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TEMPORAL AND SPATIAL VARIATIONS OF FRESHWATER RESERVOIR AGES IN THE LOIRE RIVER WATERSHED

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ABSTRACT. In order to map the freshwater reservoir effect (FRE) variability of the Loire River and its tributaries, spatial and temporal carbon isotope (¹³C and ¹⁴C) analyses of the dissolved inorganic carbon (DIC) were conducted. Sites were selected to represent the diversity of geological settings, soil type, and land use. Results show a large spatial variability of ¹⁴C FRE ranging between 135 and 2251 ± 30 yr, objectively correlated to DIC contents and alkalinity. Deeper investigations of the relationship between ¹⁴C activity of DIC and environmental variables show that the geological substrate is the dominant factor in the ¹⁴C reservoir effect, and far more influential than the river flow discharge.

KEYWORDS: freshwater reservoir effect, Loire River, dissolved inorganic carbon, ¹³C, ¹⁴C.

INTRODUCTION

The radiocarbon freshwater reservoir effect (FRE) is the difference between the age of the freshwater carbon reservoirs and the age of atmospheric or terrestrial carbon reservoirs (Ascough et al. 2010). The FRE was first described in 1949 by J Iversen in a private communication (Oana and Deevey 1960). Aquatic plants were the first samples used to measure the FRE, in 1951 by Godwin (Oana and Deevey 1960) and in 1954 by Deevey et al. (1954). Later, FRE was mainly studied in aquatic plants and animals (Broecker and Walton 1959). In the last decade, under the leadership of archaeologists, scientists started to study the FRE in order to apply corrections on ¹⁴C dates measured in prehistoric sites. This effect leads to aging of the ¹⁴C dates of bone collagen of freshwater fish consumers but is also recorded in nonhuman materials (e.g. ceramic or pottery food crusts, wild or domestic animal remains, terrestrial/aquatic shells, sediments) (Cook et al. 2001; Bonsall et al. 2004; Shishlina et al. 2007; Boudin et al. 2009; Van Strydonck et al. 2009; Higham et al. 2010; Hollund et al. 2010; Olsen et al. 2010; Philippsen et al. 2010; Keaveney and Reimer 2012; Hart et al. 2013).

Previous studies have shown that the FRE varies between a few and several thousand years. For instance, the FRE is estimated between 400 and 5000 ¹⁴C yr in Lake Mývatn (Iceland) (Ascough et al. 2010) or several tens of thousands of years in Mammoth Mountain waters (California, USA) (Sorey et al. 1998), attributed largely to geothermal mechanisms. An FRE of 18,000 ¹⁴C yr was also reported in the Dry Valleys of Antarctica and attributed to an input of ancient glacial meltwater (Hall and Henderson 2001), and in the waters of Waddi Akarit (Tunisia) fed by Saharan fossil water tables (Fontes and Gasse 1991). The FRE is highly variable within a lake or a river and very difficult to estimate because of its multiple origins (Fontugne et al. 2009; Ascough et al. 2010; Philippsen et al. 2010; Philippsen 2012, 2013; Philippsen and Heinemeier 2013).

The FRE results from complex processes involved in dissolved inorganic carbon (DIC) cycling in river systems. These processes involve mainly the chemical weathering of geological ¹⁴C-free carbonates and silicate, leading to the so-called hardwater effect (Deevey et al. 1954). The decomposition of other rocks such as volcanic glasses and geothermal CO₂ can also cause significant aging in DIC in groundwaters (Sveinbjörnsdóttir et al. 1995) and in mineral water sources (Boineau and Maisonneuve 1971; Sorey et al. 1998). Atmospheric CO₂ also exchanges with DIC, reducing the

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FRE in well-ventilated rivers. Finally, synthesis and decomposition processes of organic matter in rivers contribute to FRE variations since organic carbon records partly the seasonal variability of the ^{14}C concentration in DIC (Buhl et al. 1991; Aucour et al. 1999). A better understanding of these variations will lead to better description of the FRE evolution.

In this study, we investigated the spatial and temporal variability of the FRE in the largest French river, the Loire, and its main tributaries in 2004, 2005, 2013, and 2014. Through measurements of ^{14}C ages and DIC $\delta^{13}\text{C}$ combined with physico-chemical parameters, we tried to assess the main factors controlling these ages on a spatial and temporal basis.

STUDY AREA

Study Site

The Loire is the largest French river with a length of 1010 km and major inputs (carbon, nutrients, and flow rate) to the northeastern Atlantic Ocean with a water discharge of $26 \text{ km}^3/\text{yr}$

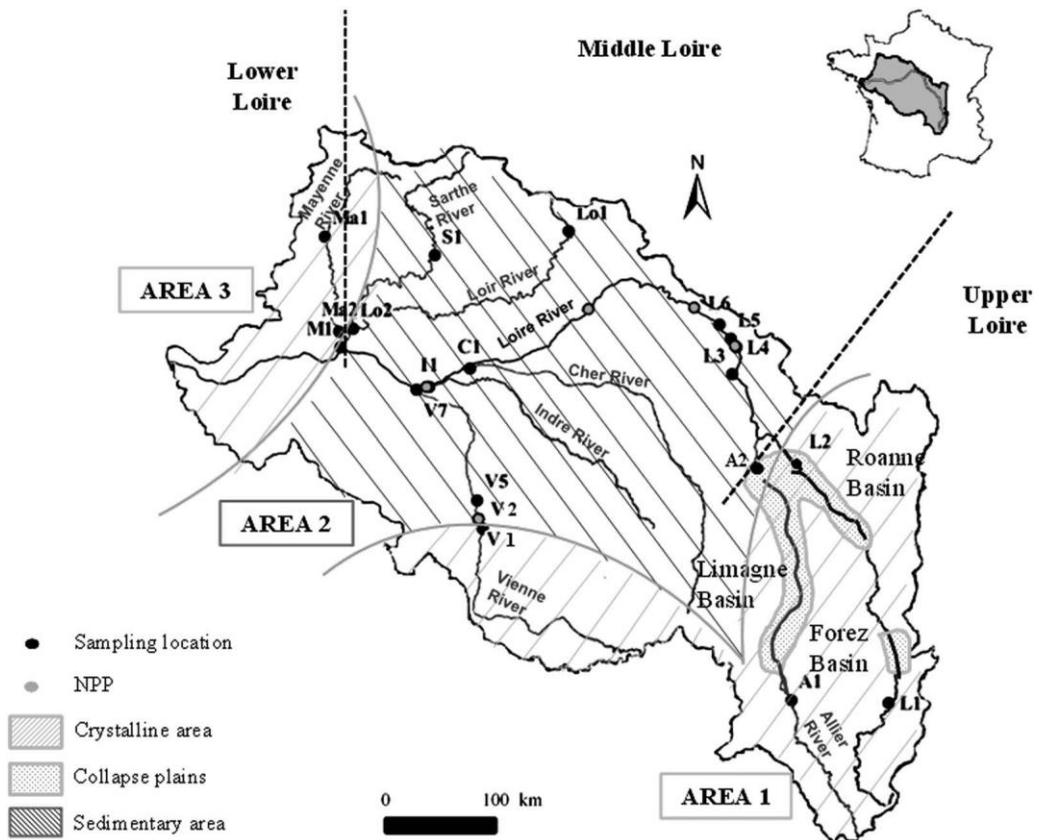


Figure 1 Loire River Basin. The upper part of the Loire River is upstream of the confluence of the Allier and Vienne rivers. The middle part of the Loire River is between the confluence of the Allier and Loire rivers and the confluence of the Maine and Loire rivers. The lower part of the Loire River is downstream the confluence of the Maine and Loire rivers. Sampling sites and nuclear power plants (NPP) are represented by black and red points, respectively (online version of the article). Three areas are identified: Area 1 and 3 are crystalline regions (striped orange zone) and Area 2 is a region with carbonaceous sediments (striped blue zone). The dotted region represents the carbonated collapse plain between the Limagne Plain, the Roanne Basin, and the Forez Basin.

(Figueres et al. 1985). The Loire River system drains a 117,800 km² basin, which represents 20% of the surface area of France (Abonyi et al. 2012; Figure 1). From its source in the Southern Massif Central, the Loire flows through agricultural regions to the Atlantic Ocean (Minaudo et al. 2013). The left bank tributaries studied here are the Allier (A), Cher (C), Indre (I), and Vienne (V) rivers. The Maine (M) River, formed by the confluence of the Mayenne (Ma), Sarthe (S), and Loir (Lo) rivers, is the only tributary studied on the right bank. These tributaries were chosen based on their differences in geological settings, land use, and flow rate.

The Loire Basin drains three areas that are significantly different in geological substrate (Figure 1; Mansy et al. 2008). In Area 1, to the west, the upper segment of the Vienne River drains the Limousin granite formation and goes towards 46°30'N, in the Jurassic limestone of the Paris Basin. South of 45°30'N, the Upper Loire and Allier rivers drain the Hercynian crystalline formation of the Massif Central, which has been characterized since the Miocene period by significant volcanic activity.

Area 2 consists of the Jurassic to Miocene sedimentary formation of the Paris Basin. These sediments are mostly limestone and constitute the substrate of the Loir, Sarthe, lower Vienne, Indre, Cher, and middle Loire riverbeds. The upstream parts of the Loire and Allier rivers enter the Forez and Limagne collapse plains, respectively. These faulted basins covered by eolian Quaternary deposits (loess) are well known for their hydrothermal activities and numerous mineral springs.

Area 3 is the eastern edge of the Massif Armoricaire Paleozoic formation, which is composed of granitic and metamorphic (gneiss or schist) rocks. Nevertheless, some fractures may be filled by carbonate deposits as is the case for the Changé formation in the upper course of the Mayenne River (Aertgeerts et al. 2011a).

The Loire River and its five tributaries are situated in the central part of France where the climate is temperate. The annual mean temperature in the Loire Basin is 11°C. The rivers are supplied either by groundwater and/or precipitation, and melting snows during the spring only in the upper course of the Allier and Loire rivers. The altitude along the Loire River is from 1408 m near the source to 0 m above sea level (asl) at the estuary (Grosbois 1998).

Sampling Sites

In this study, 20 sampling sites were selected in the Loire Basin (Table 1, Figure 1). They cover a wide range of geological substrates and agricultural practices. Six sampling sites are situated in the headwater and in the beginning of the middle part of the Loire River from Aurec-sur-Loire (L1) to Briare (L6). Several nuclear power plants are located on the Loire and Vienne rivers, and can potentially release liquids containing ¹⁴C in DIC form and tritium, mainly (Siclet et al. 2002). Tritium is commonly used as a tracer for these releases and was measured in this study to identify a potential release. These values were indeed closely related to the periods of releases communicated by the energy industry. Two sites presented in this study (L5 and L6) were located downstream of a nuclear power plant. The samples used in this study were strictly selected during nonrelease periods. In previous studies, no memory effect was observed after a release (Fontugne et al. 2007).

A few sites are located on noncarbonaceous bedrock. In Area 1, two sites (L1 and A1) are located in the crystalline formation. Lussac (V1) is located at the boundary between Area 1 and 2. At this location, the Vienne River flows out from the Limousin crystalline formation and does not reach the Lias and Jurassic limestone formations situated in the northeastern part of

Table 1 Sampling sites location on the Loire River Basin. Kilometric Point 0 is situated at Saint Nazaire near the estuary (47°16'04"N; 2°11'08"W).

Rivers	N°	Location	Latitude N	Longitude	Kilometric points (rkms)*
Loire	L1	Aurec-sur-Loire	45°22'09"	4°11'39"E	847.0
	L2	Decize	46°49'40"	3°27'27"E	553.4
	L3	Saint Satur	47°20'19"	2°51'33"E	497.2
	L4	Belleville-sur-Loire	47°30'16"	2°53'13"E	477.1
	L5	Bonny-sur-Loire	47°33'01"	2°50'06"E	474.1
	L6	Briare	47°37'55"	2°44'14"E	447.4
					Confluence with Loire River
Allier	A1	Auzon	45°23'08"	3°21'23"E	536.5
	A2	Le Veurdre	46°45'28"	3°2'56"E	
Cher	C1	Savonnières	47°20'54"	0°32'34"E	241.8
Indre	I1	Le Neman	47°13'55"	0°11'50"E	216.6
Vienne	V1	Lussac-les-Châteaux	46°24'16"	0°42'07"E	206.0
	V2	Civaux upstream	46°27'31"	0°39'49"E	
	V5	Chauvigny	46°34'10"	0°38'29"E	
	V7	Candes-Saint-Martin	47°12'36"	0°04'45"E	
Maine	M1	Bouchemaine	47°26'40"	0°35'47"W	134.0
Mayenne	Ma1	Changé	48°05'57"	0°47'06"W	—
	Ma2	Montreuil-Juigné	47°32'24"	0°36'50"W	
Sarthe	S1	Le Mans	48°00'47"	0°11'56"E	—
Loir	Lo1	Bonneval	48°10'44"	1°23'22"E	—
	Lo2	Briollay	47°33'29"	0°30'03"W	

the plateau. Similarly, Decize (L2) is located at the junction of a crystalline and a sedimentary formation and Loire River waters come out of a sandy clay zone north of the Roanne Basin before running on Jurassic limestones. All the other sites are in the carbonate sedimentary context of Area 2, except for sites Ma1 and Ma2, which are partially in the metamorphic context (shale) of Area 3 (Aertgeerts et al. 2011a). Sites L2 (Area 1) and A2 (Area 2) are in the collapse basins. Site C1 is on the Cher River at Savonnières near the Mesozoic carbonate petrified caves (Couderc 1968). Site M1 at Bouchemaine on the Maine River reflects the mixing of its different tributaries: the Mayenne (Ma1, Ma2), Sarthe (S1, Aertgeerts et al. 2011b), and Loir (Lo1, Lo2) rivers. Four sampling sites are distributed on the Vienne River: V1 at the limit of the granitic area and V2, V5, V7 in a carbonate complex area, downstream from a nuclear power plant (SAGE 2006).

For this study, four sampling campaigns were conducted in April, July, and October 2013 and March 2014. According to hydrological and meteorological conditions, the July and October 2013 sampling represented summer conditions while April 2013 and March 2014 represented winter/early spring conditions. All sites were sampled during these campaigns, except V2 (upstream Civaux) that was sampled only in July and October 2013 and upstream sites of the Loire and tributaries (L1, A1, Ma1, S1, and Lo1) that were sampled in March 2014. We also used unpublished data from three other campaigns conducted in September 2004, May 2005, and November 2005 in which the sampling sites were located in the middle Loire River and the samples were collected on the riverbank (Fontugne et al. 2007; Marang et al. 2011).

METHODS

In this study, surface water samples were collected from bridges in the main water flow on the Loire River and its tributaries. They were taken from 0–0.5 m depth using a bucket (Garnier et al. 2001; Sato et al. 2006).

For chlorophyll-a (hereafter chl-a) analysis, water was immediately filtered using a precombusted (450°C) Whatman glass fiber filter (GF/F, 0.7- μm pore diameter). The filter was stored at -80°C in aluminum foil to prevent light degradation until analysis, around 1 week later. Chl-a was then analyzed by spectrofluorimetry according to Neveux and Lantoiné (1993) at the Station Marine d'Arcachon (University of Bordeaux I).

For alkalinity analysis, water was immediately filtered using a precombusted (450°C), 47-mm-diameter Whatman quartz fiber filter (QM/A, 2.2- μm pore diameter) and stored at 4°C until analysis. The analysis was performed within 1 week by potentiometric titration with HCl 0.01N, using the Gran method. We expressed the results in meq/L assuming that alkalinity is mainly represented by bicarbonates and carbonates. The precision was around 5%.

For the DIC concentration and $\delta^{13}\text{C}$ and ^{14}C analysis, water samples were transferred to precleaned (TBF4, 10% HCl, pure water) and combusted (450°C, overnight) 250-mL borosilicate ground neck bottles and poisoned with 1 mL of a saturated solution of mercury (II) chloride (Leboucher et al. 1999). The borosilicate bottles were then sealed with greased ground glass stoppers (Apiezon H).

In the laboratory, 80 to 200 mL of water sample and 2 mL of 85% H_3PO_4 were introduced in a glass reactor in a vacuum line for the extraction of DIC as free CO_2 (Leboucher et al. 1999). The sample was purged using ultra-high-purity (6.0) helium gas. The CO_2 was dried by passing through two water traps (ethanol/dry ice) before being trapped in a liquid nitrogen trap. Then, the CO_2 was manometrically quantified in a calibrated volume and separated in 2 aliquots: one for ^{14}C measurement and the other for stable carbon isotope measurement. $\delta^{13}\text{C}$ values were determined at LSCE using a dual-inlet VG-Optima isotopic ratio mass spectrometer (typical precision below 0.08‰). The DIC concentration was calculated from the amount of carbon extracted and the volume of extracted water and expressed in mgC/L with a precision of 1%.

^{14}C measurements were performed with the Artemis accelerator mass spectrometry (AMS) facility at the Laboratoire de Mesure du Carbone 14 in Saclay (France). Prior to measurement, the evolved CO_2 was converted to graphite (Cottéreau et al. 2007). The ^{14}C activities are reported in fraction modern ($F^{14}\text{C}$) and ^{14}C age (Stuiver and Polach 1977; Reimer et al. 2004). All ^{14}C values were corrected from the delay between sampling and measurement years and background subtraction. The total uncertainty for the ^{14}C activity values was $\pm 0.003 F^{14}\text{C}$, corresponding to an age of ± 30 yr. According to the definition, the FRE was calculated as follows:

$$\text{FRE} = 8033 \ln F^{14}\text{C}_S = F^{14}\text{C}_A$$

where $F^{14}\text{C}_S$ and $F^{14}\text{C}_A$ are the sample modern fraction and the atmospheric sample modern fraction, respectively (Keaveney and Reimer 2012). We used the conventional values of Levin et al. (2013) and unpublished data (Samuel Hammer and Ingeborg Levin, personal communication, 2015) for the atmospheric sample age. We calculated the mean annual value of the atmosphere activity in 2004, 2005, 2013, and 2014 and obtained $F^{14}\text{C}$ values of 1.0674, 1.0644, 1.0284, and 1.0258, respectively.

River Discharge

River discharge data of the Loire River were taken from the national BanqueHydro database (<http://www.hydro.eaufrance.fr>). Data collected between 2004 and 2014 were used to estimate the mean discharge at each sampling site for this period. We then calculated the mean discharge percentage according to the following equation to evaluate the streamflow river states in flood or low water:

$$\% \text{ of mean discharge} = \frac{\text{Discharge}}{\text{Mean discharge}} 100$$

RESULTS AND DISCUSSION

River discharge, chlorophyll-a concentration, alkalinity, DIC concentration, DIC $\delta^{13}\text{C}$, ^{14}C activity, and reservoir age are reported in Table 2. Unpublished values obtained during the 2004 and 2005 LORA experiments (Fontugne et al. 2007) are also reported in italics in Table 2. Some reservoir age values are missing because sampling sites were under the influence of a nuclear power plant release or because the measurement failed.

Chlorophyll-a

Chl-a concentrations showed large variations ranging between 0.4 and 152.8 $\mu\text{g/L}$ in the Loire River Basin. The highest concentrations ($>44 \mu\text{g/L}$) were recorded in the Maine Basin (M1 and tributaries) in the early spring (March 2013 and April 2014) and are likely associated with spring phytoplankton blooms when the optimal sunlight conditions trigger an intense photo-synthetic activity. This high chl-a concentration can also be explained by the water composition of the Maine River's tributaries, which drain large areas of cereal crops involving fertilizers that may promote an even higher rate of aquatic photosynthesis. Low values (below 10 $\mu\text{g/L}$) were observed in wine-growing zones and cattle-breeding areas, in the upper and the beginning of the middle Loire as well as in the Allier, Indre, Cher, and Vienne tributaries. This low chl-a concentration is consistent with previous studies (Aleya et al. 1994; Jugnia et al. 2004) that indicated eutrophic water in headwater due to the nature of the phytoplankton assemblage (lake-like) that does not survive in the turbulent and quite turbid river (Abonyi et al. 2012, 2014). A few high values between 22.0 and 37.9 $\mu\text{g/L}$ were observed in these rivers occurring typically at the beginning of spring and summer. In the Loire River, higher chl-a concentration mean values (16.8 $\mu\text{g/L}$) were observed in spring and summer 2004–2005 than during the four campaigns in 2013–2014 (10.4 $\mu\text{g/L}$). These results are consistent with the study by Minaudo et al. (2015) that showed the decline of chl-a concentration over the last decade mainly due to the continuous decline of phosphate concentrations.

Alkalinity and DIC Concentration

Alkalinity and DIC concentration values varied from 0.6 to 7.7 meq/L and from 2.0 to 56.6 mgC/L, respectively, and were highly correlated ($r = 0.92$; $n = 49$; $p < 0.05$). The alkalinity was higher in sedimentary limestone areas than in crystalline areas, suggesting that chemical weathering of carbonates and silicates is the main process influencing alkalinity in the Loire Basin. This seems to indicate the low contribution of atmospheric CO_2 and river exchange. The highest DIC concentrations measured in the Cher and Indre rivers are not surprising due to the presence of petrifying springs in the basin. High concentrations of DIC were also observed in the Loir. This area is mostly composed of arable land. An extensive drainage in the river catchment can be created by intensive agricultural practices, which could imply a significant increase in the export of DIC as observed by Barnes and Raymond (2009).

Table 2 River discharge (data from www.hydro.eaufrance.fr), chlorophyll-a concentration, alkalinity, DIC concentration, DIC $\delta^{13}\text{C}$, ^{14}C activity and reservoir age for the 20 sampling sites in the Loire River Basin. Sampling year and month are specified after the location name. Unpublished values obtained during the 2004 and 2005 LORA experiments (Fontugne et al. 2007) are reported in italic (nd = not determined).

Rivers	Nr	Sampling location (yy/mm)	Lab nr SacA-	Lab nr GifA-	Discharge* (m ³ /s)	Percentage of mean discharge	Chl-a (µg/L)	Alkalinity (meq/L)	DIC (mgC/L)	$\delta^{13}\text{C}$ -DIC (‰)	F ¹⁴ C-DIC * 100	Reservoir age (¹⁴ C yr)
Loire	L1	Aurec-sur Loire 14/03	38566	14089	26.0	80%	10.8 ± 1.0	1.13 ± 0.06	5.9±0.1	-7.88 ± 0.08	99.2 ± 0.2	273 ± 30
	L2	Decize 13/04	33201	13112	204.0	121%	22.0 ± 2.0	1.48 ± 0.07	7.1±0.1	-9.48 ± 0.08	95.6 ± 0.3	586 ± 30
	L2	Decize 13/07	34827	13264	91.7	55%	9.1 ± 0.8	3.78 ± 0.19	12.0±0.1	nd	94.9 ± 0.2	646 ± 30
	L2	Decize 13/10	38560	14083	42.7	25%	1.8 ± 0.2	2.42 ± 0.12	13.4±0.1	-13.00 ± 0.02	96.3 ± 0.2	525 ± 30
	L2	Decize 14/03	38571	14094	137.0	81%	9.3 ± 0.8	2.20 ± 0.11	7.7±0.1	-11.83 ± 0.05	98.6 ± 0.2	319 ± 30
	L3	Saint Satur 13/04	33203	13114	447.0	150%	15.0 ± 1.4	1.81 ± 0.09	5.6±0.1	nd	91.5 ± 0.2	941 ± 30
	L3	Saint Satur 13/07	/	/	165.0	55%	3.8 ± 0.3	3.05 ± 0.15	8.7±0.1	nd	nd	nd
	L3	Saint Satur 13/10	38563	14086	104.0	35%	2.2 ± 0.2	4.40 ± 0.22	19.0±0.2	-11.01 ± 0.03	91.4 ± 0.2	948 ± 30
	L3	Saint Satur 14/03	38758	14099	280.0	94%	9.1 ± 0.8	4.13 ± 0.21	17.3±0.2	-10.33 ± 0.05	90.6 ± 0.2	994 ± 30
	L4	Upstream Belleville-sur-Loire 04/09	2407	/	118.0	37%	14.7 ± 1.3	3.55 ± 0.18	20.8±0.2	-11.32 ± 0.07	91.5 ± 0.5	1238 ± 30
	L4	Upstream Belleville-sur-Loire 05/05	3960	/	377.0	117%	17.2 ± 1.5	3.19 ± 0.16	22.5±0.2	nd	91.0 ± 0.5	1259 ± 30
	L4	Upstream Belleville-sur-Loire 05/11	4884	/	131.0	41%	4.5 ± 0.4	2.67 ± 0.13	19.1±0.2	nd	93.0 ± 0.4	1084 ± 30
	L5	Bonny-sur-Loire 05/05	3961	/	377.0	117%	18.50 ± 1.7	3.17 ± 0.16	21.9±0.2	nd	89.7 ± 0.7	1375 ± 30
	L6	Briare 13/04	33212	13123	443.0	138%	4.5 ± 0.4	2.05 ± 0.10	8.9±0.1	-9.62 ± 0.08	90.5 ± 0.3	1032 ± 30
	L6	Briare 13/07	34837	13274	167.0	52%	37.9 ± 3.4	3.11 ± 0.16	17.6±0.2	-11.25 ± 0.06	89.9 ± 0.3	1082 ± 30
	Allier	L6	Briare 13/10	36814	14015	97.2	30%	1.7 ± 0.2	3.49 ± 0.17	19.1±0.2	-11.22 ± 0.03	nd
L6		Briare 14/03	38794	14107	330	103%	8.6 ± 0.8	3.33 ± 0.17	10.9±0.1	-10.52 ± 0.03	nd	nd
A1		Auzon 14/03	38567	14090	35.0	125%	6.2 ± 0.6	0.61 ± 0.03	2.0±0.1	-12.41 ± 0.13	100.9 ± 0.2	135 ± 30
A2		Le Veurdre 13/04	33202	13113	217.0	175%	4.6 ± 0.4	1.56 ± 0.08	3.9±0.1	nd	84.3 ± 0.3	1600 ± 30
A2		Le Veurdre 13/07	34828	13265	62.7	51%	6.1 ± 0.6	1.99 ± 0.10	17.0±0.2	-9.47 ± 0.02	86.1 ± 0.3	1427 ± 30
A2		Le Veurdre 13/09	38561	14084	42.0	34%	9.8 ± 0.9	3.63 ± 0.18	16.1±0.2	-9.32 ± 0.03	86.3 ± 0.2	1413 ± 30
A2		Le Veurdre 14/03	38570	14093	149.0	120%	10.8 ± 1.0	2.78 ± 0.14	12.2±0.1	-7.57 ± 0.10	87.6 ± 0.3	1267 ± 30
Cher		C1	Savonnières 13/04	33204	13115	127.0	161%	3.8 ± 0.3	4.37 ± 0.22	21.5±0.2	-16.00 ± 1.00	88.4 ± 0.2
	C1	Savonnières 13/07	34830	13267	35.6	45%	1.4 ± 0.1	5.26 ± 0.26	27.2±0.2	-10.30 ± 0.03	85.5 ± 0.2	1481 ± 30

Table 2 (Continued)

Rivers	Nr	Sampling location (yy/mm)	Lab nr Sac A-	Lab nr Gif A-	Discharge* (m ³ /s)	Percentage of mean discharge	Chl-a (µg/L)	Alkalinity (meq/L)	DIC (mgC/L)	δ ¹³ C-DIC (‰)	F ¹⁴ C-DIC * 100	Reservoir age (¹⁴ C yr)
Indre Vienne	C1	Savonnières 13/10	38562	14085	25.3	32%	1.6 ± 0.1	5.41 ± 0.27	17.6 ± 0.2	-12.21 ± 0.08	87.4 ± 0.2	1309 ± 30
	C1	Savonnières 14/03	38569	14092	90.2	114%	4.9 ± 0.4	6.87 ± 0.34	37.1 ± 0.2	-9.16 ± 0.04	88.3 ± 0.2	1208 ± 30
	C1	Savonnières 05/11	4894	/	16.5	21%	0.5 ± 0.1	5.54 ± 0.28	41.3 ± 0.2	-11.70 ± 0.10	88.7 ± 0.5	1465 ± 30
	I1	Le Neman 05/11	4892	/	nd	nd	0.4 ± 0.01	7.74 ± 0.39	56.6 ± 0.2	-10.90 ± 0.09	87.5 ± 0.4	1574 ± 30
	V1	Lussac les chateaux 13/04	33208	13119	145.0	195%	2.0 ± 0.2	0.99 ± 0.05	2.1 ± 0.1	nd	97.0 ± 0.3	473 ± 30
	V1	Lussac les chateaux 13/07	34831	13268	32.7	44%	1.6 ± 0.1	1.23 ± 0.06	4.3 ± 0.1	nd	94.7 ± 0.2	667 ± 30
	V1	Lussac les chateaux 13/10	38564	14087	32.5	44%	1.1 ± 0.1	1.31 ± 0.07	7.1 ± 0.1	-12.64 ± 0.04	100.9 ± 0.3	150 ± 30
	V1	Lussac les chateaux 14/03	38763	14104	133.0	179%	6.8 ± 0.6	0.85 ± 0.04	4.0 ± 0.1	-11.42 ± 0.06	100.1 ± 0.2	200 ± 30
	V2	Amont Civaux 13/07	36811	13281	32.7	44%	0.7 ± 0.1	1.45 ± 0.07	10.3 ± 0.1	-13.25 ± 0.03	94.2 ± 0.4	703 ± 30
	V2	Amont Civaux 13/10	36809	14011	32.5	44%	1.4 ± 0.1	1.50 ± 0.08	7.5 ± 0.1	-12.24 ± 0.05	94.4 ± 0.3	690 ± 30
	V5	Chauvigny 13/04	33211	13122	147.0	177%	6.1 ± 0.6	1.29 ± 0.06	4.7 ± 0.1	-12.18 ± 0.06	87.4 ± 0.2	1307 ± 30
	V5	Chauvigny 13/07	/	/	38.6	47%	1.3 ± 0.1	1.90 ± 0.10	nd	nd	nd	nd
	V5	Chauvigny 13/10	38797	14110	29.4	35%	0.9 ± 0.1	2.14 ± 0.11	9.0 ± 0.1	-11.57 ± 0.03	nd	nd
	V5	Chauvigny 14/03	38764	14105	138	166%	6.2 ± 0.6	1.07 ± 0.05	6.5 ± 0.1	-11.48 ± 0.05	nd	nd
Mayenne	V7	Candes saint Martin 05/11	4895	/	nd	nd	0.6 ± 0.1	4.39 ± 0.22	32.3 ± 0.3	-10.45 ± 0.09	80.5 ± 0.4	2244 ± 30
	V7	Candes saint Martin 13/04	33205	13116	279.0	171%	8.0 ± 0.7	2.53 ± 0.13	16.1 ± 0.2	nd	89.7 ± 0.2	1101 ± 30
	V7	Candes saint Martin 13/07	38804	13282	96.9	59%	8.0 ± 0.7	4.53 ± 0.23	19.4 ± 0.2	-11.42 ± 0.03	nd	nd
	V7	Candes saint Martin 13/10	38808	14117	81.1	50%	1.3 ± 0.1	5.19 ± 0.26	19.3 ± 0.2	-11.78 ± 0.03	nd	nd
	V7	Candes saint Martin 14/03	38762	14103	328	201%	4.9 ± 0.4	3.05 ± 0.15	14.7 ± 0.1	-11.42 ± 0.06	nd	nd
Ma1	Changé 14/03	38761	14102	34.3	116%	15.1 ± 1.2	1.06 ± 0.05	5.4 ± 0.1	-11.16 ± 0.03	85.2 ± 0.2	1496 ± 30	
Ma2	Montreuil-Juigné 13/04	33207	13118	158.0	417%	32.7 ± 2.9	1.90 ± 0.10	7.7 ± 0.1	-13.61 ± 0.06	96.7 ± 0.3	492 ± 30	

	Ma2	Montreuil-Juigné 13/07	34834	13271	9.1	24%	11.7 ± 1.1	3.50 ± 0.17	8.5 ± 0.1	nd	97.7 ± 0.2	412 ± 30
	Ma2	Montreuil-Juigné 13/10	36812	14013	6.5	17%	53.4 ± 4.8	2.62 ± 0.13	16.4 ± 0.2	-10.70 ± 0.02	100.6 ± 0.3	180 ± 30
	Ma2	Montreuil-Juigné 14/03	38759	14100	42.9	113%	44.7 ± 4.0	1.70 ± 0.09	8.2 ± 0.1	-10.22 ± 0.01	99.0 ± 0.2	285 ± 30
Sarthe Loir	S1	Le Mans 14/03	38568	14091	37.5	189%	6.7 ± 0.6	5.89 ± 0.29	26.2 ± 0.3	-11.04 ± 0.04	93.6 ± 0.3	740 ± 30
	Lo1	Bonneval 14/03	38565	14088	1.8	65%	119.7 ± 10.8	4.63 ± 0.23	20.3 ± 0.2	-8.74 ± 0.03	77.5 ± 0.2	2251 ± 30
	Lo2	Briollay 13/04	33206	13117	130.0	463%	54.8 ± 4.9	6.30 ± 0.32	33.5 ± 0.3	-10.26 ± 0.06	82.0 ± 0.2	1823 ± 30
	Lo2	Briollay 13/07	34835	13272	16.4	58%	3.0 ± 0.3	7.54 ± 0.38	53.4 ± 0.5	nd	82.0 ± 0.3	1817 ± 30
	Lo2	Briollay 13/10	36813	14014	22.5	80%	1.3 ± 0.1	7.46 ± 0.37	45.5 ± 0.5	-11.92 ± 0.04	79.8 ± 0.6	2041 ± 30
Maine	Lo2	Briollay 14/03	38757	14098	33.2	118%	152.8 ± 13.8	6.62 ± 0.33	35.6 ± 0.4	-9.57 ± 0.04	84.3 ± 0.2	1580 ± 30
	M1	Bouchemaine 13/04	33209	13120	nd	nd	51.4 ± 4.6	3.70 ± 0.18	15.9 ± 0.2	-10.49 ± 0.08	91.0 ± 0.3	987 ± 30
	M1	Bouchemaine 13/07	34833	13270	nd	nd	11.0 ± 1.0	3.95 ± 0.20	35.4 ± 0.4	-12.36 ± 0.02	86.0 ± 0.2	1440 ± 30
	M1	Bouchemaine 13/10	36810	14012	nd	nd	6.4 ± 0.6	6.62 ± 0.33	39.6 ± 0.4	-12.28 ± 0.10	84.7 ± 0.3	1562 ± 30
	M1	Bouchemaine 14/03	38760	14101	nd	nd	48.0 ± 4.3	4.92 ± 0.25	25.9 ± 0.3	-11.25 ± 0.04	89.0 ± 0.2	1140 ± 30

The lowest DIC concentrations and alkalinities were observed upstream of the other rivers (except the Mayenne River because of a carbonate inclusion upstream) due to their localization in the crystalline area (Areas 1 and 3).

DIC $\delta^{13}\text{C}$

These first data of DIC $\delta^{13}\text{C}$ in the Loire Basin present high temporal and spatial variations ranging from -7.66‰ to -13.61‰ with one low value of $-16 \pm 1\text{‰}$ in Savonnières (C1) in April 2013 and the highest DIC $\delta^{13}\text{C}$ value of -7.57‰ at Le Veurdre (A2) in March 2014. This variability is wide no matter the geological substrate. However, our DIC $\delta^{13}\text{C}$ values are consistent with the results of studies conducted on other French rivers such as the study by Buhl et al. (1991) on the Rhine ($-10.7\text{‰} < \text{DIC } \delta^{13}\text{C} < -4.4\text{‰}$), the study by Aucour et al. (1999) on the Rhône River ($-11.3\text{‰} < \text{DIC } \delta^{13}\text{C} < -4.1\text{‰}$), and the study by Amiotte-Suchet et al. (1999) on the Strengbach River ($-24.4\text{‰} < \text{DIC } \delta^{13}\text{C} < -9.3\text{‰}$). Our seasonal variation analyses of DIC $\delta^{13}\text{C}$ indicate an amplitude variation of about 5‰ with a trend toward lower values in late summer. This trend is consistent with a higher contribution in late summer from the decomposition of soil organic matter compared to a higher contribution of carbonate weathering during the spring. As the carbon isotopic composition of DIC in freshwater is controlled by different processes such as carbon exchanges with the atmosphere, CO_2 degassing in volcanic areas, dissolution of carbonate from the geological substrate, decay of organic matter in continental soils or in phytoplanktonic production, no direct relation could be established. Other proxies and parameters are needed to discriminate between these processes.

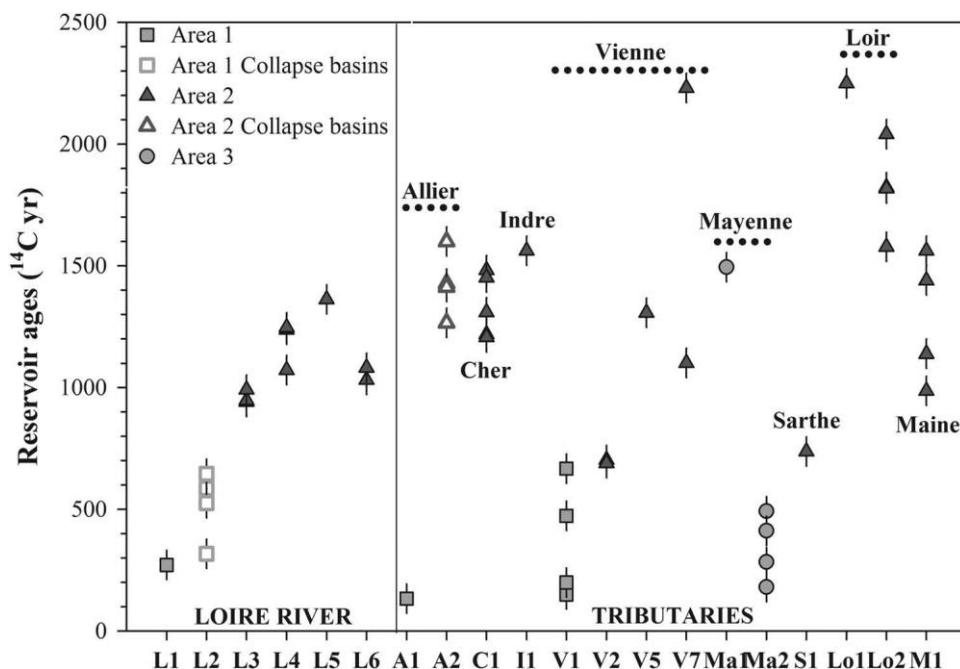


Figure 2 Reservoir ages evolution during the four campaigns from upstream to downstream for the Loire (L), Allier (A), Cher (C), Indre (I), Vienne (V), Mayenne (Ma), Sarthe (S), Loir (Lo) and Maine (M) Rivers. The orange markers correspond to sites in Areas 1 and 3, the blue markers to the sites in Area 2 (online color version). The error is expressed at 2σ .

Reservoir Ages

The reservoir age values were highly variable across the Loire Basin, ranging between 135 and 2251 ^{14}C yr. The FRE did not exceed 667 ^{14}C yr in Areas 1 and 3, except at Ma1 (1496 ^{14}C yr). In Area 2, higher FRE (>690 ^{14}C yr) was recorded (Figure 2), ranging from 690 and 2251 ^{14}C yr, except upstream of the Vienne (V1 and V2).

Spatial Variability

The DIC concentrations, alkalinity, and stable carbon isotope ratios combined with the geological substrate can be used to explain the difference in FRE values between the sedimentary Area 2, mainly composed of limestone containing old calcium carbonate, and the two different crystalline Areas 1 and 3 as well as the exceptional data.

Higher FRE offsets in Area 2 are consistent both with high alkalinity values (and DIC content) as indicated by the good correlation ($r = 0.61$; $n = 49$; $p < 0.05$) obtained between FRE and these parameters, shown in Figure 3.

Limestone dissolution seems to be the main process that controls DIC in the Area 2 rivers. The fact that the highest reservoir age was recorded in the Loire River corroborates the assertion that limestone dissolution is the main process controlling DIC in these waters. Indeed, the Loire River crosses the limestone area of the Beauce Plateau where agricultural practices promote extensive drainage as shown by the high values of chl-a concentrations observed related to the heavy runoff of fertilizers (Barnes and Raymond 2009). This drainage also results in high carbonate dissolution.

High FRE offsets, well correlated with alkalinity and DIC concentration, were also observed in crystalline areas, e.g. at L2, Ma1, S1, V1, and V2 (Figure 2). At these five sites, the results can be explained by more precise geological information. At L2, the Loire crosses the Forez and Roanne basins. The collapse basins are rich in carbonates even if the basement is plutonic (Derruau 1949; Boineau and Maisonneuve 1971; Cochet and Belkessa 1972; Landry 1988; Négrel et al. 2003; Rivé et al. 2013). The high FRE offsets observed (mean of 519 ^{14}C yr) could be the result of two processes: the percolation of groundwater through the marl faulted

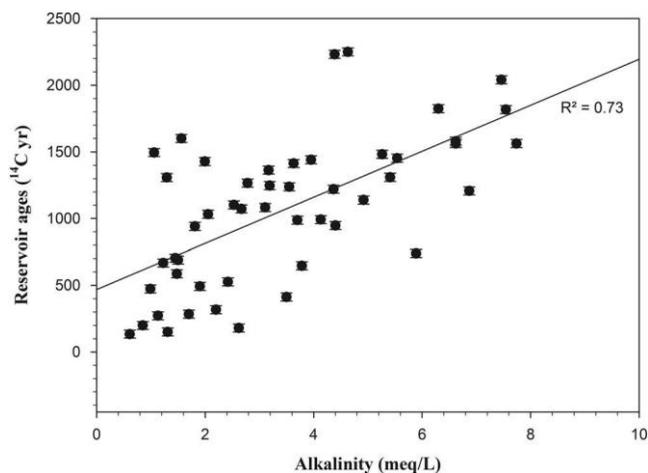


Figure 3 Reservoir ages and alkalinity correlation

substrate or volcanic CO₂ degassing well known in this region of the Massif Central (Anonymous 1997), or both. At Le Veudre (A2) on the Allier River located also in the collapse basins, the DIC $\delta^{13}\text{C}$ values, from -7.5 to -9.5‰ (Table 2), are the least depleted values recorded in the Loire Basin and its tributaries, suggesting a potentially higher contribution of volcanic CO₂ with DIC $\delta^{13}\text{C}$ values around -6‰ (Assayag 2006). At Changé (Ma1) in Area 3, a high FRE was observed due to the presence of carbonates that permeate the sedimentary matrix and are dissolved in the outcrop (Aertgeerts et al. 2011a). At S1, the FRE was lower (740 ¹⁴C yr) than at other sampling sites in Area 2 because the S1 station is situated at the exit of a schist area poor in carbonates (Aertgeerts et al. 2011b). Finally, upstream of the Vienne (V1 and V2), the Vienne River starts running through Area 2 at V1, explaining the still young reservoir age at V1 and the increase in age along the Vienne River. Spatial changes in FRE values depend mainly on the geological substrate and agricultural practices. Indeed, we observed a systematic increase in FRE values between upstream and downstream of the sedimentary area due to the increase in the dissolution of carbonate and silicate along the river. This increase can be very pronounced within a few kilometers, as on the Vienne River, where the FRE values increased from 200 yr at V1 to more than 1300 yr (V5) in only 20 km (SAGE 2006).

This rapid increase in FRE values may not be related to the dissolution of substrate alone and cannot also be attributed to organic inputs. Fast changes are often due to a mixing of different waters with different ¹⁴C signatures. Currently, the rapid changes in river characteristics are related to the arrival of new sources of water with different properties. These changes in the characteristics and ¹⁴C signature of water were observed on the Maine River, which is at the confluence of the Mayenne, Sarthe, and Loir rivers. The waters of these three tributaries have different signatures (FRE, DIC content, and alkalinity values), and the Maine River values vary between these three sources depending on their relative contributions. If we apply a simple mass balance equation of two source water masses for the Vienne River, it seems that between site V1 and V5, the arrival of ¹⁴C-depleted underground water can explain this rapid aging of FRE. Further investigations are necessary to validate this hypothesis, however.

Temporal Variability

Temporal variability over 1 yr and four campaigns was obtained at each sampling point, except in the middle course of the Loire River (L3 to L6). The observed variability is high, ranging from 257 yr at Savonnières upstream of the Cher River (C1) to 575 yr at Bouchemaine on the Maine River (M1), except on the middle Loire (L3, L4, L6). In this area, the temporal variation of the FRE ranges from 50 to 165 yr, but is not statistically significant, as indicated by the chi-squared test.

Contrary to expectations, the reservoir age and alkalinity data (Table 2) did not show any correlation with the flow of rivers expressed as a percentage of mean discharge. These data showed no evidence of a decrease in alkalinity or FRE resulting from dilution by meteoritic water during flood periods. This finding is valid for sites both in crystalline and in limestone sedimentary areas.

One explanation is the fact that the meteorological data in the days preceding the sampling are not known and we do not know in which phase of the flood the sampling was done. It is also possible that while runoff directly feeds the river during floods in the crystalline area, it is not the same for the rivers in a limestone substrate where rainwater can pass through the water table and be recharged in ¹⁴C-dead bicarbonate. Nevertheless, our data for the crystalline area tend to decrease with increasing percentage of the average flow.

CONCLUSION

The FRE in the Loire River Basin shows a wide range of variation between 135 to 2251 yr. The FRE is mainly influenced by the geological substrate and especially by the dissolution of old carbonate. Consequently, it is positively correlated with the alkalinity and mineral carbon contents of waters. Seasonal variations in reservoir ages were observed, but no direct link with river flows was noticed. This finding is valid for sites both in crystalline and in limestone sedimentary areas. Due to the large spatial and temporal variability of DIC reservoir ages in the Loire Basin, it appears difficult to use this parameter to establish a wide-ranging baseline of reservoir age. According to Keaveney and Reimer (2012) and Fernandes et al. (2014), biological or particulate organic carbon samples that integrate the DIC variations would be a better approach to propose ^{14}C FRE corrections for the establishment of reliable chronologies.

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