Isotopic characteristics of the Garonne River and its tributaries[†]

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The Garonne is the largest river in the south-west of France, and its drainage basin stretches between the Pyrénées and the Massif Central mountains. Until now, no water stable isotope study has been performed on the whole Garonne river basin which is composed of different geological substrata, and where the water resources are limited during the dry summer period. This study focuses on the Garonne river and its tributaries from the Pyrénées foothill upstream to its confluence with the Lot River downstream. The aim of the study is to determine the origins of the surface waters using their chemical and stable isotopic compositions (^{18}O, D and ^{13}C), to better understand their circulation within the drainage basin and to assess the anthropogenic influences. The Garonne displays a specific ^{18}O seasonal effect, and keeps its Pyrénean characteristics until its confluence with the Tarn River. The difference in the dissolved inorganic carbon (DIC) comes mainly from the change in lithology between the Pyrénées and the Massif Central mountains. Agriculture activity is only detected in the small tributaries.

With a mean annual discharge of $630\,m^3/s$, the Garonne is the third greatest French river by water volume after the Rhone and the Loire. Without the Dordogne tributary, the Garonne basin covers 10% of the territory of France, i.e. $55\,400\,km^2$. The source of the Garonne is in the central Pyrénées and it flows northwards before receiving tributaries from the Massif Central and then turning westwards in the direction of the Atlantic Ocean. Even if the Atlantic rainfalls are dominant, there is a Mediterranean influence in the eastern part of the basin as a result of the Autan wind blowing from the south-east through the Lauragais opening.

The 478 km long Garonne river rises on the Spanish side of the Pyrénées and flows through the limestone of the Tuca Blanco de Pomèro before re-emerging in the Val dera Artiga above the Aran Valley.[1] It follows the Aran Valley northwards into France, and then receives the Pique tributary (river length 33 km, basin area: $325\,km^2$). Near Mazères de Neste it receives its more westerly tributary, the Neste ($75\,km$, $906\,km^2$). Further downstream as it leaves the Pyrénées foothills, it is joined by the Salat ($70\,km$, $1570\,km^2$). Just before the city of Toulouse it is joined by

the last and most important Pyrénées tributary, the Ariège ($150\,km$, $3450\,km^2$). All these Pyrénean tributaries have their sources close to the Franco-Spanish border at elevations ranging between 2800 and $3200\,m$, where some high valleys receive as much as $1500–2000\,mm$ of rain per year. At Toulouse (Portet gauging station), the inter-annual mean (1910–2009) Garonne discharge is around $188\,m^3/s$.

After Toulouse, the main low-altitude tributaries with low discharges come from the Lannemezan plateau on the west. This is also the driest part of the whole Garonne basin with a mean annual rainfall of $600\,mm$ and, thus, the river depends completely on the upstream water. First the Save ($137\,km$, $1105\,km^2$) joins the Garonne at Grenade and then the Gimone ($136\,km$, $827\,km^2$). After the confluence with the Tarn (an easterly tributary) the third Lannemezan tributary is the Gers ($176\,km$, $1190\,km^2$) which joins the Garonne at Layrac and the last is the Baïse ($180\,km$, $2910\,km^2$). The total mean discharge of these four rivers does not exceed $30\,m^3/s$. The Massif Central tributaries then bring high discharge and a more constant water level to the Garonne network. The first Massif Central tributary is the Tarn ($375\,km$, $9100\,km^2$), which has its source near Mount Lozère ($1699\,m$) and a discharge of $210\,m^3/s$, including that from the Aveyron ($59\,m^3/s$). The Aveyron River itself ($292\,km$, $5170\,km^2$) joins the Tarn just less than $20\,km$ before the Garonne-Tarn junction. The last tributary, the Lot ($491\,km$), has a wide drainage basin ($9170\,km^2$), and also has its source in Mount Lozère quite close to that of the Tarn. The Truyère, one of the tributaries of the Lot, flows in a more northerly direction and it receives water from the old volcanic peak of the Plomb du

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Cantal. The Lot joins the Garonne at Aiguillon and brings a mean discharge of $144 \, \mathrm{m^3/s}$.

The water isotopes (^{18}O and D) are useful tools for the study of river basins.[2–5] Apart from our own work,[6–8] there have been very few studies of the Garonne Basin. Some studies on Pyrénean thermal springs were, however, published in the 1970s and 1990s.[9–11]

The δ^{13}C value of riverine dissolved inorganic carbon (DIC) is used as a tracer of carbon origins: biogenic CO_2 produced by soil organic matter decay and roots respiration, dissolution of carbonate rocks and atmospheric CO_2.[12–29] Contrary to what is found with ^{18}O and D, carbon isotopic signatures are not conserved from the soils to the river systems because different biogeochemical processes in the river itself, such as photosynthesis/respiration[30] and CO_2 evasion,[31,32] can affect the δ^{13}C.

In contrast to what is known for other large river basins of the world, no isotopic data on water and carbon exists for the whole Garonne river basin. The main objectives of this study are first to get some basic data on the DIC carbon isotopes and the ^{2}H, and ^{18}O isotopes of water for the Garonne River and its major tributaries from upstream to downstream, and second, to use these first isotopic data to determine the water and carbon origins, and to assess the different hydroclimatogical and biogeochemical processes controlling the isotopic signatures (^{2}H, ^{13}C and ^{18}O) and the influence of anthropogenic activities such as agriculture.

EXPERIMENTAL

Field sites

Seventeen sampling sites were selected over the whole basin (see Fig. 1): 7 along the Garonne River itself, 3 on tributaries from the Pyrénées, i.e. the Neste, Salat and Ariège Rivers, 4 on tributaries coming from the Lannemezan Plateau, i.e. the Save, Gimone, Gers and Baïse Rivers, and 3 on tributaries from the Massif Central mountains, i.e. the Tarn, the Aveyron and the Lot Rivers.

In order to assess the seasonal variations, and the influence of local rains, three sampling series were undertaken during February 2004, September 2004 and March 2007. The first of the series had an average monthly discharge ($179 \, \mathrm{m^3.s^{-1}}$ at the Portet gauging station on the Garonne River) slightly (14%) lower than the inter-annual February mean ($207 \, \mathrm{m^3.s^{-1}}$ during the period 1910–2009), whereas the other sampling periods were relatively dry ($50 \, \mathrm{m^3.s^{-1}}$ and $156 \, \mathrm{m^3.s^{-1}}$, respectively, for September 2004 and March 2007) compared with the inter-annual means ($85 \, \mathrm{m^3.s^{-1}}$ and $218 \, \mathrm{m^3.s^{-1}}$, respectively), i.e. 41% and 28% lower, respectively. In addition, all the Garonne ^{18}O data collected between 2000 and 2007 just after Toulouse were compiled with the view of obtaining precise information about any seasonal effects (see Fig. 4(a)).

Stable isotopes from water

The river waters were sampled in their middle stream during the low water period, i.e. in February–March for the winter period, and September for the summer period. Aliquots of

the water were put into capped 10-mL Exetainer vials (Labco Ltd., High Wycombe, UK).

To measure the ^{18}O values of the water samples, the samples and the internal standards were flushed off-line with a gas mixture of 2% CO_2 in helium. The Exetainer vials were then left to equilibrate at either 25.0°C or room temperature for a minimum of 18 h. The analytical precision of the measurements was ±0.15 per mil (‰).

To measure the ^{2}H values of the samples, Hokko beads were added to the Exetainer vials containing the water samples and the internal standards before the vials were flushed off-line with a gas mixture of 2% H_2 in helium. The Exetainer vials were left to equilibrate at either 25.0°C or room temperature for a minimum of 1.5 h. The analytical precision of the measurements was ±2.0‰.

Analysis of the samples was carried out using a Gasbench + Deltaplus XP isotope ratio mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) at the G.G. Hatch Isotope Laboratories, University of Ottawa, Ontario, Canada.

The equipment was calibrated by using two water standards that are traceable to the primary reference standards V-SMOW2 (Vienna-Standard Mean Ocean Water) and V-SLAP2 (Vienna-Standard Light Antarctic Precipitation) distributed by the IAEA, Vienna, Austria. A third traceable water standard was analysed alongside the samples to check the accuracy of the data.

The results are expressed in per mil on the V-SMOW/SLAP scale, for oxygen:

$$\delta^{18}O_{V-SMOW2}(‰) = ((^{18}O/^{16}O_{sample})/(^{18}O/^{16}O_{standard})-1)*1000;$$

and for deuterium:

$$\delta^2H_{V-SMOW2}(‰) = ((^2H/^1H_{sample})/(^2H/^1H_{standard})-1)*1000.$$

For the calculation of the deuterium excess, the equation for the Global Meteoric Water Line defined by Craig was used.[33]

Carbon stable isotopes

Water samples were filtered in the field through a 0.45 μm Millipore filter (Millipore, Billerica, MA, USA). The samples were collected in 125 mL polyethylene bottles, carefully sealed taking care that no trapped air remained in contact with the sample, and stored at a temperature between 0 and 5°C prior to the extraction. To extract the DIC,[34] an aliquot of the sample (10–15 mL, depending of the alkalinity) was acidified inside a vacuum line with concentrated phosphoric acid. The evolved CO_2 was purified and trapped with liquid nitrogen in a glass tube. The analyses were run on a 602 VG Optima Mass spectrometer (Isoprime Ltd., Cheadle Hulme, UK) at the Centre de Geochimie de Surface (CGS), Strasbourg, France. The resulting analytical precision of the measurements was ±0.2‰.

The results are reported as δ values with reference to Vienna Pee Dee Belemnite (VPDB):[35]

$$\delta^{13}C_{VPDB}(‰) = ((^{13}C/^{12}C_{sample})/(^{13}C/^{12}C_{standard})-1)*1000.$$
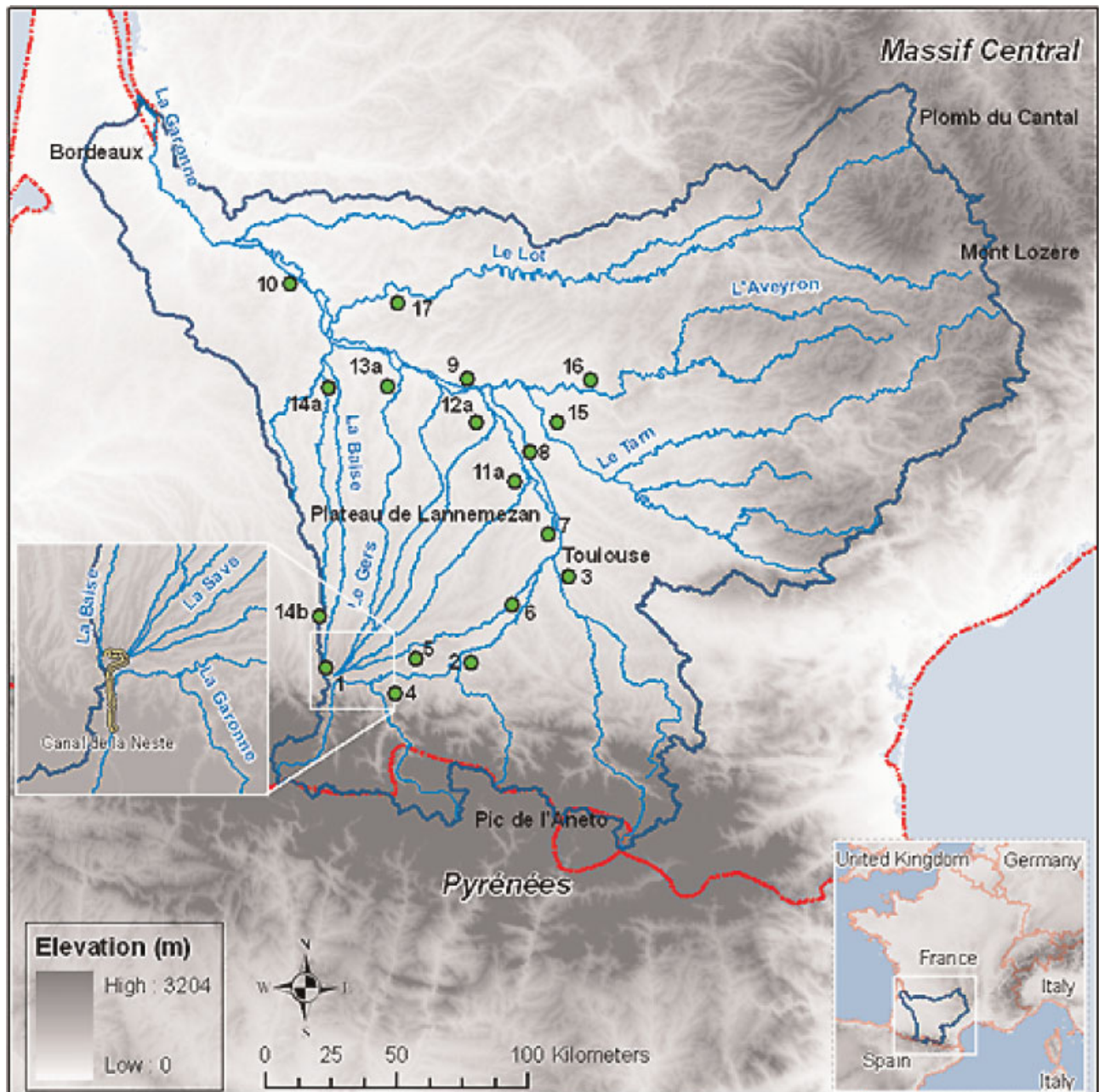
Figure 1. Location of the 17 sampling sites over the Garonne Basin. The Pyrénées Garonne tributaries 1: Neste River at Mazère, 2: Salat River at Roquefort, 3: Ariège River at Lacroix-F. The Garonne river itself 3: Valcabrère, 4: Valentine, 5: Carbone, 6: Carbonne, 7: Pinsaguel, 8: Verdun, 9: Lamagistère, 10: Mas d'Agennais (a for uphill, b for downstream station). The Lannemezan Plateau rivers 11: Save River, 12: Gimone River, 13: Gers River, and 14: Baïse River; (a) is for downstream and (b) for upstream. The Massif Central tributaries 15: Tarn River at Villemur, 16: Aveyron River at Loubejac, and 17: Lot River at Aiguillon.

RESULTS AND DISCUSSION

The different water pools

Three different water pools can be seen from the δ^{18}O isotopic characteristics reported in Table 1 and shown in Fig. 2. The first pool corresponds to the higher Pyrénées water. The only glacier area melting in the Garonne Basin can be found for the Neste River, Pic Long (3192 m) and Munia (3133 m), and for the upper Garonne River itself, Perdiguère (3222 m) and Aneto (3404 m). Effectively, the most negative values of

δ^{18}O are found for these two rivers, respectively −10.0‰ and −10.25‰. The other Pyrénean rivers such as the Salat and Ariege are only fed by neve and snow, and display slightly less negative values (−9.23 to −8.75‰). This area provides the main inflow of water to the mid-Garonne Valley before the inflow of the second important pool from the Massif Central river group.

The Tarn and Aveyron Rivers nearly double the discharge of the Garonne with an mean input of 207 m³/s. Together with the Lot River, these rivers, which come from moderate

Table 1. $\delta^{18}O$ values for the 17 sampling points over the 3 dates

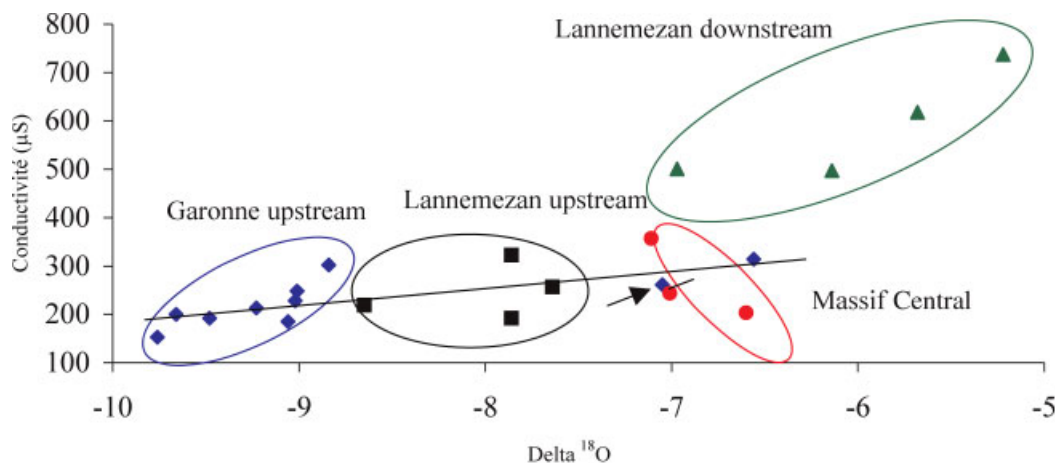|		2004	2004	2007
		Feb	Sep	March
		$\delta^{18}O_{\text{V-SMOW}}$ (‰)	$\delta^{18}O_{\text{V-SMOW}}$ (‰)	$\delta^{18}O_{\text{V-SMOW}}$ (‰)
	Pyrenees			
1	Neste (Mazere)	−10.00	−9.86	−9.48
2	Salat (Roquefort)	−8.98	−8.79	−9.06
3	Ariège (Lavroix F)	−8.75	−9.36	−9.23
	mean	**−9.25**	**−9.34**	**−9.26**
	±sd	*0.67*	*0.53*	*0.21*
4	Garonne (Valcabrere)	−10.25	−10.23	−9.76
5	Garonne (Valentine)	−9.59	−9.92	−9.66
6	Garonne (Carbonne)	−9.36	−9.42	−9.02
7	Garonne (Pinsaguel)	−8.64	−9.20	−9.01
8	Garonne (Verdun)	−8.62	−8.94	−8.84
9	Garonne (Lamagistere)	−7.91	−7.20	−6.56
10	Garonne (Mas d'Agennais)	−8.10	−7.38	−7.05
	mean	**−8.92**	**−8.90**	**−8.56**
	±sd	*0.84*	*1.18*	*1.25*
	Lannemezan downstream			
11a	Save (Grenade)	−5.79	−6.74	−6.97
12a	Gimone (Castelferrus)	−6.20	−6.37	−5.22
13a	Gers (Layrac)	−6.40	−9.64	−5.68
14a	Baise (Nerac)	−7.03	−7.67	−6.14
	mean	**−6.35**	**−7.61**	**−6.00**
	±sd	*0.52*	*1.46*	*0.75*
	Lannemezan upstream			
11b	Save (Grenade)			−7.64
12b	Gimone (Castelferrus)			−8.65
13b	Gers (Layrac)			−7.86
14b	Baise (Nerac)			−7.86
	mean			**−8.00**
	±sd			*0.44*
	Massif Central			
15	Tarn (Villemur)	−6.80	−6.59	−7.11
16	Aveyron (Loubejac)	−6.74	−5.75	−6.60
17	Lot (Aiguillon)	−8.29	−7.47	−7.01
	mean	−7.28	−6.60	−6.91
	±sd	*0.88*	*0.86*	*0.27*

Figure 2. $\delta^{18}O$ values versus conductivity for the 2007 data. The ellipses represent the different water pools: the upper Garonne River and tributaries with more negative isotope values and the smaller conductivity, the Massif Central tributaries (Tarn, Aveyron and Lot) with higher isotopes values and moderate conductivity, and the Lannemezan Plateau tributaries (downstream) with the higher isotopes values and conductivity. The upper stream of these four rivers is on the Garonne line, certainly due by the income of the Neste Canal. The downstream Garonne sites are located at the right end of the line and correspond to the mixing of these different water pools.

altitudes (775 to 1815 m), display lower $\delta^{18}O$ values: -8.29 to -6.6‰, with an even less negative value for the Aveyron in September: -5.75‰.

The third water pool is formed by the four rivers coming from the Lannemezan Plateau with a mean altitude of around 600 m. For these rivers the $\delta^{18}O$ values would expected to be in the range of -7.5 to -6.5‰ due to the lower altitude origin of the water as measured in the local wells. However, for irrigation purpose, these rivers can be fed by the Neste Canal, bringing Pyrénées water, which displays high altitude heavy isotope depletion with values as low as -10.3‰. Thus, for the upper part of these rivers, the water isotopic signature involves a mixing of these water sources with value ranging between -8.65 and -7.64‰. Downstream, the evaporation process and the inflow of local rainfall and groundwater discharge give rise, in general, to less negative ^{18}O values: from -6.97 to -5.22‰. Even in September 2004, the Neste water contribution could be detected at the end of the Gers River with a value of -9.64‰.

Other than these surface river waters, some karstic buffer systems also exist, mainly in the Ariège, Arize and Salat Valleys for the Pyrénées side, and around the Tarn River (Causses) for the Massif Central side. For instance, at the end of the Arize River in 2006 and 2002, the groundwater values ($\delta^{18}O = -6.7$ to -5.4‰) measured in the stream during the dry period suggest that the water came from the karstic buffer, as the normal value is around -7.4‰.

Origin of the rainfall and evaporation process

Table 2 gives the deuterium amount and the calculated D excess for all the sampling undertaken, while Fig. 3 reports $\delta^{18}O$ versus $\delta^{2}H$ only for the March 2007 period. In this figure, the dotted line represents the GWML with a slope of 8; a proportion of the sampling points from 2007 are above this line, and this is also the case for 2004 (data not shown). It can also be seen in Table 2 that many rivers display a D excess above 10‰ and this could suggest an influence of Mediterranean rainfall inputs characterised by a higher D excess of 14‰, although none of the eastern rivers such as the Tarn are implicated in this shift. According the IAEA rainfall data over Toulouse, the local water meteoric line (LWML) presents an equation of $y = 7.2x + 5.7$, and with these values all the experimental points are located beneath this line. It thus seems certain that all the rainfall originates from the

Table 2. δD and calculated D excess for the 17 sampling points over the 3 dates

| | | 2004 | | 2004 | | 2007 | |
| | | Feb | | Sep | | March | |
		$\delta^{2}H_{V\text{-}SMOW}$ (‰)	D excess	$\delta^{2}H_{V\text{-}SMOW}$ (‰)	D excess	$\delta^{2}H_{V\text{-}SMOW}$ (‰)	D excess
	Pyrenees						
1	Neste (Mazere)	-64.59	15.44	-66.37	12.49	-64.70	11.14
2	Salat (Roquefort)	-62.06	9.77	-57.15	13.21	-63.60	8.88
3	Ariège (Lavroix F)	-62.15	7.89	-63.20	11.67	-65.80	8.04
	mean	**-62.93**	**11.03**	**-62.24**	**12.46**	**-64.70**	**9.35**
	±sd	1.44	3.93	4.69	0.77	1.10	1.60
4	Garonne (Valcabrere)	-68.73	13.26	-69.45	12.36	-67.30	10.78
5	Garonne (Valentine)	-65.64	11.04	-67.68	11.66	-67.80	9.48
6	Garonne (Carbonne)	-62.73	12.14	-62.85	12.51	-63.40	8.76
7	Garonne (Pinsaguel)	-63.68	5.43	-60.82	12.80	-65.70	6.38
8	Garonne (Verdun)	-59.16	9.80	-59.19	12.30	-64.20	6.52
9	Garonne (Lamagistere)	-48.87	14.38	-49.79	7.83	-50.70	1.78
10	Garonne (Mas d'Agennais)	-51.02	13.78	-49.53	9.51	-49.20	7.20
	mean	**-59.97**	**11.40**	**-59.90**	**11.28**	**-61.19**	**7.27**
	±sd	7.46	3.08	7.87	1.88	7.84	2.91
	Lannemezan downstream						
11a	Save (Grenade)	-46.04	0.26	-47.13	6.80	-50.20	10.92
12a	Gimone (Castelferrus)	-41.00	8.57	-47.18	3.77	-59.30	9.90
13a	Gers (Layrac)	-42.08	9.13	-66.37	10.77	-53.70	9.18
14a	Baise (Nerac)	-40.97	15.27	-55.10	6.25	-52.70	10.18
	mean	**-42.52**	**8.31**	**-53.94**	**6.90**	**-53.98**	**10.05**
	±sd	2.40	6.16	9.09	2.90	3.84	0.72
	Lannemezan upstream						
11b	Save (Grenade)					-47.80	7.96
12b	Gimone (Castelferrus)					-39.60	2.16
13b	Gers (Layrac)					-41.50	3.94
14b	Baise (Nerac)					-41.10	8.02
	mean					**-42.50**	5.52
	±sd					3.63	2.94
	Massif Central						
15	Tarn (Villemur)	-49.25	5.15	-43.26	9.45	-48.00	8.88
16	Aveyron (Loubejac)	-51.43	2.46	-38.64	7.33	-47.70	5.10
17	Lot (Aiguillon)	-54.78	11.54	-50.77	9.00	-51.20	4.88
	mean	**-51.82**	**6.38**	**-44.22**	**8.59**	**-48.97**	**6.29**
	±sd	2.79	4.67	6.12	1.12	1.94	2.25
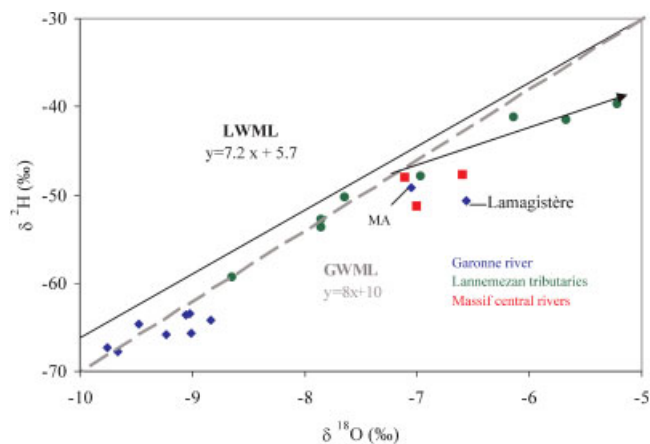
Figure 3. $\delta^{18}O$ values versus δ^2H values for the 2007 data. The straight line represents the Local Water Meteoric Line (LWML) as obtained from the IAEA network for the city of Toulouse. Diamonds: Garonne River; circles: Lannemezan Plateau tributaries; squares: Massif Central rivers.

Atlantic Ocean, and that the Mediterranean inputs are quantitatively negligible.

Krimissa et al.[11] found a LWML relation of $y = 7.7x + 9.9$ for the East-Pyrénées spring, and only the more eastern samples exhibit a high deuterium excess (14.2‰), thus showing Mediterranean rainfall input.

Most of the samples from the upstream Garonne and the upper Lannemezan rivers are close to the GWML, and this is also the case for the Garonne samples for September 2004, showing that there is no important evaporation process. On the contrary, for the downstream Lannemezan rivers, a shift is clearly seen in Fig. 3, and there are many low D excess values shown in Table 2, suggesting that evaporation has taken place. The calculation of the slopes between upstream and downstream for these four rivers gives effectively lower values with values ranging from 6.7 for the Baise River, to 5.7 for the Gimone River, 5.6 for the Gers River and 3.6 for the Save River. The arrow in Fig. 3 shows this mean lower slope. The evaporation is also confirmed by the water concentration as seen by the high conductivity, and the anthropogenic influence by the high nitrate (28–49 mg/L) and chlorine (30–50 mg/L) levels. The Tarn River is quite close to the GWML line, whereas the Aveyron and Lot Rivers are shifted slightly downwards, also suggesting evaporation. In February 2004, the Aveyron and the Tarn also displayed low D excess values. The consequence is that after the arrival of these Lannemezan and Massif Central rivers, the Garonne loses its altitude characteristics with strong negative ^{18}O values, and begins to incorporate evaporated water. The specific value found in Lamagistère with a D excess value of 1.78 can be generated by the evaporation and heating of the Nuclear power station at Golfech, working at full capacity during this cold March month.

Seasonal variations

In Fig. 4(a) for the Garonne River sampled a little downstream of Toulouse, a slight seasonal effect (around 0.5 units for the mean value) is seen, with the more depleted ^{18}O values being observed in April–June with the snow
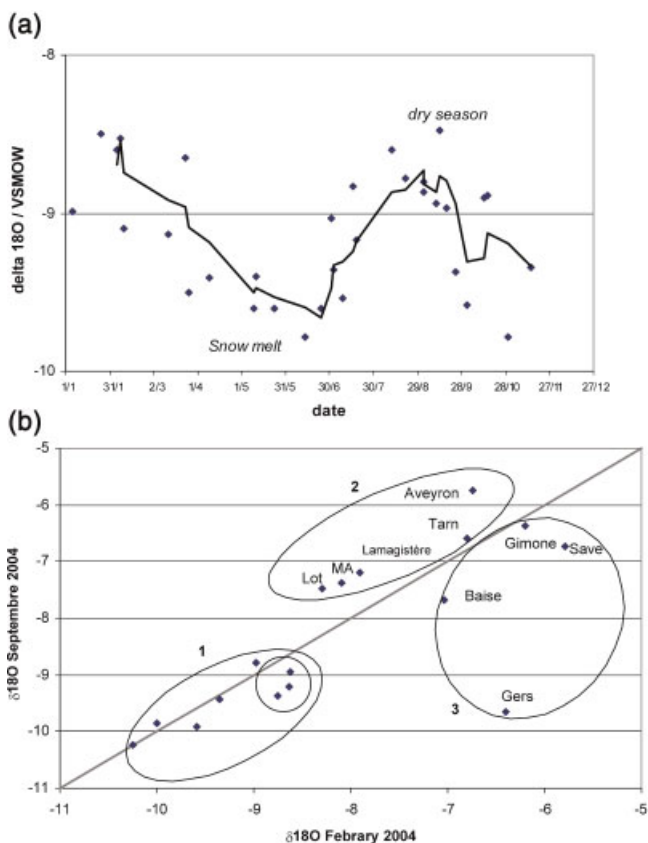

Figure 4. (a) Compilation of the 29 Garonne River $\delta^{18}O$ values taken downstream of Toulouse during the 2000–2007 period. The solid line represents the mobile mean value, to detect a seasonal effect. (b) Comparison of $\delta^{18}O$ values obtained in February 2004 and September 2004 sampling periods. The solid line correspond to equal values ($y = x$). Ellipse 1 corresponds to the upper Garonne Basin, ellipse 2 to the Massif Central rivers plus the two Garonne downstream sites: Mas d'Agenais (MA) and Lamagistère, and ellipse 3 to the Lannemezan Plateau rivers.

melt, and the more enriched values at the end of summer with the local rainfall inputs during the river low water period. In the Pyrénées, the glacier system is too small (5 km^2) to present a typical glacial profile such as that for the Rhine River, which displays more negative $\delta^{18}O$ values in August. The Pyrénées profile could then be more properly called a snow-firn profile.

Figure 4(b) reports the $\delta^{18}O$ variations between the winter low water (February 2004) and the summer low water (September 2004). The solid line represents no variation ($y = x$). The three ellipses correspond to three water pools: 1 – the upper Garonne River; 2 – the Massif Central rivers plus the downstream Garonne River; and 3 – the Lannemezan Plateau rivers. The upstream part of the Garonne River shows no wide seasonal variation with a shift lower than 0.2 units. In fact the high altitude snow and glacier melt during May and June is not seen here, and more negative ^{18}O values are found. The next pool of this upper Garonne (Garonne at Pinsaguel, Ariège and Garonne at Verdun, in the small circle in Fig. 4(b)) is located further beneath the $y = x$ line and this could be due to low altitude rainfall which increases the February values (less depleted in ^{18}O isotopes). At the level of

Toulouse the rainfall, according to the IAEA database, varies from $-7.1‰$ in February to $-5.2‰$ in September, with a maximum of $-8.2‰$ in December and a minimum of $-4.3‰$ in July. The second group with the Massif Central rivers and the downstream rivers is located above the 1:1 line. This means that here the February values are more depleted in heavy isotopes than the September values, and in consequence so too are the downstream Garonne values. Except for the more stable Tarn River, this shift is between 0.7 and $1‰$. The third group presents the wider isotopic difference, with more negative values in September, which can be only explained by the remaining Pyrénées water being brought by the Neste Canal to sustain the summer low water level.

Dissolved inorganic carbon

The isotopic composition of the DIC was only investigated over two sampling missions: September 2004 and March 2007, and the results of the second campaign have not been completed. All the available data are given in Table 3.

The $\delta^{13}C_{DIC}$ values show a small range from $-7.4‰$ to $-11.6‰$, with the majority falling between $-9‰$ and $-10‰$. The samples with the lightest $\delta^{13}C_{DIC}$ are those from the

Table 3. $\delta13C$ (‰) of DIC over the two missions (September 2004 and March 2007)

	2004	2007
	Sep	March
	$\delta^{13}C$ DIC (‰)	$\delta^{13}C$ DIC (‰)
Pyrenees		
1 Neste (Mazere)	−8.5	−8.9
2 Salat (Roquefort)	−9.1	−9.5
3 Ariège (Lavroix F)	−9.6	−9.6
mean	**−9.1**	**−9.3**
±sd	0.56	0.38
4 Garonne (Valcabrere)	−8.9	−7.4
5 Garonne (Valentine)	−8.8	−10.0
6 Garonne (Carbonne)	−9.5	−9.8
7 Garonne (Pinsaguel)	−9.4	
8 Garonne (Verdun)	−9.6	
9 Garonne (Lamagistere)	−9.5	
10 Garonne (Mas d'Agennais)	−9.8	
mean	**−9.4**	**−9.1**
±sd	0.37	1.45
Lannemezan downstream		
11a Save (Grenade)	−11.2	
12a Gimone (Castelferrus)	−11.2	
13a Gers (Layrac)	−10.4	
14a Baise (Nerac)	−10.7	
mean	**−10.9**	
±sd	0.39	
Lannemezan upstream		
11b Save		−11.8
12b Gimone		−10.7
13b Gers		−10.7
14b Baise		−10.6
mean		**−11.0**
±sd		0.57
Massif Central		
15 Tarn (Villemur)	−9.5	−11.6
16 Aveyron (Loubejac)	−8.8	
17 Lot (Aiguillon)	−10.9	
mean	**−9.7**	**−11.6**
±sd	1.09	

Lannemezan Plateau rivers and the Tarn and Lot Rivers. Along the Garonne fluvial continuum (from Valcabrere to Mas d'Agenais), a small decrease in $\delta^{13}C_{DIC}$ is observed from $-8.9‰$ to $-9.8‰$ in March 2004. This trend is the inverse of that observed for other large river basins, like the Saint Lawrence,[29] the Danube (Pawellek and Veizer),[22] the Patagonian rivers,[14] or the Nyong River (Brunet et al., in press). In these large river basins, a progressive enrichment in ^{13}C is generally observed, caused by degassing of CO_2 to the atmosphere. In the case of the Garonne River, this process is not highlighted by the $\delta^{13}C_{DIC}$ values, probably due to the contribution of the tributaries which supply DIC with more negative $\delta^{13}C$ values.

The differences in the DIC isotopic composition in the different tributaries can be attributed to the regional lithology. In the upper basin, limestones and dolomites are dominant, whereas the lithology of the Lamnemezan Plateau rivers is dominated by molasses, consisting of conglomerate, marl and shale, detrital sediments supplied by the erosion of the Pyrénées mountains. For the tributaries draining from the Massif Central Mountains, the lithology is a mixture of carbonate rocks, granites and volcanic rocks. The DIC resulting from carbonate dissolution has a $\delta^{13}C$ on average of about $0‰$,[37] Dandurand et al.[38] report carbonate rocks with a $\delta^{13}C$ between $+2.9‰$ and $+3.9‰$ in the Ariege Basin, near the village Roquefort les Cascades. In the Gascogne region (central part of the Garonne Basin), at Aurade, an average $\delta^{13}C$ value of $-7.9 \pm 0.6‰$ ($n = 11$) has been measured in this study (unpublished data) in the small Montoussé (sub-tributary of the Save River) experimental catchment, which drains Miocene calcareous molassic deposits. The variability of the isotopic composition of the principal DIC sources is recorded by riverine $\delta^{13}C_{DIC}$.

Even if some data are lacking, it is interesting, like Kendall et al.,[36] to examine separately the two sampling periods to determine if they exhibit possible seasonal variations. This regional variation in $\delta^{13}C_{DIC}$ can be coupled with the distribution of water pools, observed with oxygen isotopes, illustrated in Figs. 5(a) and 5(b). For the Garonne River from upstream to downstream, for the Pyrénean tributaries and the Lannemezan Plateau rivers, there is a general decreasing trend between $\delta^{13}C_{DIC}$ and $\delta^{18}O_{H2O}$ showing a progressive mixing of waters from the Pyrénées with a high $\delta^{13}C_{DIC}$ due to carbonate rock and a low $\delta^{18}O_{H2O}$ due to snow melting, and from the Massif Central and the Lannemezan Plateau with lower $\delta^{13}C_{DIC}$ (particularly for the Lannemezan Plateau rivers) due to Miocene sedimentary deposits and higher $\delta^{18}O_{H2O}$ due to evaporation processes and low altitude rainfall inputs. It can be clearly seen in Fig. 5(a) that the Garonne River at lower stations (Lamagistère and Mas d'Agenais) is a mixing of three main sources: the upper Garonne River and the Pyrenean tributaries, the Lanneme-zan Plateau tributaries, and the Lot, the Tarn and its main tributary, the Aveyron, which have higher $\delta^{13}C_{DIC}$ values during September 2004 (very dry month: -41% compared with the inter-annual monthly mean) than during March 2007. This can be explained by a very important contribution from the ground waters draining important carbonate reservoirs in the upper Tarn and Aveyron drainage basins during the driest period.
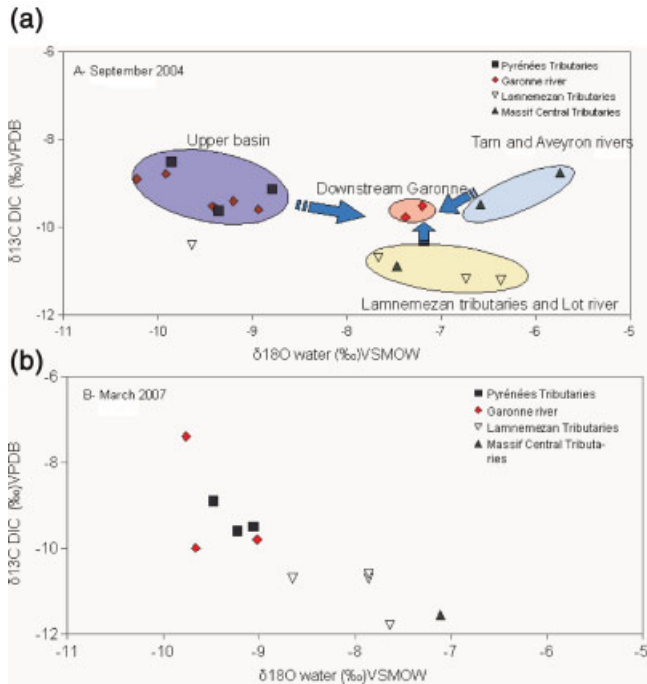
(a)

(b)

Figure 5. $\delta^{13}C_{DIC}$ versus $\delta^{18}O_{H2O}$ for the September 2004 (a) and March 2007 (b) periods.

CONCLUSIONS

This study should contribute to a better understanding of the carbon and water origins, but also of the carbon and water balance over the whole Garonne Basin. Such a study has also shown the necessity of coupling water and carbon cycles at the scale of a large river basin such as the Garonne.

The main results obtained in this study are:

– The Garonne River keeps its upstream water isotopic characteristic far beyond the city of Toulouse, until its junction with the first Massif Central tributaries, the Tarn and Aveyron Rivers.

– A seasonal effect is found with the most depleted values obtained in March–April due to the snow melting, and lesser ones in August corresponding to the warmer low altitude rainfall.

– Agriculture activity is mainly detected in the small tributaries on the left side (Gascogne region), from the Save to the Baïse Rivers, with higher conductivity and nitrate concentrations, and lower D excess. The refilling of these rivers in the upper basin by the Neste Chenal is also indicated by the most negative $\delta^{18}O$ values.

– Along its fluvial continuum, the Garonne River displays a small decrease in $\delta^{13}C_{DIC}$, contrary to what is found for other large rivers.

– The $\delta^{13}C_{DIC}$ values in the Garonne Basin reflect mainly the DIC contribution resulting from dissolution of carbonate rocks, with some regional variations.

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