ELSEVIER

Surface water–groundwater interactions in an alluvial plain: Chemical and isotopic systematics

Ph. Négrel[a,*], E. Petelet-Giraud[a], J. Barbier[a], E. Gautier[b]

[a]BRGM, Water Department, Avenue C. Guillemin, BP 6009, 45060 Orleans cedex 02, France
[b]CNRS UMR 8591, Physical Geography Laboratory, Meudon, France

Abstract

Our work on the Loire River forms part of a French National Research Program dedicated to wetlands and aims to better understand the global functioning of the system from the hydrological, geochemical, ecological and sociological aspects. The present study, using a coupled hydrological and geochemical (stable and Sr isotopes) approach, focuses on the 'Soulangy' site with its secondary anastomosing channels just below the confluence of the Loire and Allier rivers, and also on the 'Dorna''nt' site with two unconnected oxbow lakes 50 km upstream of the confluence. The stable isotopes of water (δ^{18}O, δ^2H) show that the alluvial (or riverbank) aquifer feeds the Loire River during the summer, but is not recharged by the river during flood periods in the winter; the alluvial groundwater thus has a purely local origin from precipitation. The major elements reveal an anthropogenic input of Cl and more importantly of NO_3, especially near farms. The ^{87}Sr/^{86}Sr isotopes identify different groundwater layers in the alluvium, i.e. an upper and a lower alluvial aquifer, and a perched aquifer at Dornant, that have relatively complex relationships with the surface water. The two main rivers (Loire and Allier) present distinct geochemical characteristics reflecting the different lithologies that they drain upstream. In addition, the secondary channels, lying parallel to the Loire main stream at the Soulangy site, give different geochemical signatures, which shows that they are not fed by the same overflows of the Loire; they are more-or-less well connected to the upper level of the alluvial plain, and a longitudinal study of one of these channels has revealed a Loire River influence progressively replaced by a water contribution from the upper alluvial aquifer. Similarly, the two oxbow lakes at the Dornant site are not supplied by the same water during the summer months. A conceptual scheme of the Loire hydrosystem based on δ^{18}O and ^{87}Sr/^{86}Sr suggests that the isotopic variations of the Loire River can be related to a Massif Central surface-water supply for the Loire and Allier main streams and to a groundwater supply from the alluvial plains.
© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Wetlands serve as water-storage areas that reduce flooding by retaining water excess and releasing it to streams, and their importance for the future of our living world is becoming increasingly recognized. Not only are wetlands areas of exceptional biodiversity, but they also play a key role in the conservation and management of fresh-water resources (Whittaker and Likens, 1975; Holland et al., 1990; Mitsch and Gosselink, 1993; Hunt et al., 1998). As wetlands are

* Corresponding author.
   E-mail address: p.negrel@brgm.fr (Ph. Négrel).

complex and sensitive ecosystems, a slight change can have a strong impact not only on the wetlands themselves, but also on large areas of the enclosing catchment (Fustec and Frochot, 1996).

The hydrology and water quality of rivers, lakes and wetlands are strongly controlled by the exchanges of water and solutes with adjacent river banks and uplands, and detailed studies dedicated to evaluating mechanisms of water and solute transfer between the wetland and surrounding upland have been carried out in different environments (Kehew et al., 1998; Hayashi et al., 1998; Hunt et al., 1998). In France, where wetlands have been listed as being highly sensitive areas from the biological and water-resources stand-points, a National Research Program dedicated to wetlands (the Programme National de Recherche sur les Zones Humides[PNRZH]) is currently underway. The present study, which forms part of this PNRZH programme and concerns the Loire River, aims to better understand the global functioning of the system in terms of its hydrological, and geochemical aspects.

Previous geochemical investigations of the Loire were focused on the middle part of the river near Orleans and Tours, and characterized the temporal variations in the dissolved and suspended loads with regard to natural and anthropogenic inputs (Négrel and Grosbois, 1999; Négrel et al., 2000; Grosbois et al., 2000, 2001). The present study has targeted the transition between the upper and middle parts of the Loire catchment. It ranges from just below and to some 50 km above the confluence of river's main upstream tributary, the Allier. As one aim of the work has been to determine geochemical constraints on the hydrological functioning of a wetland, we used water chemistry and isotopic tracing (stable isotopes of water, strontium) to characterize spatial heterogeneity in the different fluxes between the Loire River and the riverbank [alluvial] aquifers, between the main and secondary channels and the wetland area composed essentially by abandoned channels, etc. as well as the temporal variations in bottom-water level and over-flow discharge. A second major aim of the work, based on a specific approach combining hydrology, hydrochemistry and geomorphology, was to integrate the results of this study of a 'transitional wetland' in the sense of Lissey (1971), i.e. having both significant inflow and outflow of groundwater, within the context of the entire Loire River basin.

2. The loire river, study sites, sampling and analysis

2.1. Hydrology of the loire river

With a catchment basin of 112,120 km^2 basin and a length of 1012 km, the Loire River is the most important fluvial hydrosystem in France (Fig. 1). The upper parts of the Loire River and Allier River (main upstream tributary of the Loire) drain the French Massif Central-Hercynian mountains that induce cold winters and warm summers. The middle part of the basin belongs to the sedimentary Paris Basin, where the climate is more temperate. Due to this double climatic influence, the mean annual discharge is relatively modest (310 m^3 s^{-1} just downstream the Loire–Allier junction) and the hydrology of the Loire River is immoderate: long droughts during the summer alternate with high-water levels during the winter, with the ratio between the driest monthly discharge and the wettest monthly discharge attaining 6.6. The seasonal variability is intensified by an interannual irregularity, which is also reflected in the intensity of the annual flooding. Two types of flood are generally distinguished. The one concerns flash floods ('crues cevenoles') in the upper catchment that are produced by Mediterranean storms at the end of summer or at the beginning of autumn; thunderstorms produce heavy rainfall giving rise to a very rapid increase in discharge. The second type of flood occurs from high winter discharges ('crues océaniques') generated by long and less intense rainfall produced by westerly storm fronts from the Atlantic Ocean.

2.2. The study sites

In the present study to constrain mechanisms and understand the functioning of fluvial units in the Loire River catchment, two different morphodynamic con-texts were examined along 50 km of the river in the transition zone between the upper and middle parts of the catchment (Bazin and Gautier, 1996; Gautier et al., 2000a,b; 2001).

– The upstream site (Dornant) is located in Burgundy, where the Loire River is characterized by a sinuous to meandering fluvial pattern.
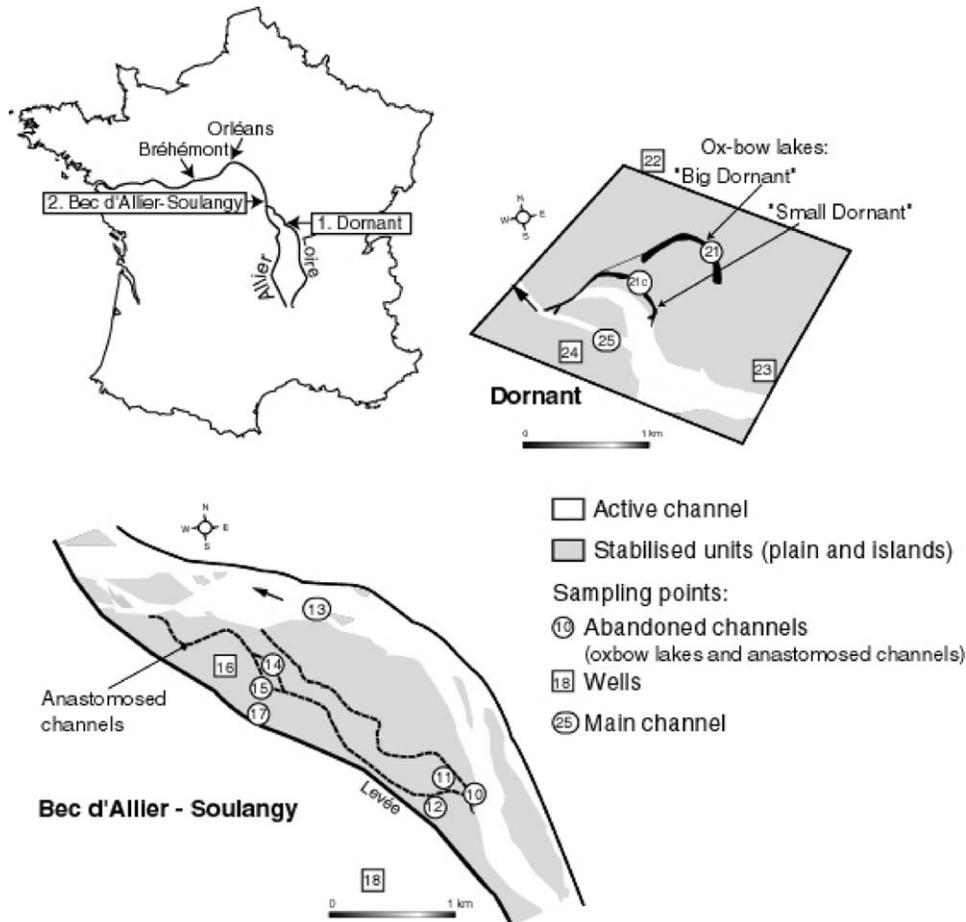
Fig. 1. Simplified map of the studied wetland area in the Loire watershed and location of the sampling sites and points upstream from Orleans.

The Dornant Lakes (Fig. 1), which are oxbow lakes, result from the rapid migration of the Loire River over about 1 km during the last 40 years. The first lake ('Big Dornant') corresponds to the position of the meander in the 1950–1960s; it is disconnected from the main channel of the Loire River during periods of low flow and is upstream-reconnected to the river channel during periods of high flow (i.e. 450–500 $m^3 s^{-1}$). The second oxbow lake ('Small Dornant'), located closer to the Loire River, is younger; it is downstream-reconnected during periods of intermediate flow (50 $m^3 s^{-1}$) and is totally submerged by the river at periods of high flow during wintertime.

– Approximately 50 km downstream is the Soulangy site, which extends for some 5 km from the Bec d'Allier, marking the junction between the Allier and Loire rivers (Fig. 1), near to Fourchambault. Here the contribution of the main upstream tributary, the Allier, causes major changes to the fluvial forms: the Loire river develops multiple active channels separating large bars and islands to form an anabranching fluvial pattern (Bridge, 1993; Nanson and Knighton, 1996; Gautier et al., 2000a). On the lateral margins, vegetated channels-namely 'anastomosing channels (Knighton and Nanson, 1993)'-are submerged

when the Loire River discharge exceeds the full-bank stage (850-850 $m^3.s^{-1}$). The channels are dry during low-water periods, except for some ponds (i.e. in the inundated portion of the wetland, Hayashi et al. (1998)) in the channel pools. The pond usually remains in the wetland even during the summer months when the water level will gradually decrease due to evaporation.

2.3. Sampling and analysis

Water sampling was carried out upstream at the Dornant site and in two areas downstream in the Soulangy site near the Loire–Allier confluence (Fig. 1). Sixteen samples were collected during the high-flow period in March 1999 (samples BA99-XX, Table 1) and 15 samples were collected during the low-flow period in June 1999 (samples BA99-XXX, Table 1). The samples included water types from the main river channels, the anastomosing secondary channels, wells in the alluvial plain, one pond, and the upstream oxbow lakes of the Loire River.

The alluvial groundwater at both the Soulangy and Dornant sites are divided into upper and lower alluvial (or riverbank) aquifers (BA99-16 and 166, 17 and 177, 18 and 188, 23 and 233, 24 and 244). The Dornant site also includes a perched aquifer (BA99-22 and 222) that is contained within Stampian lacustrine carbonates and 'Bourbonnais' sandy-clayey deposits, both encompassing silicate components of granitic-gneissic and basaltic origin from the Massif Central, i.e. they are mainly constituted by clay, sand and gravel derived from crystalline, metamorphic and volcanic rocks (Clozier et al., 1976, 1983; Delance et al., 1988). The groundwater (BA99-16 and 166, 17 and 177, 18 and 188) from the riverbank alluvial aquifers at the Soulangy site drain the Quaternary alluvial deposits of the Loire River (10 m thick; Delance et al., 1988) which overlie marine carbonaceous deposits (Toarcian, Oxfordian; Delance et al., 1988); at Dornant the alluvial deposits overlie the 'Bourbonnais' sandy-clayey deposits (Clozier et al., 1976, 1983; Delance et al., 1988).

The water samples were collected in polyethylene bottles and separated into three aliquots. Two of the aliquots were filtered through precleaned 0.22 μm Teflon (PVDF) Millipore filters using a precleaned Nalgene filter apparatus: the filter was used to determine the suspended matter concentration, and the filtrate was separated into a further two aliquots of which (i) 100 and 250 ml were acidified with twice-distilled nitric acid and stored in precleaned polyethylene bottles for (a) major-cation analysis and (b) strontium-isotope and Sr-Rb trace-element determination, and (ii) 2×100 ml were stored unacidified in polyethylene bottles for (a) anion determination, and (b) alkalinity determination. The third aliquot (250 ml) was stored non-filtered in polyethylene bottles and used for stable-isotope analysis.

The electrical conductivity and water temperature of each sample were measured on site using a WTW LF96 microprocessor conductivity meter standardized to 20 °C, and pH was measured on site using an Ingold electrode and an Orion 250 pH-meter previously calibrated using standard buffers. The chemical analyses of the water samples were performed using a capillary ionic analyser for major elements (accuracy 5%), inductively coupled plasma mass spectrometry for trace elements (accuracy 5%), and HCl titration and Gran's method for alkalinity. Chemical separation using a cation exchange column and mass spectrometric procedures (Finnigan MAT 262 multiple collector mass spectrometer) for strontium determination followed the standard method used at BRGM (Négrel and Deschamps, 1996); total blank for Sr was less than 0.5 ng for the whole chemical procedure. The $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$, and reproducibility of the $^{87}Sr/^{86}Sr$ ratio measurements was tested through replicate analyses of the NBS 987 standard—the mean value appears to be close to 0.710230 ± 17 10^{-6} ($2\sigma, n = 65$).

The D and O isotopic ratios, reported in per mil deviations from the international SMOW standard, were analysed using a Finnigan MAT 252 mass spectrometer The average precision, based on multiple analyses of various samples and laboratory standards, was $\pm 0.1‰$ for $\delta^{18}O$ and $\pm 0.8‰$ for δ^2H. Tritium samples were enriched by electrolytic enrichment and analysed by the scintillation count method; tritium concentrations are expressed in tritium units (1 TU = 0.12 mBq/ml; 1 tritium atom per 10^8 hydrogen atoms).

Table 1
Major- and trace-element concentrations (μmole/l), $^{87}Sr/^{86}Sr$ ratios, $\delta^{18}O$, δ^2H and tritium (TU) of the dissolved load in surface and ground water from the wetland area

	Ca (μmol/l)	Na (μmol/l)	Mg (μmol/l)	K (μmol/l)	Cl (μmol/l)	SO$_4$ (μmol/l)	NO$_3$ (μmol/l)	HCO$_3$ (μmol/l)	$\delta^{18}O$ ‰ SMOW	δ^2H ‰ vs SMOW	^3H T.U.	$^{87}Sr/^{86}Sr$	Sr (μmol/l)	Rb (μmol/l)	Σ^+ (μeq/l)	Σ^- (μeq/l)	NICB (%)
Winter (March 1999)																	
Anastomosed channels																	
BA99-10	503	365	160	77	321	116	115	1050	−8.1	−56.3	–	0.711436	1.06	0.04	1768	1717	3
BA99-11	788	400	276	87	406	154	177	1611	−7.9	−56.0	–	0.711162	1.67	0.03	2614	2502	4
BA99-12	433	291	148	95	307	103	79	667	−7.8	−52.7	–	0.711062	0.95	0.03	1547	1259	19
BA99-14	673	387	247	87	341	141	–	1611	−7.8	−55.1	–	0.711208	1.56	0.02	2313	2233	3
BA99-15	1030	357	453	87	459	213	224	2066	−7.5	−51.3	–	0.710444	2.27	0.02	3409	3174	7
Loire River																	
BA99-13	568	396	181	74	346	130	144	1102	−8.2	−57.1	–	0.710621	1.21	0.04	1967	1852	6
BA99-19	968	365	136	72	355	148	181	1691	−7.9	−54.4	–	0.711263	1.24	0.03	2644	2522	5
BA99-25	440	435	144	74	417	136	158	777	−8.3	−57.8	–	0.712216	1.06	0.04	1677	1624	3
Allier River																	
BA99-20	533	409	193	72	327	121	111	1188	−8.4	−57.7	–	0.711026	1.42	0.05	1932	1868	3
Wells																	
BA99-16	1670	504	420	121	451	198	895	2840	−7.1	−49.6	–	0.709360	3.74	0.05	4804	4582	5
BA99-18	2065	674	823	664	744	627	481	4562	−7.0	−48.9	–	0.709403	4.11	0.12	7114	7041	1
BA99-22	2285	470	362	985	183	419	173	5118	−7.1	−49.4	–	0.712334	2.48	0.27	6748	6311	6
BA99-23	1090	643	210	421	307	166	495	2375	−6.8	−49.3	–	0.712343	1.86	0.08	3664	3508	4
BA99-24	1055	530	284	1159	310	255	873	2415	−7.5	−53.5	–	0.710667	1.12	0.52	4367	4108	6
Dornant oxbow lake																	
BA99-21	720	474	243	51	341	128	134	1839	−7.3	−51.3	–	0.712014	1.56	0.02	2451	2570	−5
Pond																	
BA99-17	943	248	416	113	445	158	300	1770	−6.4	−45.7	–	0.710743	2.28	0.01	3077	2832	8
Summer (June 1999)																	
Anastomosed channels																	
BA99-111	660	248	247	64	290	64	–	1770	−7.3	−50.4	–	0.711291	1.44	0.03	2126	2187	−3
BA99-122	1238	234	494	192	625	164	203	2790	−5.8	−43.8	–	0.710559	2.21	0.05	3889	3946	−1
BA99-144	700	237	259	174	346	58	–	1920	−6.9	−47.9	–	0.711243	1.48	0.06	2329	2383	−2
Loire River																	
BA99-133	788	346	243	90	423	190	73	1730	−7.2	−51.8	–	0.711086	1.71	0.05	2497	2604	−4
BA99-199	848	509	181	90	428	200	68	1320	−6.9	−49.9	10	0.711018	1.43	0.04	2656	2216	17
BA99-255	660	517	181	92	420	389	126	1310	−7.2	−51.4	–	0.711880	1.42	0.05	2292	2633	−15
Allier River																	
BA99-200	783	648	296	95	504	181	56	1920	−7.5	−52.2	9	0.711067	2.18	0.08	2900	2843	2

Table 1 (continued)

	Ca (µmol/l)	Na (µmol/l)	Mg (µmol/l)	K (µmol/l)	Cl (µmol/l)	SO$_4$ (µmol/l)	NO$_3$ (µmol/l)	HCO$_3$ (µmol/l)	δ^{18}O ‰ SMOW	δ^2H ‰ vs SMOW	^{3}H T.U.	^{87}Sr/^{86}Sr	Sr (µmol/l)	Rb (µmol/l)	Σ$^+$ (µeq/l)	Σ$^-$ (µeq/l)	NICB (%)
Wells																	
BA99-166	1670	439	440	108	501	218	844	2780	−7.1	−49.3	10	0.709427	3.73	0.05	4767	4560	4
BA99-188	2038	796	432	987	532	397	363	4930	−7.1	−50.4	11	0.709232	3.40	0.19	6722	6619	2
BA99-222	2488	583	412	1087	234	521	15	5910	−7.0	−49.4	8	0.712299	2.61	0.33	7468	7200	4
BA99-233	700	700	202	236	285	169	92	1780	−7.1	−50.3	8	0.713194	1.64	0.02	2739	2494	9
BA99-244	1140	343	263	1092	417	186	84	1630	−7.2	−51.4	9	0.711308	1.47	0.46	4243	2504	
Dormant oxbow lakes																	
BA99-211	1428	596	210	74	408	116	–	3300	−6.7	−48.3	–	0.712284	2.17	0.02	3945	3940	0
BA99-211C	475	422	148	69	310	92	–	1210	−6.1	−46.9	–	0.711659	1.08	0.02	1737	1703	2
Pond																	
BA99-177	985	278	506	77	572	210	16	2280	−4.9	−40.4	–	0.710697	2.37	0.01	3338	3289	1

3. Results and discussion

3.1. Isotopic (δ^2H, ^{18}O) signature and origin of the water

Variations in the stable isotope composition of components in a catchment water balance are caused by (a) natural variations in the isotopic composition of rainfall, (b) mixing with previous water, and (c) evaporation (Kendall and McDonnell, 1998; Guglielmi et al., 1998; Hunt et al., 1998; Huddard et al., 1999). Considering the temperatures encountered in catchment studies, the stable isotopes of water can be considered as conservative and as not being affected by exchange with soils or rocks (Barth, 2000). The relationships δ^2H (‰ vs. SMOW) and δ^{18}O (‰ vs. SMOW) are shown in Fig. 2a for water collected at the end of the winter period and in Fig. 2b for water collected during the summer period. All points in these δ^2H vs δ^{18}O diagrams clearly show an enrichment of heavy isotopes with respect to the Global Meteoric Water Line (GMWL, Craig, 1961) for both surveys. It is worth noting that more local rain surveys agree with the GMWL (IAEA/WMO, GNIP Database, 2001).

The different water collected from the two study sites at the end of the winter period (Table 1) display the most negative values for the water in the main Loire and Allier river channels (δ^{18}O around −8.2‰), intermediate values for the water from the secondary channels, and the most enriched values for the water from pond with δ^{18}O close to −6.4‰ in winter BA99-17) and around −4.9‰ in summer (BA99-177)—the pond corresponds to an outlet of the upper riverbank aquifer in the alluvial plain. Groundwater from the alluvial aquifers and the perched aquifer display enriched values (δ^{18}O around −7.0‰), possibly indicating that the groundwater may originate from precipitations with a more enriched δ^{18}O than that providing the δ^{18}O signature upstream in the Loire and Allier catchments.

Barbaud (1983) gave a mean annual weighted δ^{18}O of around −7.84‰ at the Volvic raingauge (475 m altitude) near the head of the Loire catchment. Consequently, the sampled water from the Loire and Allier rivers probably correspond to a recharge at higher altitude. Based on a gradient close to 0.3‰ per 100 m of altitude (Guglielmi et al., 1998), the average

recharge altitude is estimated at 600 m, which corresponds to the mean altitude bordering the Limagne and Forez plains located in the upper Loire basin. The intermediate $\delta^{18}O$ values ($-7.3/-8‰$) in water from the anastomosing secondary channels in the Soulangy site and the abandoned meanders in the Dornant site reflect a mixing of river and riverbank-aquifer water. Such relationships between streamflow and groundwater are often described in catchment (Rodhe, 1984; Turner et al., 1990).

During the summer period, water from the anastomosing channels and some wells in the alluvial plain are characterized by evaporation. Other river and aquifer water samples display $\delta^{18}O$ values of around $-7.5/-7‰$. The range of $\delta^{18}O$ values in

the aquifer water corresponds to that determined during the winter period from the same wells and reflects the capacitive effect classically observed in many aquifers that buffer variation in the different inputs (Huddard et al., 1999).

The stable isotopes confirm that, in summer, both the Loire and Allier rivers and the oxbow lakes are fed by the alluvial aquifers. Moreover, water from the alluvial aquifers display a different isotopic signature from that of the river water during winter (i.e. $\delta^{18}O = -8.2‰$). This demonstrates that the riverbank aquifers in the alluvial plain are not recharged by winter overflows, but probably by local precipitations mainly during the spring and autumn.

(a)
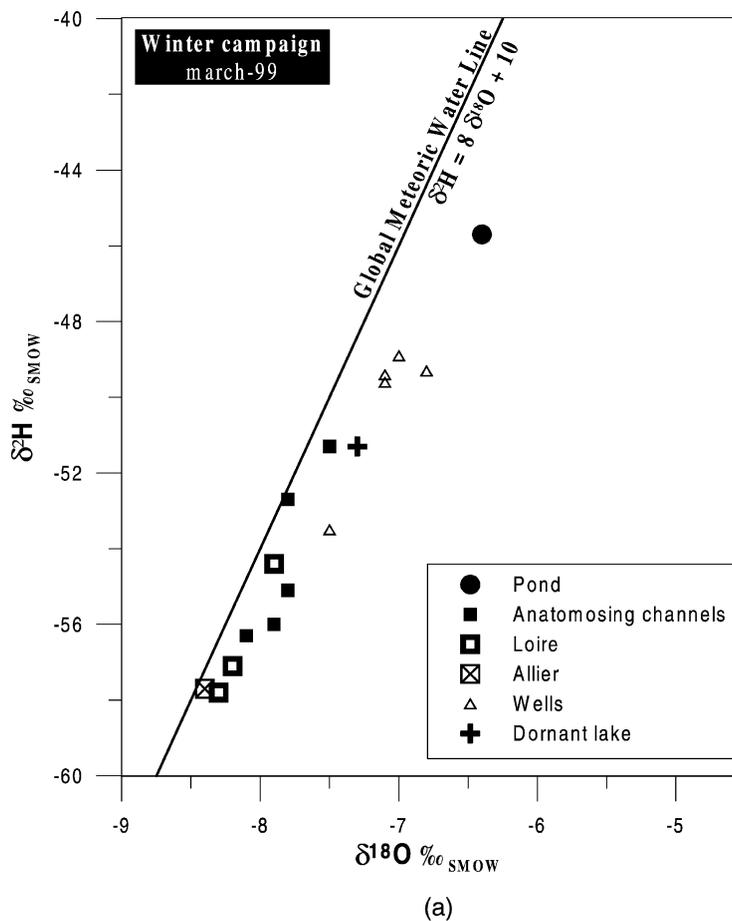
Fig. 2. Relationships between δ^2D (‰ vs. SMOW) and $\delta^{18}O$ (‰ vs. SMOW) in water collected from the Soulangy and Dornant sites at the end of the winter period (a) and during the summer period (b).
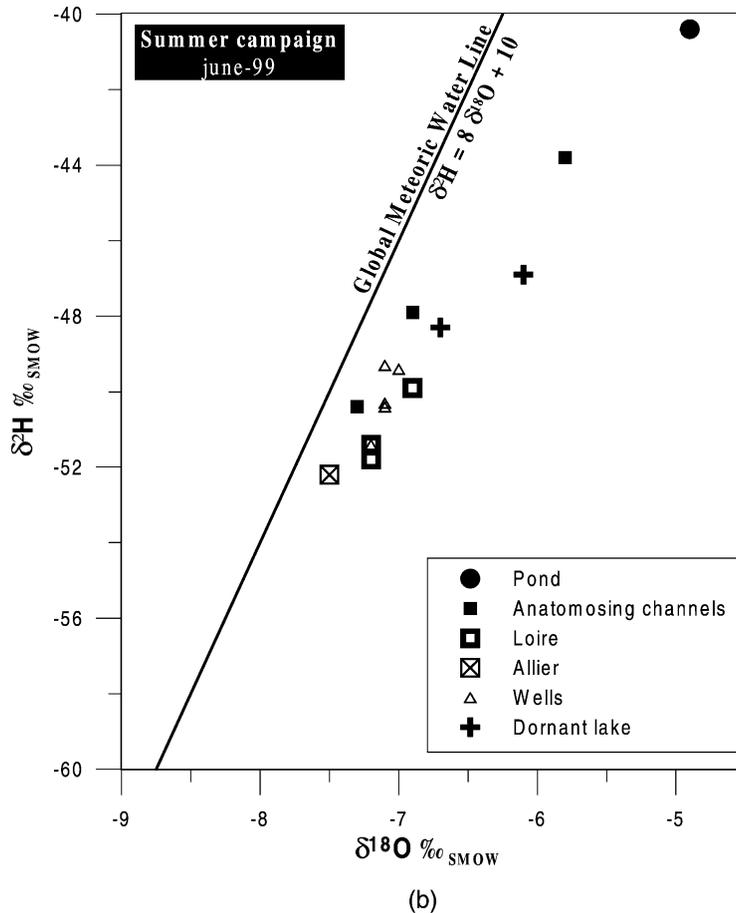
Fig. 2 (*continued*)

The tritium concentrations in the alluvial aquifers and perched aquifer fluctuate weakly between 8 and 11 TU (Table 1) and indicate groundwater recharge from modern water (i.e. water in equilibrium with an atmosphere contaminated by nuclear testing). Distribution of ^3H values of the groundwater samples does not show a definite pattern and is similar to that of a river (French National Isotopic Data Base®) reflecting contemporaneous water.

3.2. Major ion behaviour

The water chemistry (Table 1) shows a great variation and a major chemical contrast is observed between the lowest total cationic charge value ($\Sigma^+ = 1550$ µeq/l) obtained in one anastomosing secondary channel sample collected during wintertime (BA99-12) and the highest value (7470 µeq/l) in a sample collected from the perched aquifer collected during the summer (BA99-222). Although the secondary channels show large fluctuations in their total cationic charge (Σ^+), the fluctuations observed in wells tapping the alluvial aquifers (BA99-18 and 188) and perched aquifer (BA99-22 and 222) are even greater. This may reflect the longer water-rock interaction with surrounding deposits in the alluvial plain and hillside (gravel, sand and clay). The Dornant lakes also revealed a large difference in their total cationic charges ($\Sigma^+ = 3945$ and 1737 µeq/l). As for cations, the total anionic charge (Σ^-) ranges from 1259 in the secondary channels (BA99-12) to 7200 µeq/l in the perched aquifer (BA99-22).

The Normalized Inorganic Charge Balance (Table 1), NICB (Huh et al., 1998), is defined as $\{\Sigma^+ - \Sigma^-/\Sigma^+\}$ and represents the fractional difference between the total cations and total anions (Edmond et al., 1995). As exemplified by Huh et al. (1998) the measured major ions (Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-) are generally enough to give a charge balance. Most of the water samples showed a charge imbalance mainly in favour of a positive charge excess, but some inversely with a negative charge deficit. NICB in the range $\pm 5\%$ cannot be interpreted as it fall within the range of analytical uncertainties (Edmond et al., 1995; Huh et al., 1998; Roy et al., 1999). Positive charge excess higher than 5% (Table 1) agrees with the database of the dissolved load of the Loire River at Orleans (Grosbois et al., 2000) and Tours (Grosbois et al., 2001) where the greater imbalance appeared during the low-flow periods. This deficit of negative charges could be related to the fact that no analysis was made of organic matter (Berner-Kay and Berner, 1987; Edmond et al., 1995; Huh et al., 1998) which is mainly produced by biological activities during spring and summer. Only the sample from the Loire River upstream of the Dornant lakes (BA99-25) exhibits an imbalance in favour of a negative charge excess. This could be attributable to the lack of NH_4^+ measurements, which can cause a significant cation deficit (Négrel and Roy, 1998; Grosbois et al., 2000), and/or the presence of a large amount of PO_4^{3-} ($\Sigma PO_4^{3-} = 84$ μmol/l) which is not accounted for in the anionic budget and therefore may induce an anion deficit. It is worth noting that ΣPO_4^{3-} was only detected in this sample. Grosbois (1998) revealed high P contents in the dissolved load at Tours, mainly in relation to fertilizer applications. A similar anion deficit observed by Roy et al. (1999) in the Seine River could be related to the lack of ΣPO_4^{3-} measurements.

The major element chemistry of the water reveals Na/Cl ratios depleted with respect to that of the seawater (0.87, Berner-Kay and Berner, 1987) and in rainwater samples collected in the Massif Central (France) over a period of one year (0.68, Négrel and Roy, 1998) reflecting a significant anthropogenic Cl^- source. This involves an anthropogenic contribution in one of the secondary channels and in a pond within the alluvial plain where the high NO_3^- levels in excess of the French limitation for drinking water (810 μmol/

l, i.e. 50 mg/l) agree with a contamination linked to agricultural practices. Conversely, the groundwater show a greater Na^+ enrichment reflecting a release of Na^+ through weathering of the surrounding deposits. Furthermore, clear anthropogenic inputs are indicated in groundwater where NO_3^- contents higher than the limitation value are associated with large amounts of potassium. The NO_3^- contents decrease in the upstream samples in summer (BA99-233 and 244), together with a decrease in the bicarbonate and sodium contents.

The EQ3NR geochemical code (Wolery, 1992) was used to compute the saturation indices (SI). The values obtained for the relevant solid phases were used as criteria for determining the solids likely to precipitate under the measured physico-chemical conditions. A SI of zero indicates equilibrium, a positive value indicates oversaturation and a negative value undersaturation, with respect to the solid phases. The thermodynamic calculations show that the studied water are slightly saturated ($pCO_2 = 3 - 11 \times 10^{-3}$ atm) with respect to the atmospheric pCO_2 (3.2×10^{-4} atm). The SI values with respect to calcite ($-0.03/-1.32$) indicate that the water is slightly undersaturated with respect to this solid phase, as are other carbonate species (Table 2). With regard to surface water, it is well known that biochemical processes influence the water chemistry (Drever, 1988). Grosbois (1998) recognised areas of algal production in the Loire catchment; the algae occur mainly as diatoms between May to October, as in the Seine River (Meybeck, 1998). The process needed to explain HCO_3^- and Ca^{2+} behaviour in the Loire, as revealed at Orleans and Tours (Négrel and Grosbois, 1999; Négrel et al., 2000; Grosbois et al., 2000, 2001), is the precipitation of an authigenic component that might have a direct impact on dissolved calcium and carbonate species. Grosbois et al. (2001) demonstrate that the carbonate precipitates that were sampled during the summer period in the Loire at Tours are large (between 20 and 40 μm long) and have a very specific shape that reflects an authigenic polynuclear crystalline growth. A lot of these carbonate grains contain diatoms in their centre, which may act as a nucleus for the authigenic growth. This processes was also described in the Seine River (Meybeck, 1998).

Biological activity also induces a decrease in NO_3^- and PO_4^{3-} contents, as well as in SiO_2 because of

Table 2

Water saturation indices (SI) with respect to calcite at the end of the winter period and during the summer period. The EQ3NR geochemical code (Wolery, 1992) was used to compute the saturation indices

	SI/calcite winter		SI/calcite summer
Winter (March 1999)		*Summer (June 1999)*	
Anastomosed channels			
BA99-10	−0.62		
BA99-11	0.57	BA99-111	−0.65
BA99-12	1.12	BA99-122	0.69
BA99-14	−0.47	BA99-144	−0.36
BA99-15	0.26	BA99-155	1.12
Loire River			
BA99-13	−0.76	BA99-133	0.97
BA99-19	−0.23	BA99-199	0.38
BA99-25	−0.92	BA99-255	1.39
Allier River			
BA99-20	−0.74	BA99-200	1.26
Wells			
BA99-16	−0.03	BA99-166	−0.18
BA99-18	−0.42	BA99-188	0.38
BA99-23	−0.84	BA99-233	−1.32
BA99-24	−0.97	BA99-244	−0.70

diatom growth (Grosbois, 1998; Meybeck, 1998). In the present study, three secondary channels at the Soulangy site showed an oversaturation with respect to calcite (SI = 0.26/1.12; Table 2) at the end of wintertime, while water from main Allier and Loire river channels were undersaturated (SI = −0.23/−0.76; Table 2). Coupled with the low NO_3^- content and high dissolved oxygen concentration, the calcite oversaturation could be related to photosynthesis and bacterial activity (Meybeck, 1998; Grosbois et al., 2000, 2001). The shallow depth of water (several decimetres) in the secondary channels, together with the low amount of suspended-matter compared with the main river channels, may explain the difference in calcite saturation; this agrees with the work by Grosbois (1998) in the wetland of the Loire River near Tours, which demonstrated an increase of the fluvial activity each year from April. Another factor to be taken into account is the calcium-bicarbonate type of the groundwater. Moreover, the silicate nature of the bedrock in the Massif Central (i.e. granite-gneiss and basalt) induces a low Ca^{2+} content in the river water flowing over this area (Négrel and Deschamps, 1996,

1997a,b, 1999), and specially the Allier and Loire rivers. The surface water is thus Ca-poor compared to the groundwater. Consequently the input of Ca-rich groundwater into the anastomosing secondary channels increases the Ca^{2+} (and HCO_3^-) content and leads to the water's SI being oversaturated (SI = 0.26 in BA99-15, and 1.12 in BA99-12; Table 2).

During the summer months, some of the anastomosing secondary channels are dry and others contain only very shallow water. Decomposition of the organic matter in these channels results in an emission of CO_2 followed by a decrease in both pH and dissolved oxygen. This induces an undersaturation with respect to calcite, as exemplified by samples BA99-111 and BA99-144 with a dissolved oxygen close to 1.8 and 3 mg/l, respectively, and SI in the −0.36/−0.65 range (Table 2). These fluctuations are accompanied by a decrease in the NO_3^- and SO_4^{2-} contents.

The main channels of the Loire and Allier rivers show the opposite situation with a lower amount of suspended matter during summer (Négrel and Grosbois, 1999) and very high photosynthetic activity yielding a high pH (>9) and dissolved oxygen content (>11 mg/l). The water is thus oversaturated with respect to calcite (SI range 0.38/1.39; Table 2), and an oversaturation with regard to the various species of dolomite is indicated by the relationship between pH and Mg^{2+} (not shown)—the river water display the lowest Mg content, which is taken to indicate Mg removal by the carbonate precipitation.

3.3. Surface water–groundwater relationships: Sr isotope constraints

The Sr isotopic composition of water from the alluvial aquifers, the main and secondary river channels, the pond, and the abandoned oxbow lakes can be compared in order to construct a model of groundwater/surface water system (Bullen et al., 1996; Kehew et al., 1998). This is based on the fact that (a) the $^{87}Sr/^{86}Sr$ ratio varies according to the Rb/Sr ratio and the age of the material (Faure, 1986), and (b) since natural processes do not fractionate Sr isotopes, the measured $^{87}Sr/^{86}Sr$ ratio differences are due to a mixing of Sr derived from various sources with potentially different isotopic compositions (Faure, 1986). Thus, $^{87}Sr/^{86}Sr$ ratio variations within

a hydrosystem can provide information about sources of Sr and different mixing processes involved (Fisher and Stueber, 1976; Albarède and Michard, 1987; Palmer and Edmond, 1992; Bullen et al., 1996; Négrel et al., 1997a,b; Négrel, 1999; Roy et al., 1999; Semhi et al., 2000).

In the present study the Sr isotopic composition shows large fluctuations of around 4×10^{-3} (Table 1), which is higher than the analytical errors for the procedure (2×10^{-5}), and the $^{87}Sr/^{86}Sr$ ratio varies largely from 0.70923 (BA99-188) − 0.70936 (BA99-16) to 0.71319 (BA99-233). The different sources of Sr that may control the $^{87}Sr/^{86}Sr$ found in all the water types in the hydrosystem can be constrained, according to Négrel et al., 1993; Gaillardet et al. (1997); Roy et al. (1999), by the relationships between the Sr isotopic composition and concentration ratios. The use of X/Y ratios (X and Y being dissolved species), rather than absolute concentrations alone, allows us to circumvent the variations due to dilution or concentration effects on the chemical characteristics of the water (Négrel et al., 1993; Gaillardet et al., 1997). We shall use the Na/Sr ratios (Négrel and Deschamps, 1996; Gaillardet et al., 1997) as shown in Fig. 3 (river water), Fig. 4 (groundwater), Fig. 5 (Dornant site) and Fig. 6 (Soulangy site), which is the most useful to discriminate in this study.

3.3.1. The loire and allier rivers

Analyses were made on three samples of Loire River water, collected 50 km upstream (BA99-25), a few kilometres upstream (BA99-19) and downstream (BA99-13) of the confluence of the Loire and Allier rivers, and one sample of Allier River water (BA99-20) collected upstream the confluence. The $^{87}Sr/^{86}Sr$ and the Na/Sr ratios vary less in the Allier River than in the upstream Loire River (sampling site 25) between winter and summer (Fig. 3), and both ratios increase during wintertime in the Loire River (sampling site 25), which could reflect a greater drainage of granitic basement. These points enable us to define two end-members, termed the 'Allier MC' and 'Loire MC', reflecting the drainage of the upstream part of the Massif Central. Note that the $^{87}Sr/^{86}Sr$ and Na/Sr ratios of the 'Loire MC' are higher than those of the 'Allier MC', but are roughly similar to those obtained from a survey of the Allier River around 50 km upstream of the confluence

(Négrel et al., 1997a) with a mean value ($n = 15$) close to 0.71172 for the $^{87}Sr/^{86}Sr$ ratio and close to 200 ± 100 for the Na/Sr ratio. Sample BA99-19, which represents the Loire River just above the Loire-Allier confluence, is characterized by lower $^{87}Sr/^{86}Sr$ and Na/Sr ratios than the upstream sampling point 25 (Fig. 3). This illustrates the variations in the drained lithologies that could influence the $^{87}Sr/^{86}Sr$ and Na/Sr ratios, as pointed out by Roy et al. (1999) for the Seine River. However, conversely to sampling point 25, the $^{87}Sr/^{86}Sr$ and Na/Sr ratio fluctuations between winter and summer time at sampling point 19 reveal an decrease in the Sr isotopic ratio associated with an increase in the Na/Sr ratio.

Sampling point 13 corresponds to the mixing between the Allier and Loire river water. However, this point never plots on a theoretical pure mixing line between sampling points 19 and 20. During summer, the mixture has a similar $^{87}Sr/^{86}Sr$ ratio to the end-members and a lower Na/Sr ratio. Conversely, during winter, the Na/Sr ratio of the mixture is higher than in the Allier and Loire river water and the $^{87}Sr/^{86}Sr$ ratio (0.71062) is always lower than in the end-members. This implies that the water at sampling point 13 is not a pure binary mixture between the Allier and Loire river water, and that at least a third Sr end-member is required (groundwater input?).

3.3.2. The groundwater

The scatter of the groundwater data in Fig. 4 allows the definition of three different fields with weak $^{87}Sr/^{86}Sr$ and Na/Sr ratio variations

− The perched aquifer located on the right bank of the Loire River (BA99-22 and 222) with low Na/Sr ratios and high $^{87}Sr/^{86}Sr$ close to 0.7123. The constancy of the $^{87}Sr/^{86}Sr$ ratio through time is well correlated with a stability in the Sr content (2.5 μmol/l). The high Sr isotopic ratio in the groundwater reflects the composition of the surrounding rocks (i.e. the Stampian lacustrine carbonates and the 'Bourbonnais' sandy-clayey deposits)-both deposits encompass silicate components of granitic-gneissic and basaltic origin from the Massif Central.

− The groundwater from the riverbank alluvial aquifers around the Soulangy site constitute two fields. Samples BA99-16 and 166, and BA99-18 and 188 display the lowest $^{87}Sr/^{86}Sr$ ratios

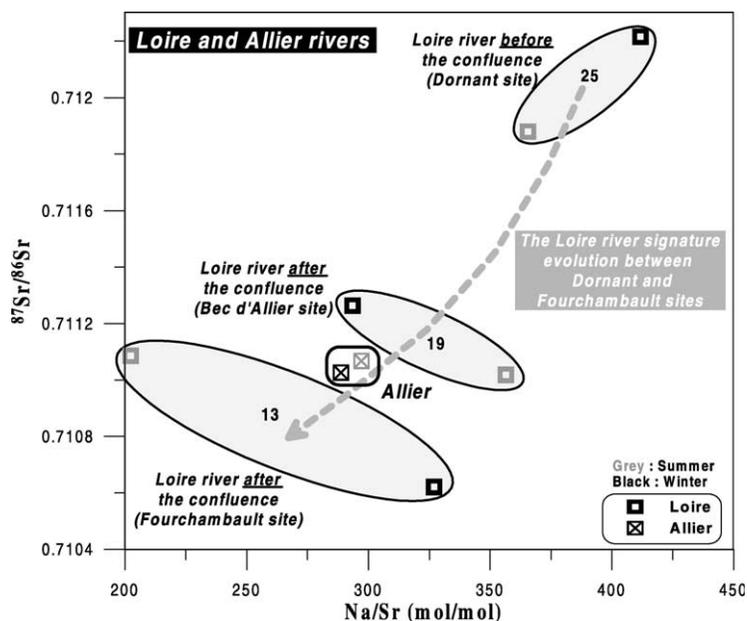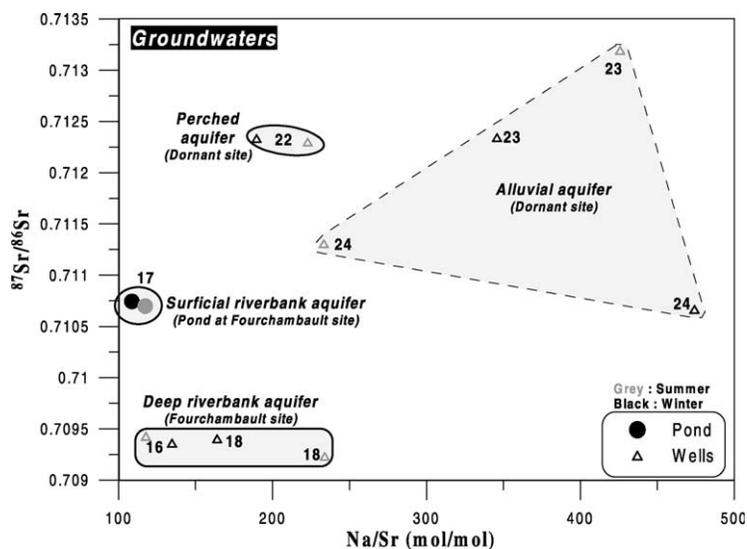Fig. 3. Relationship between the $^{87}Sr/^{86}Sr$ ratio and the Na/Sr ratio of the dissolved load in river water from the Soulangy and Dornant sites.

(< 0.70943) and high Sr contents (Table 1). Moreover, the $^{87}Sr/^{86}Sr$ ratios show weak variations between winter and summer (0.70923–0.70942) and the Na/Sr ratio falls in the 118–235 range. The range of the $^{87}Sr/^{86}Sr$ ratios partly agrees with the drainage of marine

carbonaceous deposits (Toarcian, Oxfordian; Delance et al., 1988) whose values are close to 0.70675 and 0.70790 (Koepnick et al., 1990; Jones et al., 1994), although a contribution of fertilizers on the Sr budget cannot be ruled out. Négrel (1999); Böhlke and Horan (2000)

Fig. 4. Relationship between the $^{87}Sr/^{86}Sr$ ratio and the Na/Sr ratio of the dissolved load in the alluvial groundwater from the Soulangy and Dornant sites.
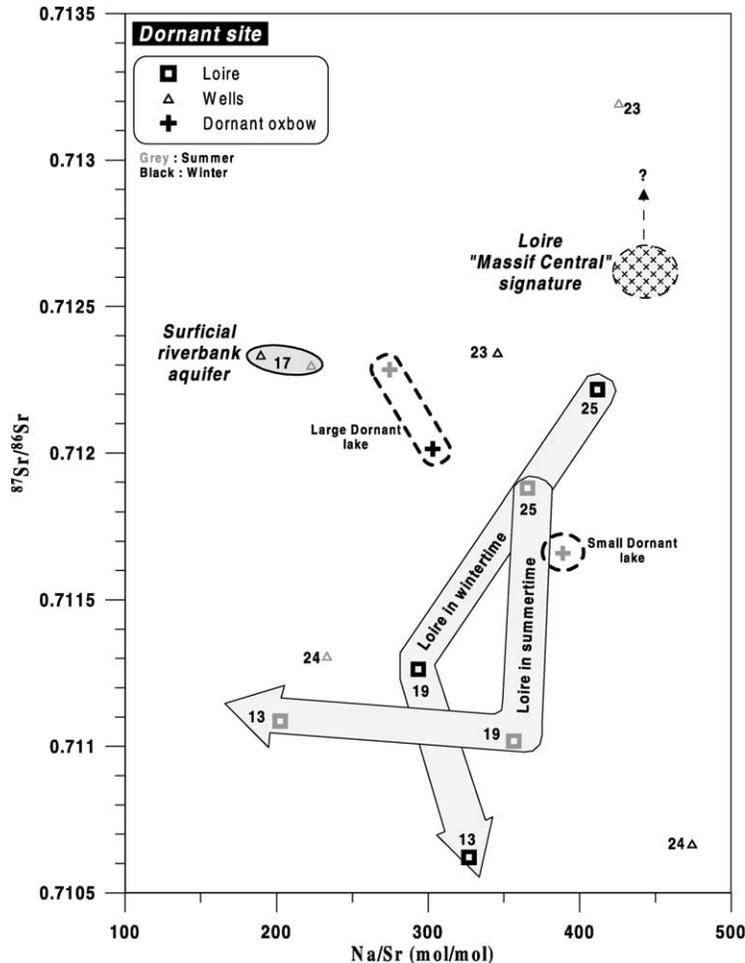
Fig. 5. Relationship between the $^{87}Sr/^{86}Sr$ ratio and the Na/Sr ratio of the dissolved load in water from the Dornant site.

estimate that anthropogenic disturbance through agricultural activity induces an input of Sr that can be important with respect to the range of Sr contents ($3-1500 \mu g\ g^{-1}$) with an isotopic ratio ranging from 0.70794 to 0.7095. The pond water (samples BA99-17 and 177) displays constant $^{87}Sr/^{86}Sr$ ratios between winter and summer (0.710743 and 0.710697, respectively), along with a constancy of the Na/Sr ratio implied by the weak Na^+ and Sr^{2+} variations.

The groundwater of the riverbank alluvial aquifers around the Dornant site were investigated in wells located on both the left bank of the Loire River (sampling point 24) and the right bank (sampling point 23) upstream the lakes. The $^{87}Sr/^{86}Sr$ ratios range from 0.71067 (BA99-24) to 0.71319 (BA99-233). The right bank system (BA99-23 and 233) is characterized by high and variable $^{87}Sr/^{86}Sr$ ratios (0.71234 in winter and 0.71319 in summer) and by Na/Sr ratios ranging from 300 to 400; the left bank system (BA99-24 and 244) has lower and less variable $^{87}Sr/^{86}Sr$ ratios (0.71067 in winter and 0.71131 in summer) and large variations in the Na/Sr ratios (200–500). The probable influence of fertilizer applications, as indicated by the NO_3^- contents, would lower the natural $^{87}Sr/^{86}Sr$ ratio (Négrel, 1999; Böhlke and Horan, 2000).

The description of the different groundwater systems illustrates the difficulty that can be associated
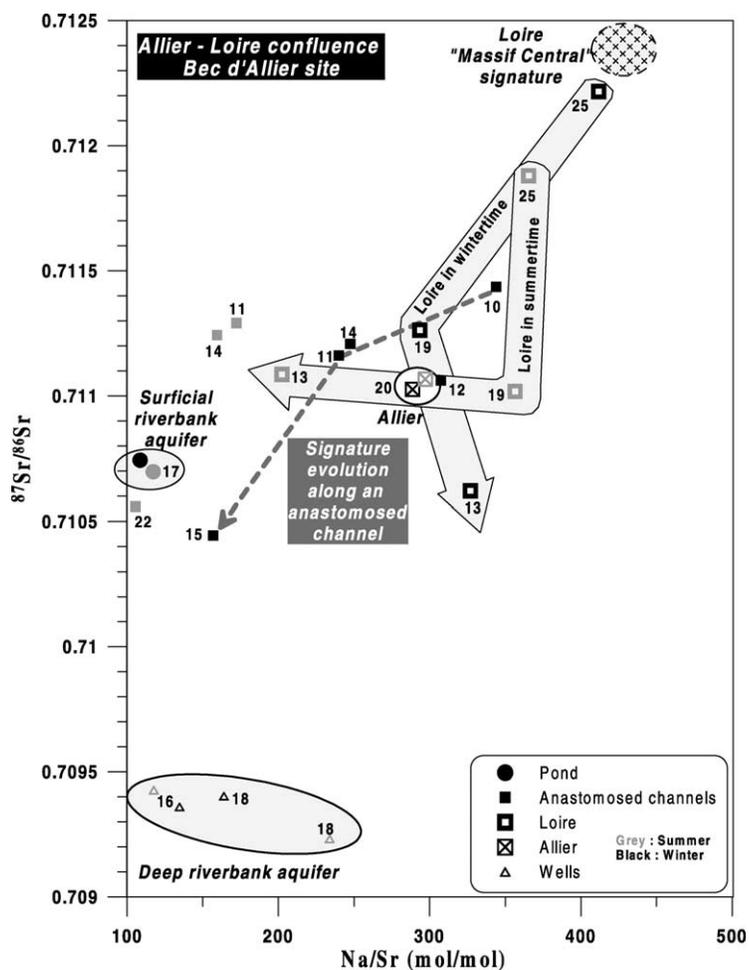
Fig. 6. Relationship between the $^{87}Sr/^{86}Sr$ ratio and the Na/Sr ratio of the dissolved load in water from the Soulangy site.

with characterizing the riverbank alluvial aquifers. It is obvious from Fig. 4 that two different signatures in the $^{87}Sr/^{86}Sr$ ratio are revealed by the groundwater of the riverbank alluvial aquifer in the alluvial plain around the Soulangy site. The pond water may represent the upper riverbank alluvial aquifer, whereas water from sampling points 16 and 18 may represent the lower alluvial aquifer. For the pond, the upper aquifer representation is corroborated by the enriched stable isotopes of water. The alluvial aquifer around the Dornant site is also heterogeneous in its signature. Variations are observed both between the different sampling points and with regard to the season. A large heterogeneity in the nature of

the alluvial deposits ('Bourbonnais' and Quaternary alluvial deposits) could be envisaged to explain the dispersion of the chemical and isotopic signatures. Another hypothesis is to envisage different aquifer levels within the alluvium, as for the riverbank aquifer at the Soulangy site.

3.3.3. The Dornant site

The $^{87}Sr/^{86}Sr$ ratio in the Dornant lakes ranged from 0.71166 to 0.71228 in relation to the hydrological conditions, with the highest value being in summer. Sample BA99-211C corresponds to the 'Small Dornant' lake that could only be sampled during summer. It displays a lower $^{87}Sr/^{86}Sr$ ratio

(0.71166) than the Big Dornant lake (0.71228), but which is accompanied by an increase in the Na/Sr ratio, mainly due to a decrease of the Sr^{2+} content by a factor 2 when compared to the Big Dornant. The summer signature of the lake water is higher than the winter signature and may reflect groundwater inputs with a high $^{87}Sr/^{87}Sr$ ratio. This can be seen in Fig. 5 where the sample collected in the Big Dornant lake plots near the field of groundwater from the perched aquifer (BA99-22 and 222).

Another feature concerns the difference in the $^{87}Sr/^{86}Sr$ ratio between the two lakes in summer. This difference can be explained either by a variation in the drained lithologies, inducing a change in the $^{87}Sr/^{86}Sr$ ratio, or by a time shifted input of the Loire River water into the two lakes. The $^{87}Sr/^{86}Sr$ ratio of the dissolved load in the Loire River (as well as that of the Allier River, Négrel et al., 1997a) fluctuates with the discharge of the river (Grosbois and Négrel, 2000). If the river did not fill up the two lakes at the same time, the $^{87}Sr/^{86}Sr$ ratio could display differences.

3.3.4. The soulangy site

The anastomosing secondary channels display $^{87}Sr/^{86}Sr$ ratios ranging from 0.711436 to 0.710444 in association with large fluctuations in the Sr^{2+} contents (0.9–2.3 μmol/l). The Na/Sr ratio also shows large fluctuations from 100 to 350 (Fig. 8). One channel was sampled from upstream (i.e. sample BA99-10 from the Loire riverbank) to downstream (sample BA99-15) during the winter. It should be noted that the channel was not connected to the Loire River during this period. As shown by Fig. 6, Sample BA99-10 displays both $^{87}Sr/^{86}Sr$ and Na/Sr ratios intermediate between those of the Loire (BA99-25) and Allier (BA99-19) rivers above their confluence. This suggests that the signature of the upstream sample may correspond to the one of the river that filled the channel. Both the $^{87}Sr/^{86}Sr$ and Na/Sr ratios decrease from the upstream sample to the downstream one. From sampling point 10 to sampling point 11, an influence of the upper alluvial aquifer (represented by samples BA99-17 and 177) should be considered. Likewise, from sampling point 11 to sampling point 15, a supplementary influence of the lower alluvial aquifer (represented by samples BA99-16 and 166, and BA99-18 and 188) may explain the observed

$^{87}Sr/^{86}Sr$ and Na/Sr ratios. Fluctuation of the chemical and isotopic signature of the water along the secondary channel reveals the gradual contribution of groundwater.

Sample BA99-14, corresponding to an anabranch of this plot near sampling point 11, suggests a similar hydrological pattern. During the summer, only sampling from points 11 and 14 was feasible, the other parts being dewatered. The two samples (BA99-111 and BA99-144) plot close to one another in Fig. 6, revealing an increase in the $^{87}Sr/^{86}Sr$ ratio and a decrease in the Na/Sr ratio-the only way to explain this shift is to envisage a coupled feed by the riverbank alluvial aquifers (both upper and lower) and a groundwater of the perched-aquifer type.

Sample BA99-12, corresponding to an anastomosing secondary channel and collected during the winter, plots within the field defined for the 'Allier MC' end-member; this merely reflects a larger contribution from the Allier River. On the other hand, water from this anastomosing channel during the summer shows a shift towards the upper riverbank alluvial aquifer, suggesting a major feed by this groundwater type. Such an origin of the water collected in the anastomosing channel is supported by the stable isotopes of groundwater that give enriched values.

3.4. Conceptual scheme of the loire hydrosystem through isotopic tracing

A conceptual scheme of the Loire hydrosystem can be proposed on the basis of its isotopic patterns relative to $^{87}Sr/^{86}Sr$ and $\delta^{18}O$. Measurement of the strontium and oxygen isotopic ratios on the dissolved load at Orleans over a period of one year (Grosbois et al., 2000) showed that the ratios are highest during low flow and decrease with increasing discharge, as shown in Fig. 7. Négrel and Grosbois (2001) interpret this kind of relationship as a mixing with two signatures. The first signature, present during the high flow, was the highest of the hydrological cycle and agreed with the geochemical signature of the weathered silicate bedrock of the Massif Central. The second signature, present during the low flow, was the lowest of the hydrological cycle and agreed with the geochemical signature of weathered carbonate bedrock, carbonate groundwater and fertilizer inputs.
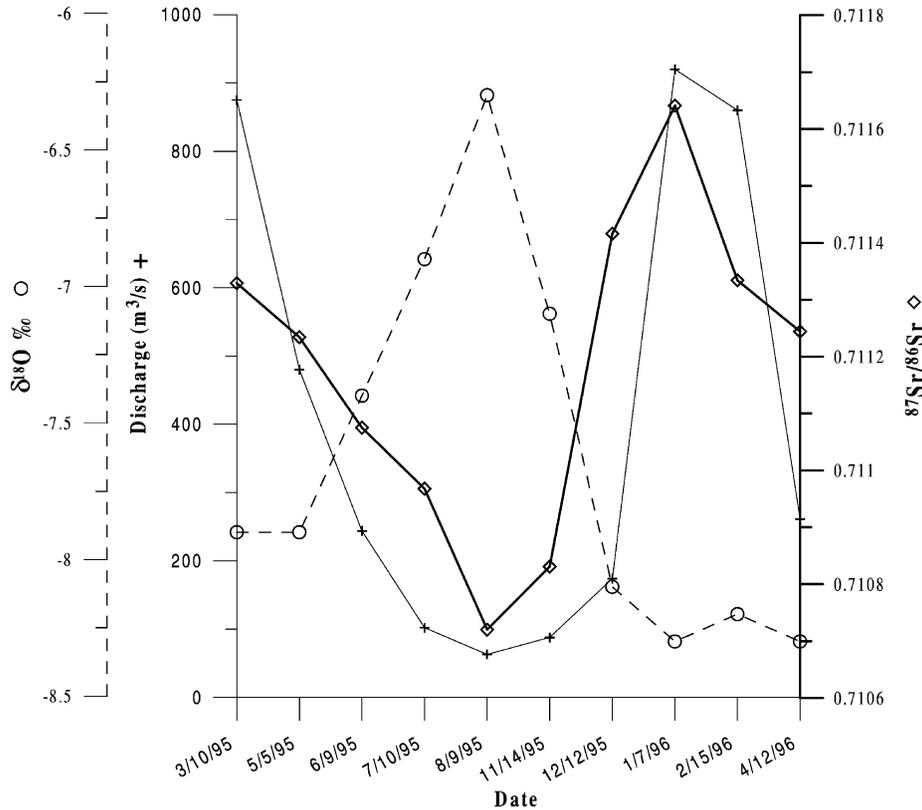
Fig. 7. Fluctuations of $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and discharge in the dissolved load obtained during the monthly survey at Orleans (data are from Grosbois et al., 2000).

Different groundwater systems may contribute to the Loire River budget. Firstly those described above, i.e. groundwater from the upper riverbank alluvial aquifers located in Quaternary deposits, from the lower riverbank alluvial aquifers showing an influence of the drained Mesozoic deposits, and from perched aquifers located in Tertiary deposits. Secondly, the groundwater located in the Aquitanian lacustrine carbonates (Beauce aquifer) and in the Cretaceous chalk.

A complete dataset for the Loire River and its alluvial groundwater is plotted in a $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ diagram (Bullen et al., 1996) in Fig. 8. As shown by Figs. 7 and 8, the $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ measured on the dissolved load at Orleans show a good correlation. The highest $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ observed during the winter well reflect the mixing between the Loire and Allier rivers (respectively,

the 'Loire MC' and 'Allier MC'). Decreasing flow in the Loire River is accompanied by a decrease in the $^{87}Sr/^{86}Sr$ ratio and an enrichment in the $\delta^{18}O$ towards the field defined by the upper riverbank alluvial aquifer. We can therefore postulate that the isotopic variations in the Loire River at Orleans are explained mainly by two different water inputs: one originating from the Loire and Allier rivers flowing over the Massif Central, and the second corresponding to a groundwater contribution from the alluvial plain. Groundwater from (a) the perched aquifers draining lacustrine carbonates (Stampian) and sandy-clayey deposits ('Bourbonnais'), and (b) from the lower riverbank alluvial aquifer marked by the drainage of marine carbonaceous deposits (Toarcian, Oxfordian; Delance et al., 1988) and from the Upper Cretaceous Chalk aquifer and overlying Beauce aquifer, extensively developed in Tertiary lacustrine carbonates
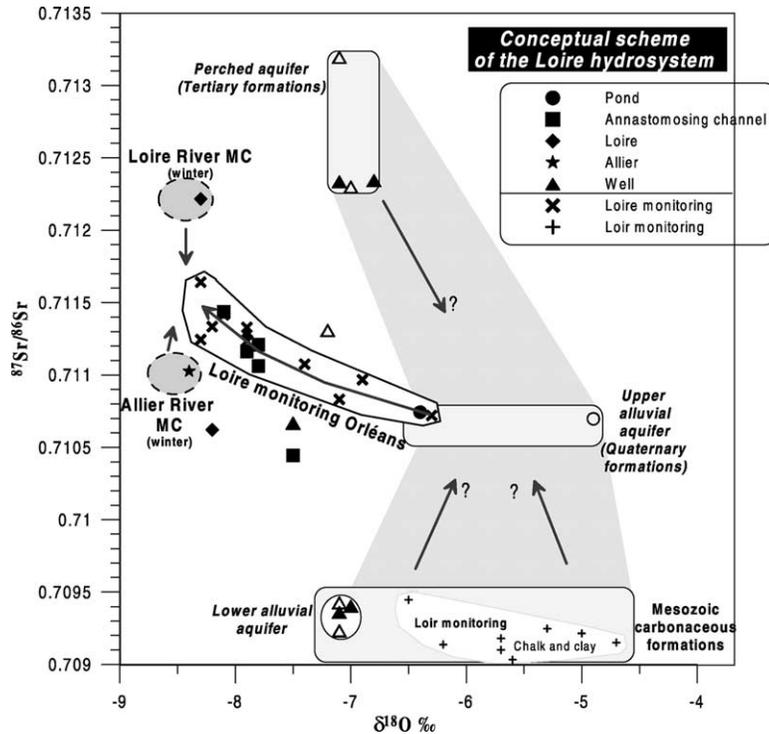
Fig. 8. Relationship between the $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ and discharge in the dissolved load obtained during the monthly survey at Orleans (data from Grosbois et al., 2000) and in surface and groundwater from the wetland site. Also plotted are data of groundwater located in the Upper Cretaceous Chalk aquifer and overlying Beauce aquifer (Négrel, unpublish data).

from which it is tapped for intense wheat farming (Négrel, unpublished data), seems to play a negligible role in the mixing model.

4. Conclusions

This study of the Loire-Allier hydrosystem has been conducted using a coupled geochemical and hydrological approach to enable a better understanding of the wetland function (a) upstream of the Loire and Allier confluence, (b) at the confluence itself, and (c) immediately downstream of the confluence. The stable isotopes ($\delta^{18}O$ and δ^2H) reveal not only that the alluvial aquifer is not recharged by the Loire River during flood periods, but that the groundwater has a local origin. Fluctuations in the Sr isotopes discriminate different groundwater levels (i.e. a perched aquifer, an upper alluvial aquifer and a lower alluvial

aquifer) that have variably complex relations with the surface water. The Loire and Allier rivers have distinct isotopic signatures derived from the drainage of different lithologies in the upper part of the catchment. The oxbow lakes of the Loire alluvial plain have different geochemical signatures, suggesting a time-delayed water input by the main stream.

The study also emphases the complexity in the functioning of perifluvial wetlands and the role of geomorphological inheritance. In the case of the Dornant site, the migration of the meanders and the connection between the lakes and the other water reservoirs has induced a strong lateral variability: the youngest lake ('Small Dornant') seems to be more influenced by the Loire River because of its downstream connection, whereas the Big Dornant, due to its wide upstream alluvial plug, is more dependent on the groundwater. In the case of the Loire River

downstream at the Soulangy site, the long anastomosing secondary channel shows a pronounced longitudinal variation: the Loire influence is progressively substituted by the water from the perched alluvial plain aquifer.

A conceptual scheme of the Loire hydrosystem based on two distinct isotopic tracers (δ^{18}O and ^{87}Sr/^{86}Sr) is proposed. It suggests that the isotopic variation of the Loire River can be related to a Massif Central surface-water supply (headwater of the Loire and Allier rivers) and an alluvial-water supply. This conceptual scheme should be improved by ongoing investigations into the rivers and groundwater.

Acknowledgements

References

Albarède, F., Michard, A., 1987. Evidence for slowly changing ^{87}Sr/^{86}Sr in runoff from freshwater limestones of southern France. Chem. Geol. 64, 55–65.

Barbaud, J.Y., 1983. Etude géochimique et isotopique des aquifères du nord de la Chaine des Puys. Temps de transit et vulnérabilité des systèmes de Volvic et d'Argnat. Doctoral thesis, University of Avignon, p. 209.

Barth, S.R., 2000. Stable isotope geochemistry of sediments-hosted groundwater from a Late-Proterozoic-Early Mesozoic section in Central Europe. J.Hydrol. 235, 72–87.

Bazin, P., Gautier, E., 1996. Un espace de liberté pour la Loire et l'Allier: de la détermination géomorphologique à la gestion. Rev. Géograp. de Lyon 71/4, 377–386.

Berner-Kay, E., Berner, R.A., 1987. The Global Water Cycle, Geochemistry and Environment, Prentice Hall, Englewood Cliffs, p. 396.

Böhlke, J.K., Horan, M., 2000. Strontium isotope geochemistry of groundwater and streams affected by agriculture, Locust Grove. MD. App. Geochem. 15, 599–609.

Bridge, J.S., 1993. The interactions between channel geometry, water flow, sediment transport and deposition in braided rivers. Braided Rivers, Geological Society Special Publication, vol. 75., pp. 13–71.

Bullen, T.D., Krabbenhoft, D.P., Kendall, C., 1996. Kinetic and mineralogic controls on the evolution of groundwater chemistry and ^{87}Sr/^{86}Sr in a sandy silicate aquifer, northern Wisconsin, USA. Geochim. Cosmochim. Acta 60, 1807–1821.

Clozier, L., Turland, M., Belkessa, R., 1976. Geological Map of France at 1:50,000 scale, Dornes Sheet. Explanatory Notes. BRGM, Orléans, p. 51.

Clozier, L., Debrand-Passard, S., Delance, J.H., Desprez, N., Lorenz, C., Lorenz, J., 1983. Geological Map of France at 1:50,000 scale, Sancoins Sheet. Explanatory Notes. BRGM, 37 p.

Craig, H., 1961. Isotopic variations in meteoric water. Science 133, 1702–1703.

Delance, J.H., Lablanche, G., Clozier, L., Debrand-Passard, S., Gros, Y., Cornet, J., Martins, Cl., Vautrelle, Ch., Gratier, M., 1988. Geological Map of France at 1:50,000 scale, Nevers Sheet. Explanatory Notes. BRGM, Orléans, p. 55.

Drever, J.I., 1988. The geochemistry of natural water, second ed., Prentice Hall, Englewood Cliffs, p. 430.

Edmond, J.M., Palmer, M.R., Measures, C.I., Grant, B., Stallard, R.F., 1995. The fluvial geochemistry and denudation rate of the Guayana shield in Venezuela. Geochim. Cosmochim. Acta 59, 3301–3325.

Fisher, R.S., Stueber, A.M., 1976. Strontium isotopes in selected streams within the Susqehanna River Basin. Wat. Res. Res. 12, 1061–1068.

Faure, G., 1986. Principles of Isotope Geology, Wiley, New York, p. 589.

Fustec E., Frochot B., 1996. Les fonctions et valeurs des zones humides. Laboratoire de Géologie Appliquée, Univ. Paris-VI, Laboratoire d'Ecologie, Univ. Dijon, Agence de l'Eau Seine-Normandie, p. 134.

French National Isotopic Data Base: on the web: http://bdiso.infoterre.brgm.fr.

Gaillardet, J., Dupré, B., Allègre, C.J., Négrel, Ph., 1997. Chemical and physical denudation in the Amazon River Basin. Chem. Geol. 142, 141–173.

Gautier, E., Piégay, H., Bertaina, P., 2000a. A methodological approach of fluvial dynamics oriented towards hydrosystem management: the Loire and Allier rivers case study. Geodyn. Acta 13/1, 29–43.

Gautier, E., and the project team., 2000. La détermination d'un espace de liberté pour le système fluvial ligérien: identification et spatialisation des unités morphodynamiques et écologiques fonctionnelles dans les vals libres et endigués de la Loire, enjeux et acteurs sociaux. PNRZH Annual Report, p. 80.

Gautier, E., and the project team., 2001. La détermination d'un espace de liberté pour le système fluvial ligérien: identification et spatialisation des unités morphodynamiques et écologiques fonctionnelles dans les vals libres et endigués de la Loire, enjeux et acteurs sociaux. PNRZH Final Report, p. 135.

Guglielmi, Y., Mudry, J., Blavoux, B., 1998. Estimation of the water balance of alluvial aquifers in region of high isotopic contrast: an example from southwestern France. J. Hydrol. 210, 106–115.

Grosbois, C., 1998. Géochimie des eaux de la Loire: contributions naturelles et anthropiques, quantification de l'érosion. Doctoral thesis, University of Tours (France), p. 232.

Grosbois, C., Négrel, Ph., Fouillac, C., Grimaud, D., 2000. Chemical and isotopic characterization of the dissolved load of the Loire river. Chem. Geol. 170, 179–201.

Grosbois, C., Négrel, Ph., Fouillac, C., Grimaud, D., 2001. An overview of dissolved and suspended matter fluxes in the Loire river basin: natural and anthropogenic inputs. Aq. Geochem. 7, 81–105.

Hayashi, M., van der Kamp, G., Rudolph, D., 1998. Water and solute transfer between a prairie wetland and adjacent uplands; 1-water balance. J. Hydrol. 207, 42–55.

Holland, M.M., Whigham, D.F., Gopal, B., 1990. In: Naiman, R.J., Décamps, H. (Eds.), The characteristics of wetland ecotones, The Ecology and Management of Aquatic-Terrestrial Ecotones. MAB-UNESCO, vol. 4., pp. 171–198.

Huddard, P.A., Longstaffe, F.J., Crowe, A.S., 1999. (dD and $d^{18}O$ evidence for inputs to groundwater at a wetland coastal boundary in the southern Great Lakes region of Canada. J. Hydrol. 214, 18–31.

Huh, Y., Tsoi, M.Y., Zaitsev, A., Edmond, J.M., 1998. The fluvial geochemistry of the rivers of Eastern Siberia: I. Tributaries of the Lena River draining the sedimentary platform of the Siberian craton. Geochim. Cosmochim. Acta 62, 1657–1676.

Hunt, R., Bullen, T.D., Krabbenhoft, D.P., Kendall, C., 1998. Using stable isotopes of water and strontium to investigate the hydrology of a natural and a constructed wetland. Groundwater 36, 434–443.

IAEA/WMO, 2001. Global Network of Isotopes in Precipitation. The GNIP Database. Web address: http://isohis.iaea.org

Jones, C.E., Jenkyns, H.C., Hesselbo, S.P., 1994. Strontium isotopes in early Jurassic seawater. Geochim. Cosmochim. Acta. 58, 1285–1301.

Kehew, A.E., Passero, R.N., Kishanamurthy, R.V., Lovett, C.K., Dayharsh, B.A., 1998. Hydrogeochemical interaction between a wetland and an unconfined glacial drift aquifer Southwestern Michigan. Groundwater 36, 849–856.

Kendall, C., McDonnell, J.J., 1998. Isotope Tracers in Catchment Hydrology. Elsevier, 839.

Knighton, A.D., Nanson, G.C., 1993. Anastomosis and the continuum of channel pattern. Earth Surf. Proc. and Landforms 18, 613–625.

Koepnick, R.B., Denison, R.E., Burke, W.H., Hetherington, E.A., Dahl, D.A., 1990. Construction of the Triassic and Jurassic portion of the Phanerozoic curve of seawater $^{87}Sr/^{86}Sr$. Chem. Geol. 80, 327–349.

Lissey, A., 1971. Depression-focused transient groundwater flow patterns in Manitoba. Geol. Assoc. Can. Spec. Paper 9, 333–341.

Meybeck, M., 1998. Man and river interface: multiple impacts on water and particulates chemistry illustrated in the Seine river basin. Hydrobiologia 373/374, 1–20.

Mitsch, W.J., Gosselink, J.G., 1993. Wetlands, second ed., Van Nostrand Reinhold Company, New York, p. 722.

Nanson, G.C., Knighton, A.D., 1996. Anabranching rivers: their causes, character and classification. Earth Surf. Proc. and Landforms 21, 217–239.

Négrel, Ph., 1999. Geochemical study in a granitic area, the Margeride, France: chemical element behavior and $^{87}Sr/^{86}Sr$ constraints. Aq. Geochem. 5, 125–165.

Négrel, Ph., Deschamps, P., 1996. Natural and anthropogenic budgets of a small watershed in the Massif Central (France): chemical and strontium isotopic characterization in water and sediments. Aq. Geochem. 2, 1–27.

Négrel, Ph., Roy, S., 1998. Rain chemistry in the Massif Central (France). A strontium isotopic and major elements study. App. Geochem. 13, 941–952.

Négrel, Ph., Grosbois, C., 1999. Changes in distribution patterns of chemical elements and $^{87}Sr/^{86}Sr$ isotopic signatures in suspended matter and bed sediments transported out by the upper Loire River watershed (France). Chem. Geol. 156, 231–249.

Négrel, Ph., Grosbois, C., 2001. Tracing the sources of dissolved and suspended loads in the Loire river (France) by Sr isotopes. 4th International Symposium on Applied Isotope Geochemistry, June 2001, Menlo Park, California, USA, 190-192.

Négrel, Ph., Allègre, C.J., Dupré, B., Lewin, E., 1993. Erosion sources determined from inversion of major, trace element ratios and strontium isotopic ratio in riverwater: the Congo Basin case Earth. Planet. Sci. Lett. 120, 59–76.

Négrel, Ph., Fouillac, C., Brach, M., 1997a. Occurrence of mineral water springs in the stream channel of the Allier River (Massif Central, France): chemical and Sr isotope constraints. J. Hydrol. 203, 143–153.

Négrel, Ph., Fouillac, C., Brach, M., 1997b. A strontium isotopic study of mineral and surface water from the Cezallier (Massif Central France): implications for the mixing processes in areas of disseminate emergences of mineral water. Chem. Geol. 135, 89–101.

Négrel, Ph., Grosbois, C., Kloppmann, W., 2000. The labile fraction of suspended matter in the Loire river (France): multi-element

chemistry and isotopic (Rb-Sr and C-O) systematics. Chem. Geol. 166, 271–285.

Palmer, M.R., Edmond, J.M., 1992. Controls over the strontium isotope composition of river water. Geochim. Cosmochim. Acta 56, 2099–2111.

Rodhe, A., 1984. Groundwater contribution to streaflow in Swedish forested till soil as estimated by oxygen-18. In: Proceedings of Isotopic Hydrology. IAEA. pp. 55–56.

Roy, S., Gaillardet, J., Allègre, C.J., 1999. Geochemistry of dissolved and suspended loads of the Seine river France: anthropogenic impact, carbonate and silicate weathering. Geochim. Cosmochim. Acta 63/9, 1277–1292.

Semhi, K., Clauer, N., Probst, J.L., 2000. Strontium isotope compositions of river water as records of lithology-dependent mass transfers: the Garonne river and its tributaries (SW France). Chem. Geol. 168, 173–193.

Turner, J.V., Macpherson, D.K., 1990. Mechanisms affecting streamflow and stream water quality: an approach via stable isotope, hydrochemical and time series analysis. Wat. Res. Res. 26, 3005–3019.

Whittaker, R.H., Likens, G.E., 1975. In: Lieth, H., Whittaker, R.H. (Eds.), The biosphere and Man, Primary Productivity of the Biosphere, Springer, New York, p. 175.

Wolery, T.J., 1992. EQ3NR: a computer program for geotechnical aqueous speciation-solubility calculations: theoretical manual, user's guide and related documentation (version 7.0). UCRL-MA-110662-PT-I, Lawrence Livermore National Laboratory, California, p. 246.