystalline basement drained upstream, it is therefore very distinct from that of a groundwater interacting with a carbonated aquifer. Sr isotopic composition are not available in any of the springs draining the Beauce aquifer. Nevertheless, on its western part the Beauce aquifer also feeds the Loir River (a tributary of the Maine, Fig. 1) through springs and brooklets. For instance, the Conie river presents similar characteristics to the southern springs (580–790 and 900–960  $\mu\text{mol/l}$  respectively, Naiades database, Fig. 4C). The Loir river was sampled during one hydrogeological year (Table 1), and presents Sr isotopic compositions varying between 0.70901 and 0.70967 with a mean value of 0.70922, and Cl/Sr being around 500 (molar ratio) during the summer period (June to September). In the  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. Cl/Sr (Fig. 7D) the Loir signature (location L on Fig. 1) is thus assumed to represent the Beauce aquifer signature feeding the Loire river to the south. In this diagram, the Loire River  $^{87}\text{Sr}/^{86}\text{Sr}$  decreases significantly from locations 5 to 6 (0.71126–0.71072 respectively) while the Cl/Sr ratio increases. The Loire River sample in Amboise (6) plots on a binary mixing line between the Loire River sample in Orléans (5) and the Loir signature previously defined. The calculated mixing proportions give a 20% groundwater inputs into the Loire River, in agreement with estimates based on Cl and Loire flow rate measurements. Using sodium as the reference instead of chlorine, would give the same mixing proportions.

**Table 1**

Loir monitoring in St-Maur location (L, Fig. 1) over the year 1996. W refers to the river discharge.

Date	W	Cl	$\text{NO}_3$	Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
	$\text{m}^3/\text{s}$	$\mu\text{mol/l}$	$\mu\text{mol/l}$	$\mu\text{mol/l}$	$\pm 1 \times 10^{-5}$
27/03/1996	1.51	691	331	2.01	0.70967
11/04/1996	1.02	838	249	1.69	0.70928
27/04/1996	0.79	803	–	1.70	0.70925
10/05/1996	0.74	800	–	1.46	0.70918
25/05/1996	0.94	776	126	4.14	0.70901
13/06/1996	0.37	846	–	0.98	0.70925
04/07/1996	0.41	951	64	1.79	0.70922
08/08/1996	0.23	1126	–	1.65	0.70915
10/09/1996	0.35	1039	–	–	0.70917
02/10/1996	0.71	–	–	1.42	0.70910
07/11/1996	1.70	855	60	1.73	0.70903
23/12/1996	2.39	1128	627	1.63	0.70945
30/01/1997	1.09	1132	425	1.58	0.70914

Sr isotopes thus demonstrate that (1) the increase of the Loire flow rate between Orléans (location 5) and Amboise (location 6) can only be explained by groundwater inputs from the Beauce carbonated aquifer; (2) this conservative tracer allows to calculate mixing proportions in full agreement with the discharge measurements. The 26th of June, the groundwater inputs are calculated to account for about 20% of the Loire discharge measured in Amboise (location 6), i.e. about  $21 \text{ m}^3 \text{ s}^{-1}$  representing a mean value of about  $0.23 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$  along this 90 km river profile.

## 6. Conclusion and perspectives

In this study, the functioning of the Loire River Basin was studied through two snapshot sampling campaigns in low flows and during a flood event. Through a coupled hydrological and geochemical approach, we focused on surface water mixing and the interactions between ground- and surface water.

The stable isotopes of water showed the complex hydrological behavior of the Loire River system at the basin scale: (1) In the upper part of the basin, binary mixing of surface water masses explain the longitudinal evolution of the Loire signature because the contrasted isotopic signatures reflect both the continental and altitudinal effects; (2) In the middle part, groundwater contributions are required to locally explain the Loire signature; and (3) in the downstream part, the morphology of the Loire River with several branches and isles precludes rapid water mixing below the confluence of tributaries. Moreover, in the western part of the basin, the Atlantic Ocean impact tends to homogenize the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signatures so that this tracer is less discriminant in term of water mixing.

The  $\text{NO}_3$  concentration along the Loire River increases from up-to downstream and appears to be mainly controlled by the input from tributaries, especially in the middle part of the Loire basin where the diffuse agricultural sources are mostly encountered. The major elements, using Na as the reference element, allow discriminating three main end-members representing the major lithologies, i.e. basalts, granite/gneiss and carbonate, which control the chemistry of the Loire River and its tributaries through water-rock interactions. Strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) show large variation at the basin scale (0.70691–0.71395) and clearly discriminate the three main lithological endmembers.

In the Middle Loire section, previous studies focused on the quantitative impact of the groundwater discharges into the Loire River. In this study, through geochemical and isotopic tracers, (1) the groundwater inputs to the Loire River were confirmed and clearly attributed to the Beauce carbonate aquifer using the relationship between  $^{87}\text{Sr}/^{86}\text{Sr}$  and the Cl/Sr ratios, (2) the major role of the groundwater inputs on the river discharge that account for ~20% in low flow is confirmed using conservative tracers (Sr isotopes and Cl concentrations); and (3) we point out the quality impact of these groundwaters especially regarding nitrates. Groundwater impacts on surface water quality have recently been considered as a potential vector of surface water contamination, (e.g. Rozemeijer and Broers, 2007; Garrett et al., 2012; Yu et al., 2018), nevertheless they are still weakly studied and quantified. Here, we show that nitrates concentrations rapidly decrease in the Loire River (especially in low flow period) after the groundwaters inputs enriched in  $\text{NO}_3$ , probably due to a nitrate removal processes (plant/microbial uptake?). This could be further studied along this 90 km river section, in complement to the approach by Minaudo et al. (2015). N and O isotopes of  $\text{NO}_3$  could help discriminating the source of nitrate present in the Loire upstream Orléans, resulting from diffuse N inputs from agricultural practices and punctual inputs from wastewater treatment plants, and the Beauce aquifer inputs; these isotopes can also be used to study of denitrification processes. Moreover, the Beauce aquifer being highly impacted by agricultural activities, the impact of its inputs into the Loire should be further investigated, especially regarding pesticides loads and fates, and their potential impact on the Loire related

ecosystems.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.apgeochem.2018.08.028>.

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