

Export and degassing of terrestrial carbon through watercourses draining a temperate podzolized catchment

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Abstract We measured spatial and temporal variations in carbon concentrations, isotopic compositions and exports during a complete hydrological cycle in nine watercourses draining a lowland forested podzolized catchment, flowing into the Arcachon lagoon (France). In addition, integrated fluxes of CO₂ across the water-atmosphere interface were estimated to assess the relative importance of CO₂ evasion versus lateral carbon transport at the catchment scale. Watercourse similarities and specificities linked to the local catchment characteristics are discussed and compared with other riverine systems. Low concentrations of suspended particulate matter and particulate organic carbon (POC) were generally measured in all the watercourses (8.4 ± 3.4 and 1.6 ± 0.6 mg L⁻¹, respectively), reflecting limited mechanical soil erosion. The generally high POC content in the suspended matter (20 %), low Chl *a* concentrations (1.3 ± 1.4 µg L⁻¹) and the relatively constant δ¹³C-POC value (near -28 ‰) throughout the year reveal this POC originates from terrestrial C₃ plant and soil detritus. The presence of podzols leads to high levels of dissolved organic

carbon (DOC; 6.6 ± 2.2 mg L⁻¹). Similarly, high dissolved inorganic carbon (DIC) concentrations were measured in the Arcachon lagoon catchment (5.9 ± 2.2 mg L⁻¹). The δ¹³C-DIC value around -20 ‰ throughout the year in many small watercourses reveals the predominance of terrestrial carbon mineralisation and silicate rock weathering in soils as the major DIC source. With pCO₂ between 1,000 and 10,000 ppmv, all watercourses were a source of CO₂ to the atmosphere, particularly during the low river stage. Organic carbon parameters remained relatively stable throughout the year, whereas DIC parameters showed strong seasonal contrasts closely linked to the hydrological regime and hyporheic flows. In total, the carbon export from the Arcachon watershed was estimated at 15,870 t C year⁻¹ or 6 t C km⁻² year⁻¹, mostly exported to the lagoon as DOC (35 %), DIC (24 %) and lost as CO₂ degassing to the atmosphere (34 %).

Keywords Podzolized catchment · Coastal lagoon · Carbon dynamics · Carbon export · CO₂ degassing

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Introduction

Rivers deliver significant amounts of terrestrially-derived carbon from the land to the sea, representing the main linkage between these two reservoirs. Approximately 0.9 Gt C year⁻¹ is discharged by rivers to oceans (Meybeck 1982). Of this total carbon flux value, about 40 % is organic and 60 % is inorganic. Meybeck (1993) computed a carbon flow carried to the ocean by temperate rivers of 19.4, 20.3 and 60.3 % for DOC, POC and DIC, respectively, and proportions of 37:18:45 for DOC:POC:DIC in global rivers. However, the role of rivers in the global carbon cycle is not limited to passive transport. In fact, a

large part of the carbon that is lost from terrestrial systems degasses as CO₂ to the atmosphere from the surfaces of inland waters and does not reach the ocean (Cole et al. 2007; Tranvik et al. 2009). Recent data compilations suggest that, globally, the degassing of CO₂ from inland waters could be occurring at levels that are similar to or larger than the carbon export to the ocean. Cole et al. (2007) suggest that, of the at least 1.9 Pg C year⁻¹ that is received by inland waters from land, 40 % is returned as CO₂ to the atmosphere, 12 % is sequestered in sediments and the remaining 48 % is transported to the ocean. The revision of this “active pipe” hypothesis, advanced by Cole et al. (2007) by Tranvik et al. (2009), increased the total amount of organic carbon that was imported to inland waters from the terrestrial environment to 2.9 Pg C year⁻¹, of which 48 % is the degassing of CO₂ (from instream, soil and groundwater respiration), 21 % is buried in sediments and 31 % reaches the ocean.

The concentration and composition of carbon in river waters is partly a product of instream processes, but is in its majority regulated by upland, riparian and hyporheic/groundwater processes that determine solute and gaseous inputs into aquatic systems (Jones and Mulholland 1998). In most rivers, the particulate organic carbon (POC) is mainly allochthonous and originates from soil erosion. Under particular conditions, significant changes in POC sources can occur (i.e. during storms). Additionally, in eutrophic rivers, phytoplankton developments can highly contribute to autochthonous POC (Abril et al. 2002; Neal et al. 2006). Dissolved organic carbon (DOC) in unpolluted rivers mostly originates from leachable organic carbon in soils and from terrestrial vegetation (Meybeck 1993; Sobek et al. 2007). This DOC is often considered to be mainly recalcitrant to microbial degradation and is almost entirely transported to the ocean (Mantoura and Woodward 1983). However, part of this DOC serves as a substrate for heterotrophic bacteria and fuels the aquatic trophic chain through the microbial loop in freshwaters (Pace et al. 2004). Additionally, autochthonous labile DOC can be produced within rivers by phytoplankton (Bianchi et al. 2004). The DIC in river waters has three main sources: soil CO₂, bedrock and soil minerals through carbonate and silicate dissolution and atmospheric CO₂ exchange at the air/water interface (Yang et al. 1996). Most rivers and lakes are net heterotrophic and emit carbon dioxide (CO₂) to the atmosphere (Jones et al. 2003; Sobek et al. 2005; Billett and Moore 2008). CO₂ is typically supersaturated in streams or rivers that are connected to CO₂-rich groundwater and soils. It can also be due to instream respiration and organic matter decomposition which exceeds primary production in the river itself (Jones and Mulholland 1998; Cole and Caraco 2001). Thus, inland aquatic systems are almost net annual sources of CO₂ to the atmosphere (Cole

et al. 1994; Hope et al. 1994; Jones et al. 2003). The CO₂ that is found in freshwater is also influenced by silicate and carbonate rock weathering, producing carbonate alkalinity rather than dissolved CO₂ (Yang et al. 1996; Amiotte-Suchet et al. 1999). In the presence of carbonate rocks on the watershed, one half of the total alkalinity (TA) originates from the rock, with the rest being atmospheric carbon that has been fixed on land and recycled in the soils; these rivers generally have a high pH, high dissolved inorganic carbon (DIC) and TA, and a relatively ¹³C-enriched stable isotopic composition of DIC (Barth et al. 2003). When, in contrast, silicate rock weathering is dominant, a major part of the DIC originates from soil organic matter mineralisation and soil CO₂ from root respiration; these rivers are acidic, have low TA and a large fraction of the DIC is present as excess CO₂ with respect to the atmospheric equilibrium (Amiotte-Suchet et al. 1999).

Thus far, several studies on inland water carbon dynamic and export to oceans have been carried out; for instance, in estuaries (Frankignoulle et al. 1998; Abril et al. 2002), lakes (Kling et al. 1992; Cole et al. 1994), large rivers (Meybeck 1993; Hope et al. 1994; Gaillardet et al. 1999) and stream waters (Hynes 1983; Neal and Hill 1994; Jones and Mulholland 1998). A few studies have dealt with watercourses in lowland catchment, with acidic organic matter-enriched soils and attempted to estimate not only carbon lateral export as particles and solutes but also CO₂ degassing to the atmosphere along the entire watercourse (Hope et al. 2001; Billett et al. 2004). Here, we present a 1-year survey of carbon dynamics in acidic watercourses that drain a temperate, lowland, sandy, podzolized catchment and flow into the Arcachon lagoon (southwest of France). In this paper, we describe and explain the dynamics of all the carbon forms (except methane) i.e. particulate, dissolved, organic, inorganic and gaseous in these watercourses, and we quantify the carbon export to the lagoon taking into account the CO₂ degassing to the atmosphere. Finally, we establish a regional carbon budget that can be compared to other studies and to the net ecosystem production upstream inland and downstream in the lagoon.

Materials and methods

Study site

The study area is located in the Arcachon lagoon catchment in south-western France (44°78'N, 01°16'W northerly and 44°64'N 01°12'W southerly). The lagoon receives freshwater from several watercourses (Fig. 1a; Table 1); the largest, in terms of watershed and discharge, is the Leyre River located at the south-eastern corner. In addition, 17

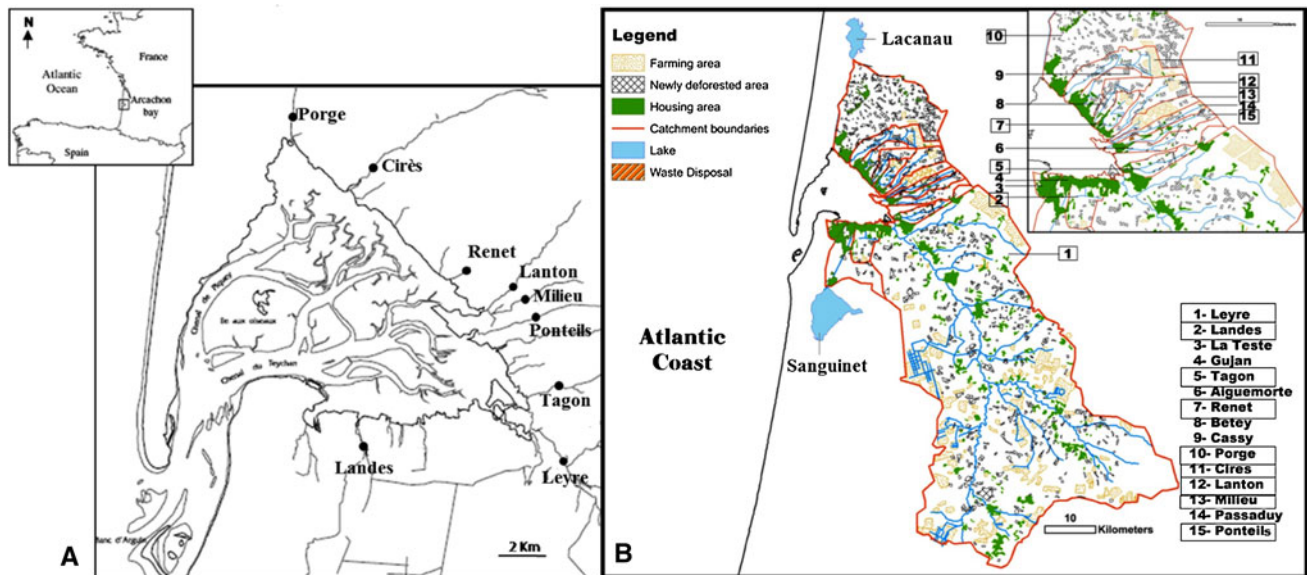


Fig. 1 Map of the Arcachon lagoon and its direct catchment basin, showing **a** the sampling stations for the nine watercourses, i.e., Porge, Cirès, Renet, Lanton, Milieu, Ponteils, Tagon, Leyre and Landes, and **b** the watercourse catchment boundaries with the soil occupation (modified from Canton et al. 2010)

Table 1 General characteristics of the nine study watercourses in the Arcachon lagoon catchment

	Surface (km ²)	Runoff (m ³ s ⁻¹)	Drainage (L s ⁻¹ km ⁻²)	Population density (inhab km ⁻²)	Inhabitants/runoff (inhab m ⁻³ s)
Porge (Arès)	221.6	3.63	18	310	17,263
Cirès (Andernos)	48.7	0.63	13	445	34,402
Renet (Lanton)	17.9	0.61	34	43	1,283
Lanton (Lanton)	36.1	0.28	8	43	5,562
Milieu (Audenge)	21.3	0.63	19	63	3,313
Ponteils (Audenge)	23.3	0.23	10	63	6,414
Tagon (Biganos)	29.6	0.67	23	113	4,939
Leyre (Biganos)	2141.4	18.16	8	113	13,360
Landes (Gujan-Mestras)	116.6	0.52	4	315	70,703
Total	2656.5	25.34	137	1,510	157,239

The Leyre average runoff was calculated from daily runoffs that were measured between the sampling period by the French institute of regional environment (DIREN). The Porge, Cirès, Lanton, Ponteils and Landes runoffs were computed using the average of the measured runoffs from 1989 to 1993 (Auby et al. 1994). Other stream runoffs were estimated from watershed areas, assuming that the surface/runoff ratio equals that of the Leyre catchment

streams with very low runoff (<1 m³ s⁻¹) are distributed all around the lagoon. Finally, two canals, Canal du Porge in the north and Canal des Landes in the south, also bring water from regulated dune lakes: the Lacanau Lake in the north and the Cazaux-Sanguinet Lake in the south (De Wit et al. 2005). The annual freshwater inputs into the lagoon average 1.25 billion m³, of which 8 % is groundwater, 13 % is rainfall and 79 % is from watercourses (Rimmelin et al. 1998).

In total, the catchment is typical of lowlands, with a surface area of 4,138 km² and slopes below 0.25 %. It is relatively homogenous topographically, climatically

(isohyets between 900 and 1,000 mm) and geologically (Auby et al. 1994). The geology of the Arcachon lagoon catchment consists of a uniform quaternary sand cover, named *Sable des Landes* (Legigan 1979) (Fig. 1b). These soils are typical of podzols that occur on coarse, poor, siliceous parent materials (on periglacial sand deposits) under temperate humid climates (Lundström et al. 2000). These podzols are characterised by high organic acidity (pH typically between 4 and 5), low inorganic nutrient availability, and high organic carbon content that can reach 50 g per kg soil (Jolivet et al. 2007). Although mainly silicate, some Miocene-carbonated outcrops can be

observed locally in this sandy catchment, particularly along the Leyre River (Folliot et al. 1993). In the Pontails catchment, carbonate precipitates that are used by the landfill of the city of Audenge, closed since 2008, can also be found inside soils (Canton et al. 2010).

The Sables des Landes contains a free and continuous water table covering more than 4,000 km², close to the Arcachon lagoon. It is formed by a homogeneous sand formation and its bottom consists of a sandy clay layer. With a variable thickness of between 10 and 130 m, the water table is usually located very close to the surface (~3 m). Nevertheless, on the edge of the streams, an important water table with a downward pull up exists, characterising a xerophilous lande (Jolivet et al. 2007).

The area has been massively drained and forested with pine trees (*Pinus pinaster*) following the imperial decree of 1,857, and currently pine forest is the major surface cover (84 % of the area, Fig. 1b). Intensive farming of corn and other vegetables is now prevalent in areas from 130 to 280 km², which have replaced traditional farming areas as well as forest (Auby et al. 1994).

Sampling strategy

Different watercourse types were sampled in this study, including the Leyre River with the highest runoff (18.2 m³ s⁻¹, representing 80 % of the total freshwater inputs), the two canals and six streams with very low runoff (annual average below 0.7 m³ s⁻¹). In total, nine watercourses from the north to the south were sampled at their outlet into the lagoon during one year, from February 2008 to February 2009 (Fig. 1a; Table 1). These nine main watercourses have been chosen for this carbon study because they cover an area spanning from the north to the south, representing about 90 % of the total catchment area and nearly the entire freshwater input into the lagoon. The streams present the highest drainages—in general above 10 L s⁻¹ km⁻²—due to their small watershed surface, and the north and south of the Arcachon catchment show the highest population densities, above 100 inhab km⁻². Consequently, these watersheds with high inhabitants to runoff ratios are subjected to more anthropogenic pressures, primarily through urban rainwater discharge, as most of the domestic load is being treated (De Wit et al. 2005).

The Renet, Pontails and Tagon streams and the Leyre River were sampled every 2 weeks, whereas the Porge and Landes canals and the Cirès, Milieu and Lanton streams were sampled every 2 weeks. During the study, organic, inorganic, particulate, dissolved carbon forms and carbon isotopic ratios were characterised, along with other parameters in the nine watercourses of the Arcachon lagoon watershed (Figs. 2, 3; Tables 2, 3).

Field techniques

In the field, conductivity and temperature of the watercourses were measured with a portable probe, Cond340i, and pH was measured using a combined electrode (Metrohm) 1 min after sampling. The CO₂ partial pressure (*p*CO₂) in watercourses was directly measured by a homemade portable equilibrator system that was used in the field following Frankignoulle et al. (2001). An Infra Red Gas Analyzer (LI-COR®, LI-820) was used to measure the *p*CO₂ in dry air that was equilibrated with freshwater. The LI-820® was calibrated at the laboratory 1 day before the field experiment using two gas standards of 0 and 2959 ± 59 ppmv. The equilibrator consists of a Plexiglas cylinder (height: 30 cm, diameter: 8 cm) that is filled with marbles to increase the exchange surface area. The system works as a closed system: water, through a portable peristaltic pump (Masterflex®, 1 L min⁻¹), runs from the top to the bottom of the equilibrator, and air is pumped upwards (1 L min⁻¹). The *p*CO₂ of air equilibrates with the *p*CO₂ of water and is then measured by the LI-COR® after being dried by a Dierite grain tube. After 7 min, the *p*CO₂ is constant and the entire equilibration between the air and water is achieved; then measurements are recorded with the datalogger LI-1400®.

The subsurface water was sampled and then filtered (0.7 µm of porosity) in the laboratory the same day to measure levels of SPM, POC, δ¹³C-POC, molar C/N ratio and Chl *a*. The filtered water was then used for a total alkalinity (TA) analysis. Dissolved organic carbon (DOC) samples were obtained after filtration in the field through pre-combusted GF/F filters (porosity of 0.7 µm) in detergent-washed and pre-combusted Pyrex vials (25 mL) and acidified with 50 µL of HCL 37 % to reach pH 2. The DOC filtrates were stored at 4 °C before analysis at the laboratory. Water required to measure the stable isotope composition of the dissolved inorganic carbon (δ¹³C-DIC) was obtained by overfilling 100 mL sealed glass serum vials, and kept poisoned with a saturated HgCl₂ solution to avoid bacterial activity. Samples were stored in the dark before analysis.

Laboratory analyses

The water for SPM and POC measurements was filtered through pre-weighed and pre-combusted Whatman GF/F glassfibre filters (0.7 µm porosity). The filters were then dried at 60 °C and stored in the dark; subsequently, SPM was determined by the weight difference. POC was measured using the same filter; the filters were acidified in crucibles with 2 N HCL to remove carbonates and were then dried at 60 °C (Etcheber et al. 2007). The POC content was measured by combustion using a LECO CS 125 analyser.

The POC in mg L^{-1} and POC in % (of SPM) were then calculated. The uncertainty was ± 0.05 % of SPM.

DOC concentrations were measured with a SHIMADZU TOC 5000 analyser (in TOC-IC mode), which in principle is based on thermal oxidation after a DIC removal step (Sharp 1993). The precision was close to 0.1 mg L^{-1} .

Water for Chl *a* measurement was filtered through GF/F filters, which were stored in the dark at -80 °C until analysis. Pigments were extracted with 90 % acetone, and the fluorescence was measured before and after acidification (Yentsch and Menzel 1963).

Total alkalinity (TA) was measured by titration with HCl 0.1 N on 100 mL filtered samples and was calculated by a Gran function linearisation (Gran 1952) between pH 4.2 and 3. The reproducibility between the measures was better than $\pm 5 \text{ } \mu\text{mol L}^{-1}$.

Water for the measurement of $\delta^{13}\text{C}$ -POC and the C/N ratio was filtered through pre-combusted GF/F filters. The filters were dried and stored in pre-cleaned glass vials; prior to the analysis, the filters were decarbonated using HCl 12N and dried overnight. Measurements were performed by coupling an elemental analyser (EA; Carlo Erba NC2500) to an Isotope Ratio Mass Spectrometer (IRMS; Micromass Isoprime). The carbon isotope ratio is expressed in the delta notation ($\delta^{13}\text{C}$) relative to Pee Dee Belemnite. The $\delta^{13}\text{C}$ -POC levels were calibrated against the lab standards of Acetanilide (-26.0 ‰), Glycine (-45.2 ‰), Caseine (-23.3 ‰) and Bassin (-17.5 ‰), which were themselves calibrated against certified standards (IAEA-CH6, IAEA-CH7 and USGS24). The C/N ratio was calibrated against certified acetanilide. The reproducibility of the $\delta^{13}\text{C}$ -POC levels and the C/N ratio was better than ± 0.2 ‰ and ± 0.2 , respectively.

The $\delta^{13}\text{C}$ -DIC measurements were made following Gillikin and Bouillon (2007). In 100 mL vials that were filled to the top, a headspace was first created with Helium gas to obtain a volume of approximately 20 % of the total volume of the vial. Then, 0.3 mL of warm 85 % phosphoric acid was added to transform the carbonate forms into CO_2 . To ensure gas equilibration, the vials were shaken and placed upside down for 1.5 h. The samples were measured using the above-mentioned EA-IRMS by injecting 3 mL of the CO_2 gas that was contained in each vial headspace through an injection port that was mounted before the water trap of the EA. $\delta^{13}\text{C}$ -DIC was calibrated against a homemade standard (45 mg of Na_2CO_3 were dissolved in a vial, flushed with He gas flow, with 3 mL of H_3PO_4) that had been calibrated against a certified standard (NBS19, -1.96 ‰) using a dual-inlet IRMS (Micromass Isoprime). The isotopic value of the standard Na_2CO_3 found was -4.5 ± 0.2 ‰. Finally, the equation of Miyajima et al. (1995) was applied to correct for the partitioning of the CO_2 between the headspace and the water

phase and to calculate the $\delta^{13}\text{C}$ of the total DIC. The repeatability was approximately ± 0.1 ‰ between samples.

DIC concentration was calculated from the $p\text{CO}_2$ and TA measurements (in addition to the water temperature) by resolving inorganic carbon system equations using dissociation constants from Mehrbach et al. (1973). The excess CO_2 , defined as the quantity of DIC that was theoretically transferred as CO_2 to the atmosphere after water–air equilibration, was calculated as the difference between the in situ DIC and a theoretical DIC at the atmospheric equilibrium (i.e. $\text{DIC}_{\text{equilibrium}}$, computed for a $p\text{CO}_2$ of 380 ppmv and the in situ TA as explained above) following Abril et al. (2000).

Hydrologic data sources, flux calculations and statistical tools

According to available hydrologic data for this study, daily runoffs measured by the French institute of regional environment (DIREN) were used to calculate the Leyre averaged runoff over the sampling period. The Porge, Cirès, Lanton, Penteils and Landes runoffs were computed using the average of the measured runoffs from 1989 to 1993 (Auby et al. 1994). Other stream runoffs were estimated and normalized using the surface/runoff relationship between the Leyre and the other watersheds. The carbon export budget (carbon exports and carbon export rates) of the Arcachon lagoon watershed was computed using the monthly averages for carbon concentrations and watercourse runoffs over the corresponding sampling points. It was calculated for each sampled watercourse in t C year^{-1} (carbon export) and then normalized by each corresponding watershed surface in $\text{t C km}^{-2} \text{ year}^{-1}$ (carbon export rate). The total carbon export rate was then computed by adding the nine watercourse carbon export values (i.e. the total carbon export from the Arcachon lagoon watershed) divided by the total catchment surface (see Tables 1, 4, 5).

The carbon export budget from these watercourses to the lagoon included the export of each carbon forms, i.e. TOC (POC and DOC), DIC (Excess CO_2 , $\text{DIC}_{\text{equilibrium}}$ and CO_2 degassing). This CO_2 degassing from watercourses to the atmosphere was calculated by the “Stream CO_2 -DEGAS” model formulated by Polsenaere and Abril (2012) that uses water–air isotopic equilibration and equation mass balance. The inversed model uses in situ data of $p\text{CO}_2$, total alkalinity (TA) and $\delta^{13}\text{C}$ -DIC and applies to small acidic and unproductive watercourses. It first makes several assumptions concerning the isotopic composition of the DIC initially released to surface waters (CO_2 from respired soil organic carbon and HCO_3^- from weathering) and on kinetic fractionation at the water–air interface ($^{12}\text{CO}_2$ degases to the atmosphere more rapidly than $^{13}\text{CO}_2$). It then computes a theoretical DIC concentration that has

evaded to the atmosphere upstream of the sampling point in order to reach the observed $p\text{CO}_2$ and $\delta^{13}\text{C}$ -DIC values due to gas isotopic equilibration (more details can be found in Polsenaere and Abril 2012).

The GraphPad Prism 5 and Xlstat softwares were used for statistical analysis. The Shapiro–Wilk test was used to test the normality of the data, followed by the Kruskal–Wallis test (in the case of nonparametric data) for analysis of variance (ANOVA) and the Dunn’s multiple comparison test (post-test). ANOVA was done to distinguish significant differences in carbon and associated parameters between watercourses and also between the four seasons (winter, periods from day 45 to 73 and from day 374 to 416; spring, period from day 85 to 168; summer, period from day 182 to 252 and autumn, period from day 267 to 351) for all watercourses.

Results

General overview of carbon concentrations and characteristics of the Arcachon lagoon catchment watercourses

General trends in terms of carbon concentrations and associated parameters have been measured throughout the study year in the nine watercourses (Tables 2, 3). Water temperatures were generally close to each other with a mean of 12.9 ± 0.5 °C and showed a typical annual trend with values ranging from 3.5 °C during the winter months (day 374, in the Porge canal) to 19.6 °C during the summer period (day 197, in Landes canal). Water conductivity showed little variation in all of the watercourses (near 205 ± 31 $\mu\text{S cm}^{-1}$), with the exception of the Porge canal, where conductivity reached 4,420 $\mu\text{S cm}^{-1}$ (salinity of 1.9) during sampling day 295 in autumn linked to the tidal rhythm; in fact, the canal links the Lacanau lake to the lagoon in the North and is sometimes affected by tidal intrusion (Fig. 1). The SPM concentrations were low over the year in all watersheds, generally below 20 mg L^{-1} . The average was 8.4 ± 3.4 mg L^{-1} ; the lowest values were found in the Landes canal (2.7 ± 1.1 mg L^{-1} on average) and the highest values were found in the other watercourses (near 10 mg L^{-1} on average). Similarly, the concentrations of POC (1.6 ± 0.6 mg L^{-1} on average) were low in these poorly turbid waters of the lowland regions, from 0.7 ± 0.3 mg L^{-1} in the Landes canal to only 2.49 ± 2.2 mg L^{-1} in the Tagon stream (Table 2). Nevertheless, the POC content of the SPM was high with a mean of 20.8 ± 2.7 %, varying from about 16 % (in Leyre River) to 24 % (in Porge canal). DOC concentrations were generally high with an annual average of 6.6 ± 2.2 mg L^{-1} and the highest values of up to 8.0 mg L^{-1} occurring in Porge canal

and Tagon and Pontails streams, and the lowest values between 4.2 and 5.8 mg L^{-1} in the other watercourses. The DOC/POC ratio ranged between 2 and 8 (Table 2). $\delta^{13}\text{C}$ -POC was somewhat constant throughout the year with an average of -28.6 ± 0.4 ‰ and values ranging from -9.2 ‰ to -28.1 ‰ in the Landes and Porge canals, respectively. Yearly averages of molar C/N ratios were above 12 and varied between 12 ± 0.9 in the Landes canal and 19.9 ± 2.2 in the Lanton stream (Table 2). Finally, Chl *a* concentrations were low in the nine watercourses, with an average of 1.3 ± 1.4 $\mu\text{g L}^{-1}$. As a consequence, the mean POC/Chl *a* ratios were always high ($2,590 \pm 1,396$ on average) from 580 to 4,200 in the Landes canal and the Milieu stream, respectively.

DIC concentrations averaged 488.0 ± 186.1 $\mu\text{mol L}^{-1}$ in all watercourses and ranged from 229.5 to 859.3 $\mu\text{mol L}^{-1}$ in the Milieu and Pontails streams, respectively (Table 3). Due to the acidic characteristic of this sandy catchment (pH of 6.55 ± 0.25 on average and values between 6.09 and 7.03, Polsenaere, unpublished data), the DIC was dominated (>99 %) by HCO_3^- and CO_2^* . TA was almost entirely composed of bicarbonates and was generally low over the year in the watercourses, with an annual average of 300 ± 135 $\mu\text{mol L}^{-1}$ and values ranged from 104.3 to 550.4 $\mu\text{mol L}^{-1}$ on average in the Milieu and Pontails streams respectively. In all cases, waters were largely supersaturated in CO_2 , with an average $p\text{CO}_2$ of $3,922 \pm 1,645$ ppmv and yearly averages ranging from 2,554 ppmv in the Milieu stream to 6,546 ppmv in the Pontails streams (Table 3). As a consequence, the excess CO_2 was also high in all watercourses with a mean of 170.2 ± 78.2 $\mu\text{mol L}^{-1}$. Finally, low values of $\delta^{13}\text{C}$ -DIC were generally observed during this annual cycle (-16.7 ± 3.5 ‰ on average) and values ranged from -20.3 to -10.6 ‰ in the Renet and Pontails streams, respectively (Table 3).

Seasonality of carbon concentrations and characteristics of the Arcachon lagoon catchment watercourses

Throughout the annual sampling period, consistent seasonal patterns in carbon concentrations and associated parameters were observed (Figs. 2, 3) and linked to the hydrological regime in the watershed. The latter consisted of short flood periods in spring (close to $30 \text{ m}^3 \text{ s}^{-1}$) related to high precipitation, then a low water flow throughout the summer period and finally, in the late autumn and winter, river runoff maxima reaching up to $100 \text{ m}^3 \text{ s}^{-1}$ (Figs. 2, 3). Organic carbon and associated parameters showed stable seasonal patterns for each watercourse with generally no clear seasonal pattern (Fig. 2). No significant differences (ANOVA, $p > 0.05$) were measured between each of

Table 2 Organic carbon and associated physical and chemical parameters in the nine watercourses entering the Arcachon lagoon; average (bold), standard deviation (in italic) and range (between brackets)

	<i>T</i> (°C)	Conductivity ($\mu\text{S cm}^{-1}$)	SPM (mg L ⁻¹)	POC (mg L ⁻¹)	DOC (mg L ⁻¹)	DOC/POC	POC/Chl <i>a</i>	$\delta^{13}\text{C-POC}$ (‰)	C/N (mol mol ⁻¹)
Porge	13.3	1113	12.0	2.4	10.9	4.5	753	-28.1	15.3
	5.0 (3.5–19.2)	<i>1166</i> (230–4420)	<i>7.2</i> (2.6–26.6)	<i>1.1</i> (1.0–4.2)	<i>1.7</i> (8.0–13.0)		<i>578</i> (60–2252)	<i>2.0</i> (–33.6 to –25.9)	<i>3.8</i> (11–24)
Cirès	12.2	203	5.1	1.2	5.8	5.0	3438	-28.4	18.9
	2.4 (6.5–16.1)	<i>27</i> (162–253)	<i>1.0</i> (3.8–7.8)	<i>0.3</i> (0.6–1.8)	<i>1.2</i> (4.0–8.1)		<i>2394</i> (1361–8–846)	<i>0.2</i> (–28.6 to –28.1)	<i>1.1</i> (17–21)
Renet	12.9	201	10.4	1.7	5.5	3.2	3825	-28.6	19.6
	2.4 (6.6–16.6)	<i>28</i> (178–277)	<i>16.9</i> (3–82.9)	<i>2.8</i> (0.1–13.4)	<i>1.1</i> (4.1–9.9)		<i>3156</i> (460–12137)	<i>0.4</i> (–29.4 to –28)	<i>1.9</i> (16–23)
Lanton	12.5	176	11.2	2.3	5.2	2.3	4140	-28.7	19.9
	2.8 (5.8–16.7)	<i>8</i> (161–193)	<i>7.9</i> (4.8–35.1)	<i>1.7</i> (0.9–7.3)	<i>1.5</i> (3.2–7.4)		<i>2530</i> (647–8169)	<i>0.4</i> (–29.1–28.0)	<i>2.2</i> (17–23)
Milieu	12.7	270	6.5	1.5	4.2	3.8	4221	-28.1	17.3
	3.5 (4.2–17.5)	<i>34</i> (215–321)	<i>4.1</i> (1.7–18)	<i>1.2</i> (0.1–4.6)	<i>1.1</i> (2.4–5.8)		<i>4004</i> (685–15218)	<i>0.9</i> (–28.9 to –26.5)	<i>1.7</i> (13–19)
Ponteils	12.8	221	6.5	1.3	8.0	6.0	2244	-28.4	16.2
	3.3 (5.1–18.6)	<i>69</i> (138–325)	<i>5.6</i> (1.6–26.3)	<i>1.2</i> (0.01–6.0)	<i>1.5</i> (5.7–11.8)		<i>1779</i> (193–6062)	<i>0.6</i> (–29.2 to –26.9)	<i>2.4</i> (11–22)
Tagon	12.6	205	12.8	2.5	8.3	3.6	2359	-29.0	17.0
	3.8 (3.8–18.6)	<i>17</i> (172–258)	<i>9.5</i> (3.5–50.3)	<i>2.2</i> (0.1–11.7)	<i>2.9</i> (3.1–12.7)		<i>1631</i> (143–6062)	<i>0.5</i> (–30.2 to –28.3)	<i>2.6</i> (12–21)
Leyre	12.7	170	8.7	1.3	5.5	4.2	1748	-28.7	14.4
	4.2 (3.8–18.6)	<i>15</i> (151–195)	<i>5.7</i> (2.3–26.4)	<i>0.9</i> (0.2–4.2)	<i>1.8</i> (2.7–10.1)		<i>1146</i> (109–5121)	<i>0.5</i> (–29.5 to –27.7)	<i>1.3</i> (12–17)
Landes	14.1	195	2.7	0.6	5.0	7.7	581	-29.2	12.0
	4.6 (4.6–19.6)	<i>21</i> (156–233)	<i>1.1</i> (1.3–4.5)	<i>0.3</i> (0.1–1.1)	<i>0.9</i> (3.3–6.5)		<i>230</i> (109–894)	<i>0.4</i> (–29.8 to –28.6)	<i>0.9</i> (11–13)

T temperature, *SPM* suspended particulate matter, *POC* particulate organic carbon, *DOC* dissolved organic carbon, *Chl a* Chlorophyll *a*, $\delta^{13}\text{C-POC}$ particulate organic carbon isotopic ratio and C/N molar carbon/nitrogen ratio of particulate organic matter. Note that values for conductivity correspond to the in situ conductivity and not to the specific conductance normalized at 25 °C

Table 3 Observed inorganic carbon parameters in the nine watercourses entering the Arcachon lagoon; average (bold), standard deviation (italic) and range (between brackets)

	$p\text{CO}_2$ (ppmv)	TA ($\mu\text{mol L}^{-1}$)	Excess CO_2 ($\mu\text{mol L}^{-1}$)	DIC ($\mu\text{mol L}^{-1}$)	$\delta^{13}\text{C-DIC}$ (‰)
Porge	4,364	374.4	181.6	573.9	-13.3
	2,775	69.5	113.5	148.3	3.8
	(1,192–8,380)	(286–569)	(48–357)	(366–924)	(-17.6 to -7.5)
Cirès	4,212	201.1	191.2	411.3	-19.5
	544.7	31.8	26.5	40.0	0.5
	(3,020–5,280)	(151–268)	(133–231)	(347–467)	(-20.3 to -18.3)
Renet	5,479	247.5	247.3	513.2	-20.3
	1,279	52.4	54.4	80.8	0.4
	(1,437–7,653)	(154–370)	(56–320)	(317–674)	(-21.2 to -19.6)
Lanton	3,167	175	136.9	330.8	-18.6
	1,057	85.6	45.8	95.7	1.4
	(1,889–6,220)	(83–444)	(73–260)	(236–612)	(-21.4 to -16.4)
Milieu	2,554	104.3	106.4	229.5	-19.7
	949.8	22.2	42.5	55.1	1.7
	(1,529–5,460)	(78–153)	(57–229)	(170–390)	(-24.6 to -17.9)
Ponteils	6,546	550.4	292.4	859.3	-10.6
	2,742	351.4	121.3	454.9	2.1
	(2,116–10,012)	(101–1,082)	(98–470)	(240–1,550)	(-15.0 to -7.6)
Tagon	5,125	394.6	228.1	640.7	-19.0
	1,425	167.6	54.0	200.7	1.3
	(2,188–7,809)	(128–648)	(108–354)	(349–949)	(-21.4 to -16.9)
Leyre	1,604	325	59.96	403.6	-15.6
	338.7	113.9	18.0	104.0	2.6
	(1,046–2,453)	(120–520)	(38–114)	(255–612)	(-21.6 to -12.5)
Landes	2,250	324.1	87.58	429.4	-13.8
	590.6	60.8	23.0	55.2	2.4
	(1,485–3,382)	(279–495)	(48–125)	(359–583)	(-16.8 to -8.0)

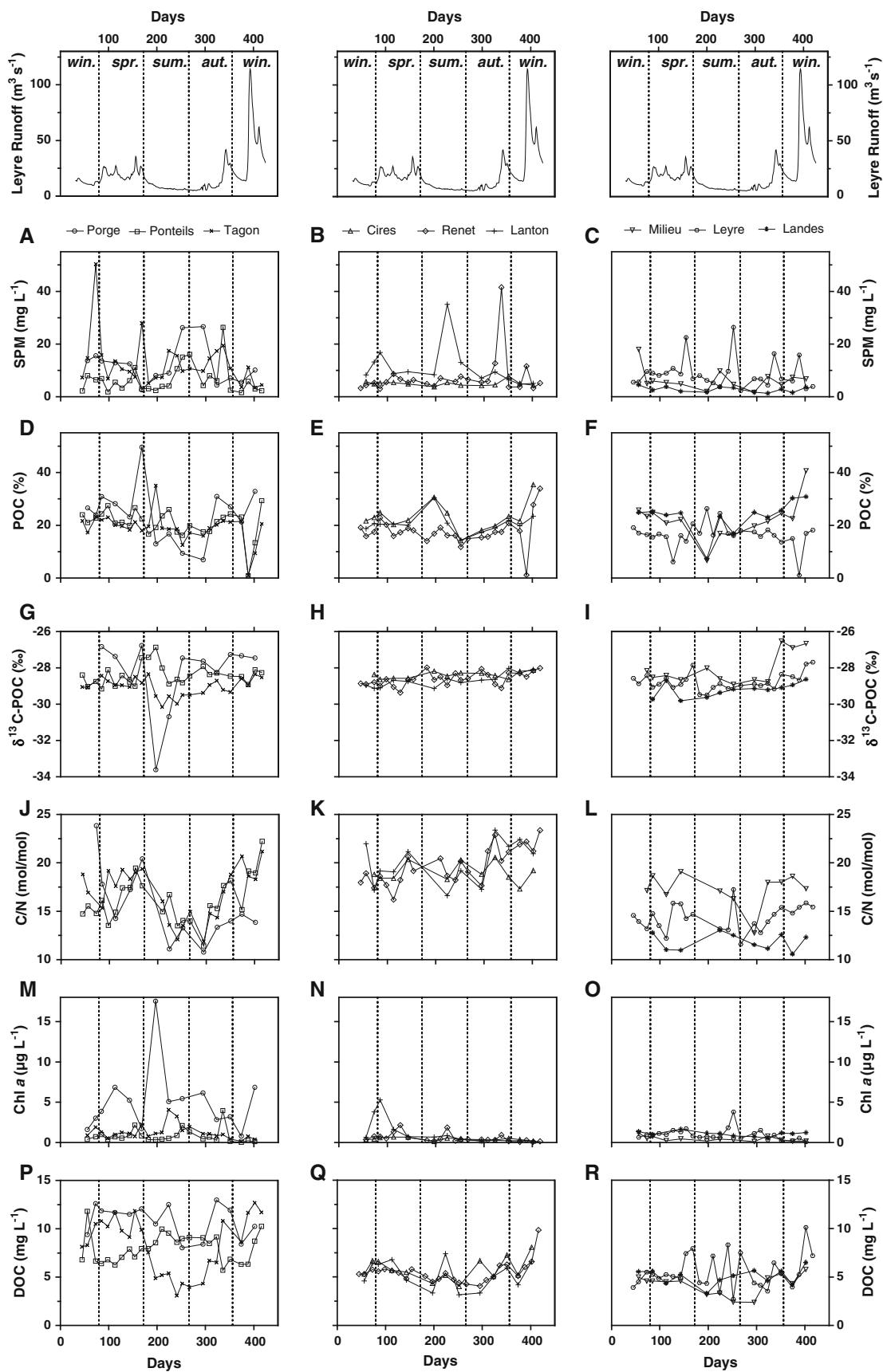
$p\text{CO}_2$ partial pressure of carbon dioxide, *TA* total alkalinity, *DIC* dissolved inorganic carbon and $\delta^{13}\text{C-DIC}$ dissolved inorganic carbon isotopic ratio

the four seasons in SPM (concentrations) and POC (concentration and %) values even if some higher SPM values were noticed during flood events (for instance in the Leyre River, day 336 with 16.4 mg L^{-1} ; Fig. 2c). Similarly $\delta^{13}\text{C-POC}$ and molar C/N ratio values showed no clear seasonal trends. However, in Porge canal during the sample day 197 in summer, a very low value of $\delta^{13}\text{C-POC}$ (-33.6 ‰) was measured compared to the constant observed values between -26 and -30 ‰ throughout the year (Fig. 2g). On the same day, a higher Chl *a* concentration was also observed in the same canal (up to $17 \mu\text{L}^{-1}$) compared to low values generally noticed in the nine watercourses (Fig. 2m). As a consequence, POC/Chl *a* ratios exhibited large differences between seasons, reflecting the annual pattern in Chl *a* concentration (plot not shown). The only clear seasonal pattern for organic carbon parameters was observed in DOC concentrations, with significant differences (ANOVA, $p = 0.0074$) between the summer and the

winter/spring, where the highest values were measured (Fig. 2p–r).

In contrast to organic carbon parameters, the observed inorganic carbon parameters in the nine watercourses showed strong seasonal patterns throughout the year (Fig. 3; Table 3). Overall, significant differences in DIC parameters were noticed between the winter and summer period (ANOVA, $p < 0.05$). In fact, $p\text{CO}_2$ was minimum during the winter months around $1,000\text{--}2,000 \text{ ppmv}$ and

Fig. 2 Seasonal variations in organic matter and its associated parameters in the nine study watercourses. **a**, **b**, and **c** Suspended particulate matter (SPM), **d**, **e**, and **f** particulate organic carbon (POC, % of SPM), **g**, **h**, and **i** stable isotope of POC ($\delta^{13}\text{C-POC}$), **j**, **k**, and **l** C/N ratio of particulate organic matter, **m**, **n**, and **o** Chlorophyll *a* (Chl *a*) and **p**, **q**, and **r** dissolved organic carbon (DOC). Panels show the daily discharge of the Leyre River. Day 0 is January 1, 2008 and win., spr., sum. and aut. indicate the winter, spring, summer and autumn seasons, respectively



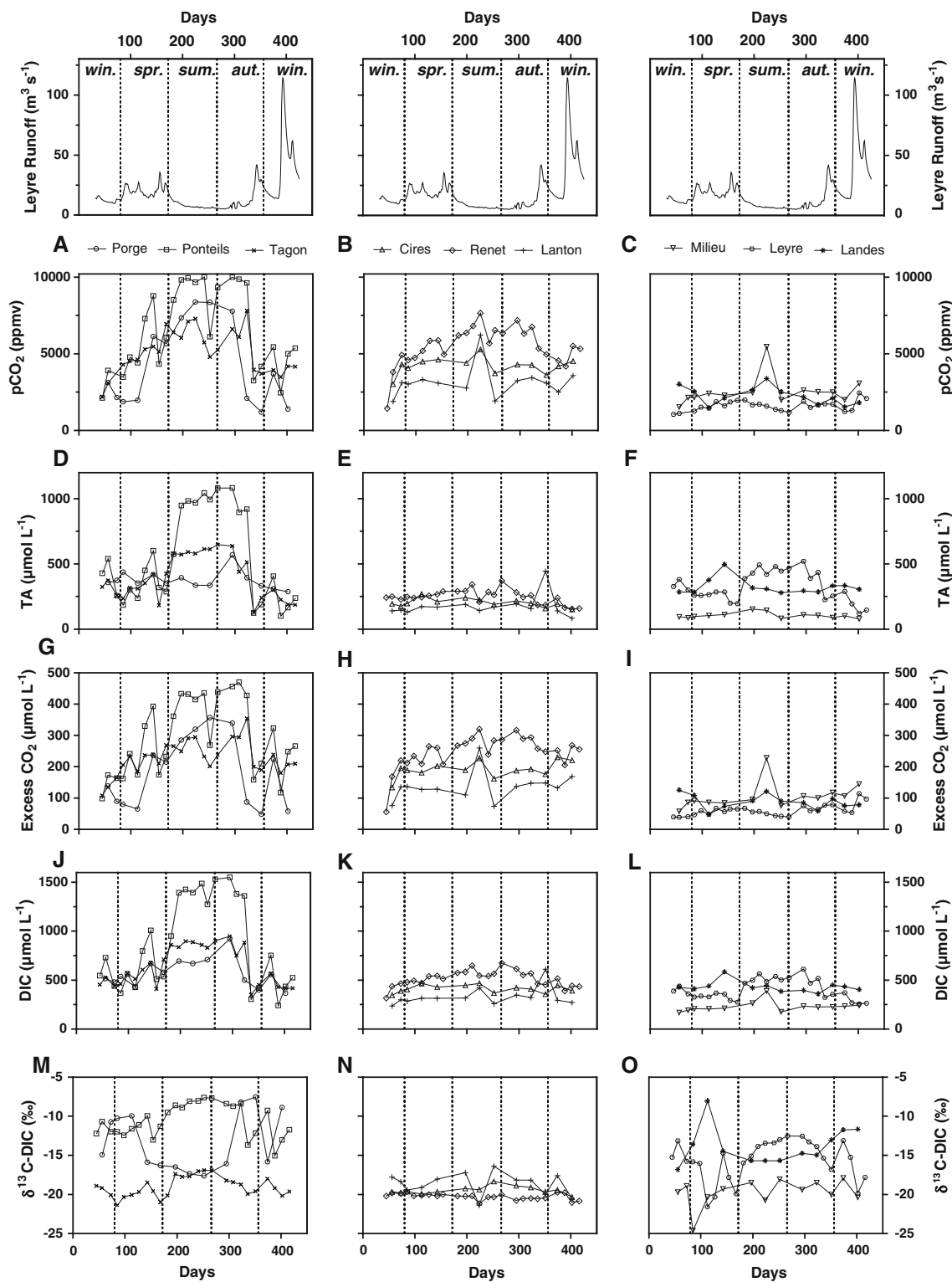
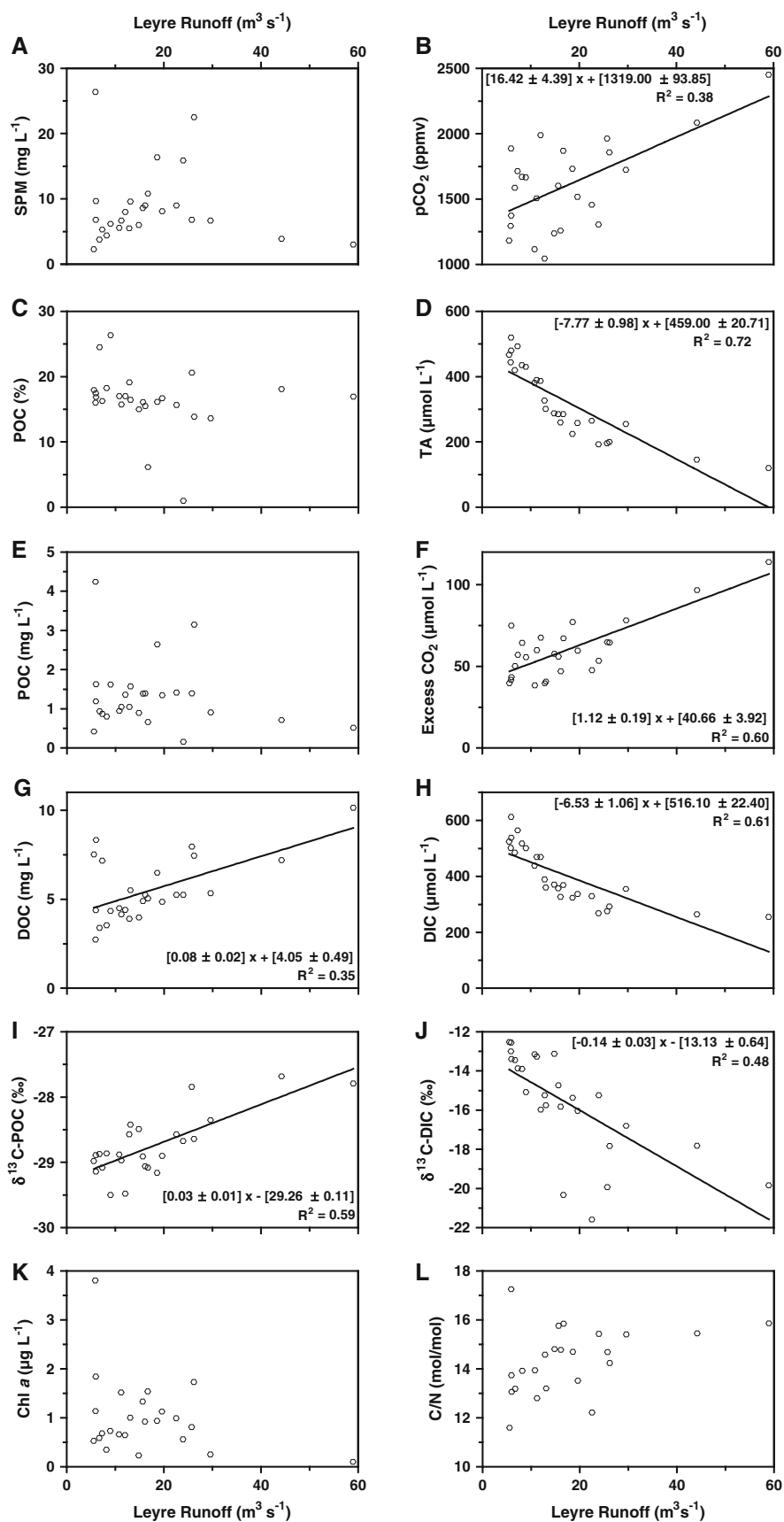


Fig. 3 Seasonal variations in the inorganic carbon and its associated parameters in the nine study watercourses. **a**, **b**, and **c** partial pressure of carbon dioxide ($p\text{CO}_2$), **d**, **e**, and **f**: total alkalinity (TA), **g**, **h**, and **i** excess of carbon dioxide (excess CO_2), **j**, **k**, and **l** dissolved

inorganic carbon (DIC) and **m**, **n** and **o** stable isotope of DIC ($\delta^{13}\text{C}$ -DIC). Panels show the daily discharge of the Leyre River. Day 0 is January 1, 2008 and win., spr., sum. and aut. indicate the winter, spring, summer and autumn seasons, respectively

Fig. 4 **a** Suspended particulate matter (SPM), **b** partial pressure of carbon dioxide ($p\text{CO}_2$), **c** particulate organic carbon (POC, % of SPM), **d** total alkalinity (TA), **e** particulate organic carbon (POC), **f** excess of carbon dioxide (excess CO_2), **g** dissolved organic carbon (DOC), **h** dissolved inorganic carbon (DIC), **i** stable isotope of POC ($\delta^{13}\text{C}\text{-POC}$), **j** stable isotope of DIC ($\delta^{13}\text{C}\text{-DIC}$), **k** chlorophyll *a* (Chl *a*) and **l** molar carbon/nitrogen ratio of organic matter (C/N ratio) versus water runoff in the Leyre River. Only significant carbon parameter/runoff linear regressions are given ($p \leq 0.001$)



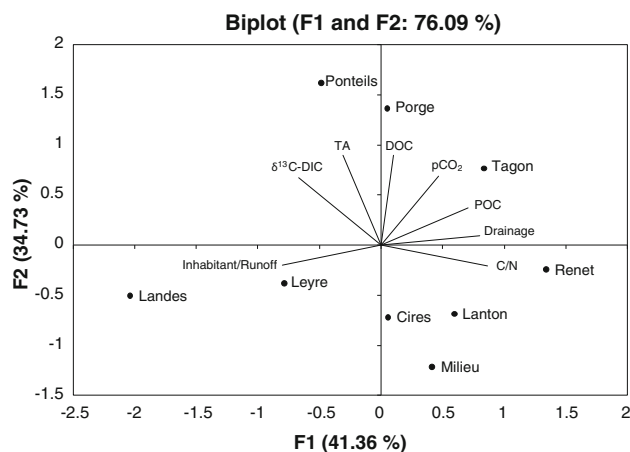


Fig. 5 Loadings plot of the principal component analysis (PCA) total variance percentage = 76.09 %. The graph shows the distribution of the nine sampled watercourses, nine observations functions to the eight measured factors (8 variables) as well as the correlations between the variables. Only eight variables were used here, as the redundancy of several variables hid the total explained variance. Six of these variables represent the measured parameters showing the greatest variations throughout the year ($\delta^{13}\text{C-DIC}$, TA, DOC, $p\text{CO}_2$, POC and C/N ratio), and two represent characteristics of river watersheds (inhabitant/runoff ratio and drainage): the inhabitant/runoff ratio ($\text{inhab m}^{-3} \text{ s}$), stable isotope ^{13}C of DIC ($\delta^{13}\text{C-DIC}$, ‰), total alkalinity (TA, $\mu\text{mol L}^{-1}$), DOC (mg L^{-1}), $p\text{CO}_2$ (ppmv), POC (mg L^{-1}), drainage ($\text{L s}^{-1} \text{ km}^{-2}$) and molar C/N ratio. Variables that are situated along the same directional axis correlate positively with each other (TA/ $\delta^{13}\text{C-DIC}$, POC/drainage); variables that are situated at opposite ends of the plot correlate negatively with each other (e.g., POC/inhabitant/runoff, C/N/ $\delta^{13}\text{C-DIC}$); variables that are situated in the centre of the plot are poorly correlated and are poor predictors. The horizontal axis explains 41.36 % of the variability and the vertical axis, 34.73 %; thus, the representation of the variables on these two axes is of good quality

increased in spring to reach maximum values during the summer and autumn, up to 10,000 ppmv in the Pontails stream (Fig. 3a–c). In the Leyre River only, an opposite $p\text{CO}_2$ pattern was noticed with higher values (around 2,000 ppmv) in winter/spring and lower values (around 1,000 ppmv) in summer/autumn, although the $p\text{CO}_2$ generally remained low over the annual cycle. The TA in the nine watercourses also followed to a lesser extent this former seasonal trend with the lowest values (approximately $100 \mu\text{mol L}^{-1}$) measured during the winter months and the highest values reaching close to $1,000 \mu\text{mol L}^{-1}$ in some watercourses during the summer months (for instance, in the Pontails and Tagon streams). The excess CO_2 (Fig. 3g–i) reflected this seasonal pattern, with minima in winter (near $100 \mu\text{mol L}^{-1}$ in the Landès canal) and maxima in the summer/autumn periods (nearly $500 \mu\text{mol L}^{-1}$ in the Pontails stream).

Seasonality of carbon concentrations, particularly in the inorganic form, could be quantitatively related to the hydrological cycle in the Leyre River, where river discharges were available during the sampling period

(Fig. 4). No clear seasonal patterns linked to water runoff were measured in SPM and POC concentrations (and %) (Fig. 4a, c, e). However, a significant increase in DOC concentrations with runoff ($p = 0.0015$) was noticed and higher values were also measured for runoffs above $15 \text{ m}^3 \text{ s}^{-1}$ (matching with winter, spring and late autumn seasons) than below $15 \text{ m}^3 \text{ s}^{-1}$ (matching with summer, autumn and start of winter) with 6.3 ± 1.6 and $4.8 \pm 1.7 \text{ mg L}^{-1}$, respectively ($p = 0.0145$, Mann–Whitney test; Fig. 4g). Similarly, a significant increase in $\delta^{13}\text{C-POC}$ values was observed in this river ($p < 0.0001$). Contrary to organic carbon parameters, all of the DIC parameters showed a clear and significant correlation with water runoff (Fig. 4). DIC and TA concentrations decreased, whereas $p\text{CO}_2$ and excess CO_2 increased with increasing runoff (Fig. 4b, d, f, h). DIC concentrations of 481.5 ± 72.7 and $312.8 \pm 40 \mu\text{mol L}^{-1}$ for runoffs below and above $15 \text{ m}^3 \text{ s}^{-1}$, respectively, were measured ($p < 0.0001$). A significant difference in TA concentrations was also observed between runoffs below and above $15 \text{ m}^3 \text{ s}^{-1}$, i.e. 411.6 ± 70.6 and $224.0 \pm 53.7 \mu\text{mol L}^{-1}$, respectively ($p < 0.0001$). On the contrary, the excess CO_2 concentrations (Fig. 4f) showed significantly higher concentrations for runoffs above than below $15 \text{ m}^3 \text{ s}^{-1}$ (68.9 ± 20.0 and $52.2 \pm 12.0 \mu\text{mol L}^{-1}$, respectively, $p = 0.0221$). Finally, lower values of $\delta^{13}\text{C-DIC}$ were measured at higher runoffs (-17.6 ± 2.3 ‰) than at lower runoffs (-13.9 ± 1.2) ($p < 0.0001$) as illustrated by the significant decrease of $\delta^{13}\text{C-DIC}$ ($p < 0.001$, Fig. 4j).

Differences in carbon concentrations and characteristics among the Arcachon lagoon watershed watercourses

In spite of the common characteristic of the carbon parameters previously shown, differences between the nine watercourses were investigated by performing a principal component analysis (PCA; Fig. 5). First, an important contrast was observed in the very low values of $\delta^{13}\text{C-DIC}$ (below -18 ‰), low TA (in general below $250 \mu\text{mol L}^{-1}$) and very high C/N ratios (above 17 mol mol^{-1}) measured in the Cirès, Renet, Lanton, Milieu and Tagon watercourses as compared to the other watercourses. On the contrary, in the four other watercourses, i.e., the Porge, Pontails, Leyre and Landès, the $\delta^{13}\text{C-DIC}$ values were higher, with values generally above -15 ‰; the TA values were also higher than the former four rivers, with values typically above $300 \mu\text{mol L}^{-1}$. Another contrast was observed in the Pontails, Porge, Tagon and Renet watercourses, where DOC and $p\text{CO}_2$ were particularly high in comparison to the others. Finally, high inhabitant/runoff ratios and low drainage values, correlated with low POC concentrations, differentiated the Leyre River and Landès canal from the other watercourses.

Table 4 Watershed carbon export and export rates (TOC: POC + DOC and DIC: excess CO₂ + DIC_{equilibrium} + CO₂ degassing); carbon exports in t C year⁻¹ (bold) and carbon export rates in t C km⁻² year⁻¹ (italic)

	Total	Organic carbon			Inorganic carbon			
	(TOC + DIC)	TOC	POC	DOC	DIC	Excess CO ₂	DIC _{equilibrium}	CO ₂ degassing
	<i>C export</i>							<i>C degassing</i>
Porge	2609 <i>19.0</i>	1658 <i>7.5</i>	306 <i>1.4</i>	1352 <i>6.1</i>	951 <i>11.5</i>	226 <i>1.0</i>	554 <i>2.5</i>	171 ^a <i>0.8</i> ^a
Cirès	608 <i>12.5</i>	149 <i>3.1</i>	25 <i>0.5</i>	124 <i>2.5</i>	459 <i>9.4</i>	47 <i>1.0</i>	50 <i>1.0</i>	362 <i>7.4</i>
Renet	603 <i>33.7</i>	144 <i>8.1</i>	29 <i>1.6</i>	115 <i>6.4</i>	459 <i>25.6</i>	56 <i>3.1</i>	55 <i>3.1</i>	348 <i>19.4</i>
Lanton	197 <i>5.3</i>	63 <i>1.7</i>	15 <i>0.4</i>	48 <i>1.3</i>	134 <i>3.6</i>	15 <i>0.4</i>	20 <i>0.5</i>	99 <i>2.7</i>
Milieu	276 <i>12.9</i>	128 <i>6.0</i>	35 <i>1.6</i>	93 <i>4.4</i>	148 <i>6.9</i>	26 <i>1.2</i>	28 <i>1.3</i>	94 <i>4.4</i>
Ponteils	233 <i>9.9</i>	66 <i>2.8</i>	9 <i>0.4</i>	57 <i>2.4</i>	167 <i>7.1</i>	23 <i>1.0</i>	36 <i>1.5</i>	108 ^a <i>4.6</i> ^a
Tagon	660 <i>22.3</i>	275 <i>9.3</i>	44 <i>1.5</i>	231 <i>7.8</i>	385 <i>13</i>	56 <i>1.9</i>	87 <i>2.9</i>	242 <i>8.2</i>
Leyre	10,446 <i>4.8</i>	4096 <i>1.9</i>	667 <i>0.3</i>	3429 <i>1.6</i>	6350 <i>2.9</i>	470 <i>0.2</i>	1985 <i>0.9</i>	3895 <i>1.8</i>
Landes	238 <i>2.0</i>	97 <i>0.8</i>	12 <i>0.1</i>	85 <i>0.7</i>	141 <i>1.2</i>	16 <i>0.1</i>	68 <i>0.6</i>	57 ^a <i>0.5</i> ^a
Total (t C year ⁻¹)	15,870	6676	1142	5534	9194	935	2883	5376
Total (t C km ⁻² year ⁻¹)	<i>6.0</i>	<i>2.5</i>	<i>0.4</i>	<i>2.1</i>	<i>3.4</i>	<i>0.3</i>	<i>1.1</i>	<i>2</i>
Percentage (%)	<i>100</i>	<i>42</i>	<i>7</i>	<i>35</i>	<i>58</i>	<i>6</i>	<i>18</i>	<i>34</i>

The CO₂ degassing was calculated using the StreamCO₂-DEGAS model, based on the *p*CO₂, total alkalinity and δ¹³C-DIC (Polensaeere and Abril 2012)

^a CO₂ degassing for the Porge, Ponteils and the Landes watercourses were estimated using *K*₆₀₀ values that were set to 5, 10 and 5 cm h⁻¹, respectively. DIC_{equilibrium} is computed as a theoretical DIC concentration in a river at atmospheric equilibrium (Abril et al. 2000). The total carbon export rate was computed as the sum of the nine carbon exports, i.e. the total carbon export (in t C year⁻¹) divided by the total catchment surface (2656.5 km², Table 1). Percentages correspond to the proportion of each carbon form within the total carbon export rate of the Arcachon lagoon watershed

Carbon exports and export rates from the Arcachon lagoon watershed

The total carbon export from the entered Arcachon lagoon watershed was estimated at 15,870 t C year⁻¹; equivalent to a carbon export rate of 6.0 t C km⁻² year⁻¹, including a CO₂ degassing to the atmosphere of 2.0 t C km⁻² year⁻¹ (Table 4). The Leyre River accounted for more than 65 % of this total carbon export (Table 4). Individual carbon export rates for subcatchments varied strongly, between 2.0 t C km⁻² year⁻¹ for Landes canal and 33.7 t C km⁻² year⁻¹ for Renet stream. The contributions of each carbon species to the total export from the catchment were 7 % for POC, 35 % for DOC and 58 % for DIC, the latter being partitioned into 6 % of excess CO₂ transported laterally, 18 % of DIC at the equilibrium with the atmosphere, and 34 % degassed as CO₂ to the atmosphere

along the watercourses (Table 4). The total POC export rate was 0.4 t C km⁻² year⁻¹ and ranged between 0.1 t C km⁻² year⁻¹ in Landes canal and 1.6 t C km⁻² year⁻¹ in Renet and Milieu streams. The total DOC export rate was 2.1 t C km⁻² year⁻¹, with a minimum of 0.7 in the Landes canal and a maximum of 7.8 t C km⁻² year⁻¹ in Tagon stream. The total DIC export rate was 3.4 t C km⁻² year⁻¹ and ranged between 1.2 t C km⁻² year⁻¹ in Landes canal to 25.6 t C km⁻² year⁻¹ in Renet stream. Lateral transport of excess CO₂ for the whole catchment account for 6 % of the total export, similar to the POC export rate to the lagoon. Finally, among the 6.0 t C km⁻² year⁻¹ exported from land, 2.0 t C km⁻² year⁻¹ escaped to the atmosphere along watercourses and did not reach the lagoon, a quantity similar to the DOC export. Degassing rates (expressed per unit area of the catchment) ranged from 0.5 t C

$\text{km}^{-2} \text{ year}^{-1}$ in Landes canal to $19.4 \text{ t C km}^{-2} \text{ year}^{-1}$ in Renet stream (Table 4).

Discussion

The nine watercourses sampled around the Arcachon lagoon showed relatively homogeneous carbon characteristics due to the relative uniformity of the catchment: low SPM and POC concentrations associated with a high contribution of POC within the SPM; a low Chl *a* concentration, high POC/SPM and molar C/N ratios, very low values of $\delta^{13}\text{C}$ -POC; a high DOC concentration and a low TA that was associated with a high $p\text{CO}_2$. However, significant seasonal patterns, linked to the water runoff and differences from one watercourse to another were noticed, in particular for inorganic carbon parameters. Variations were also observed in terms of carbon exports (and rates) from the nine watercourses with different relative contributions of each carbon form within the whole Arcachon lagoon catchment carbon budget.

Origin of carbon among the watercourses flowing to the Arcachon lagoon

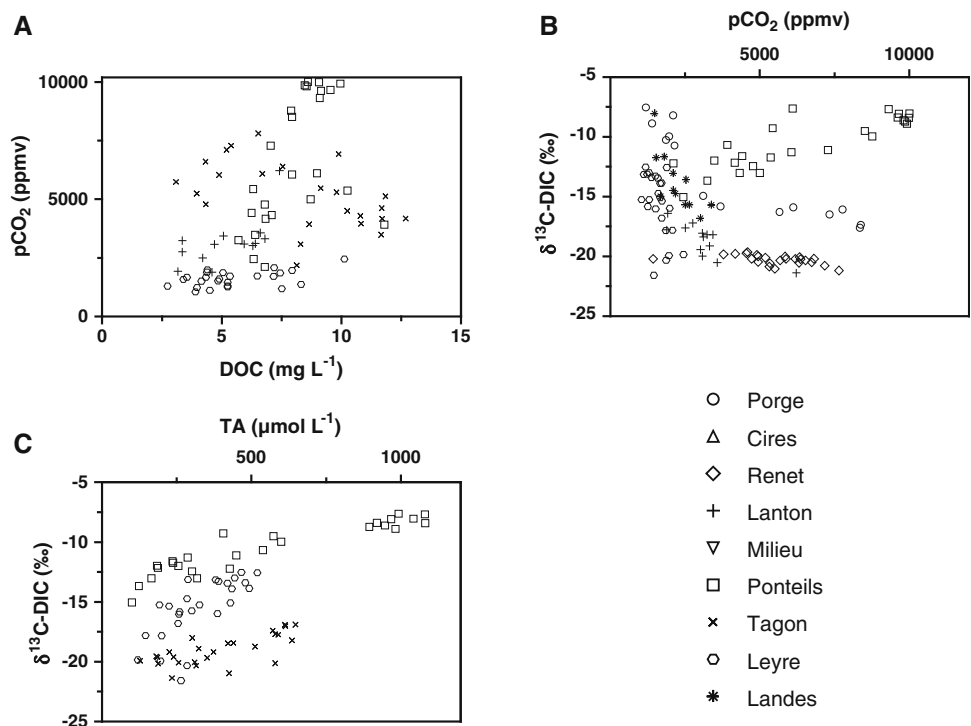
Our study reveals an almost complete terrestrial origin of POC in the Arcachon catchment. POC here is allochthonous and originates from soil and terrestrial C_3 plants, with typical molar C/N ratios higher than 12 (Bordovskiy 1965), and $\delta^{13}\text{C}$ -POC values of -27 to -30 ‰ (Mook and Tan 1991). In addition, low Chl *a* concentration and high POC/Chl *a* ratios indicate a low contribution of phytoplankton to POC contrary to eutrophic rivers for instance (Abril et al. 2002; Neal et al. 2006). Indeed, phytoplankton generally exhibits a POC/Chl *a* ratio ranging between 20 and 140, and it is generally accepted that phytoplankton-dominated POM has a POC/Chl *a* ratio that is lower than 200 (Savoye et al. 2003). Photosynthesis is likely limited by hydrological factors as shown in the rivers of eastern England by Neal et al. (2006). Additionally, these waters with low pH values and low inorganic nutrient concentrations (Canton et al. 2012) could limit phytoplankton growth, as has been shown in peatland watercourses (Greenwood and Lowe 2006). The extremely negative $\delta^{13}\text{C}$ -DIC values (Table 3; Fig. 3m–o) also confirms a weak instream net photosynthesis in these types of watercourses, as already shown in other watercourses, such as river-tributary stream systems (Atekwana and Krishnamurthy 1998).

The ubiquity of acidic podzols with high organic carbon content (Jolivet et al. 2007) lead to relatively high concentrations of DOC in the nine sampled watercourses (Table 2; Fig. 2p–r). This specificity has also been reported in boreal wetlands and temperate peatlands (Ågren et al.

2007; Billett et al. 2006). Aitkenhead et al. (1999) showed that DOC fluxes appear to strongly reflect the size of the soil organic carbon pool in the catchment. Firstly, the DOC found in the Arcachon watercourses could partly originate from high molecular weight compounds such as humic and fulvic acids. Indeed, although the podzolisation process typically results in the net retention of DOC, mature podzols continuously release DOC to rivers (Aitkenhead and McDowell 2000). This DOC background found in river waters is relatively recalcitrant (Vestin et al. 2008). Secondly, high DOC concentrations as decomposable compounds might probably be released for instance from the hyporheic zone. This DOC is derived partly from the degradation of biota and from roots and mycorrhiza exudates (Lundström et al. 2000; Van Hees et al. 2005). After hyporheic transport, this DOC constitutes an appropriate substrate for bacterial mineralisation, leading in turn to large amounts of CO_2 (Schindler and Krabbenhoft 1998; Sobek et al. 2005). This assumption is reinforced by the significant positive correlations observed between DOC concentrations and $p\text{CO}_2$ values observed in some of the watercourses as the Lanton, Pontails, Tagon streams and Leyre River (Fig. 6a). In the Arcachon lagoon catchment, all of these DOC origins and processes are probably involved but further specific analysis using stable isotopes ($\delta^{13}\text{C}$ -DOC) should be done to determine the composition of DOC in the Arcachon catchment.

The Arcachon lagoon watercourses represented a source of CO_2 to the atmosphere throughout the year; water $p\text{CO}_2$ were always oversaturated and never reached equilibrium with the atmosphere as shown in many organic-rich natural waters (Billett and Moore 2008). In small watercourses with short water residence times, water chemistry is strongly driven by terrestrial-aquatic connections (Jones and Mulholland 1998; Jones et al. 2003). Consequently, the CO_2 that is attributable to instream respiration is typically minor and the major source of CO_2 originates from root and bacterial respiration in soils followed by discharge of CO_2 enriched groundwater (Castelle and Galloway 1990; Kling et al. 1992; Johnson et al. 2008). This outstream CO_2 production probably prevails at our study sites, as already been observed in many other small head watercourses in temperate, tropical and boreal systems (Jones et al. 2003; Billett and Moore 2008; Johnson et al. 2008; Rantakari et al. 2010). The overall very negative $\delta^{13}\text{C}$ -DIC values (Table 3; Fig. 3m–o) confirm that CO_2 production is fuelled by terrestrial carbon. Indeed, in a system where the soil CO_2 is primarily derived from the decomposition of C_3 plant organic matter, the CO_2 produced has a $\delta^{13}\text{C}$ value close to the initial substrate, with means of -30 to -24 ‰ (Vogel 1993). As CO_2 progressively degasses along the watercourse, $\delta^{13}\text{C}$ -DIC becomes less negative due to water–air isotopic equilibration (Polensaere and Abril

Fig. 6 Carbon cross-parameter plots for the nine sampled watercourses. **a** The partial pressure of CO₂ versus the dissolved organic carbon ($p\text{CO}_2/\text{DOC}$), **b** the stable isotope of DIC versus the partial pressure of CO₂ ($\delta^{13}\text{C-DIC}/p\text{CO}_2$) and **c** the stable isotope of DIC versus the total alkalinity ($\delta^{13}\text{C-DIC}/\text{TA}$). Only data from rivers where significant correlations were found are shown ($p < 0.05$)



2012). This is one of the main reasons for the significant negative correlations between $\delta^{13}\text{C-DIC}$ and $p\text{CO}_2$ observed in Renet and Lanton streams, Leyre River and both canals (Fig. 6b).

Another reason for the negative $\delta^{13}\text{C-DIC}$ values in the study watersheds is the predominance of silicate rock weathering over carbonate rock weathering, consistent with the low TA values (Table 3). In monolithic watersheds, Meybeck (1987) reported a TA value of $125 \mu\text{mol L}^{-1}$ for silicate watersheds, and of $3,195 \mu\text{mol L}^{-1}$ for carbonate watersheds. If we assume these concentrations as representative of these two types of rock weathering, we can calculate that the contribution of carbonate weathering to TA does not exceed 6 % on average in the nine watercourses (0–14 % in the Milieu and Ponteils streams, respectively). However, despite these modest contributions to TA, the effect of carbonate weathering on the isotope signature of the $\delta^{13}\text{C-DIC}$ source was significant. In the Ponteils and Tagon streams and the Leyre River, we observed a significant positive correlation between $\delta^{13}\text{C-DIC}$ and TA values (Fig. 6c). This is likely explained by the greater presence of carbonates in these three watersheds. The Ponteils stream was the only site where $\delta^{13}\text{C-DIC}$ was positively correlated with $p\text{CO}_2$ and TA (Fig. 6b, c), with higher values occurring in summer (Fig. 3a, d and m). This stream hosts a landfill site, which is known to greatly affect the composition of groundwaters (Canton et al. 2010). We can thus suspect concomitant TA and CO₂ inputs from this anthropogenic source, resulting to $\delta^{13}\text{C-DIC}$

DIC values close to those found in a carbonate-dominated watershed (Barth et al. 2003). Finally, in the Porge canal where tidal intrusion occurs, a contribution of marine DIC waters from the lagoon, with a $\delta^{13}\text{C-DIC}$ value of -0.62‰ on average (Polsenaere, unpublished data), could explain the occasional high values of $\delta^{13}\text{C-DIC}$ and TA (Fig. 3d, m).

Hydrology as the main driver of carbon concentrations and characteristics in small watercourses

Temporal patterns in all watercourses (Figs. 2, 3) and concentration *versus* discharge relationships in the Leyre River (Fig. 4) reveal distinct origins and transport mechanisms for organic and inorganic carbon. Indeed, carbon concentrations are closely related to water runoffs as shown in many other watercourse systems (Meybeck 1982; Hope et al. 1997; Atekwana and Krishnamurthy 1998; Ågren et al. 2007). A specificity observed in the nine sampled small watercourses is that organic carbon parameters generally show a relative temporal stability throughout the year due to the predominance of a constant terrestrial source. Despite this constant source, POC and particularly DOC are mostly transported in a pulsed mode during periods of high discharge in autumn or winter as observed in the Leyre River (Figs. 4e, g). This was consistent with results in other small forested headwater catchments (Rantakari et al. 2010). Preferential superficial flushing transport for DOC has also been reported in many

other temperate watercourses (Tranvik and Jansson 2002; Mulholland 2003); it generally leads in turn to a dominant soil and plant organic matter source of riverine DOC (Mantoura and Woodward 1983; Aitkenhead et al. 1999).

DIC parameters showed strong seasonal contrasts, linked to patterns both in CO₂ production and transfer through the soil, groundwaters, rivers and the atmosphere, and in rock weathering pathways. Indeed, DIC composition and flux can vary accordingly to the soil horizons that are affected by transport to surface waters (Michalzik et al. 2001). Such DIC transport implies important groundwater-surfacewater connections as in the Arcachon lagoon watershed and in other river-tributary stream systems (Atekwana and Krishnamurthy 1998). In these types of watersheds, DIC parameters in watercourses are controlled by two processes with opposite effects. During high discharge periods (autumn/winter), the streamflow is a mixture of surface runoff, subsurface or hypodermic runoff and groundwater flow (Probst 1985), which results in a decrease in DIC or TA concentrations (Fig. 4h, d). On the contrary, during low flow periods (summer/autumn), DIC or TA concentrations increase with increasing groundwater discharge (Hynes 1983). During low runoff, groundwater residence time is also increased and rock-weathering products accumulate; consequently, waters are enriched in DIC (Jones and Mulholland 1998).

The decrease in DIC concentrations with runoff found in the Leyre River was also observed in a similar temperate system, i.e. the Kalamazoo River (Southwest Michigan) (Atekwana and Krishnamurthy 1998). However, in contrast to our study watercourses, *p*CO₂ increased with runoff in the Leyre river with slightly higher values during winter periods (Figs. 3c, 4b), which suggests a different CO₂ production and transport pattern. Flooding of the Leyre River in winter apparently increased heterotrophic metabolism of terrestrial organic matter, at the edge of the river or in the river itself as reported in another forested catchment by Finlay (2003). The negative correlation between δ¹³C-DIC and runoff (Fig. 4j) is also consistent with the idea of a higher soil and C₃ litter mineralisation rate during flood events, combined with carbonate weathering in groundwater in summer. In contrast, in small streams, large CO₂ inputs from the soil and groundwater mostly occur during low-flow periods (Fig. 3a–c) and are also enhanced by a longer residence time of the water in soils and groundwater. Amiotte-Suchet et al. (1999) suggested that enhanced soil organic matter oxidation in summer induces high *p*CO₂ in soils and prevents atmospheric CO₂ from penetrating the soil. This is the reason why in all of the streams except the anthropogically impacted Pontails stream, δ¹³C-DIC was negatively correlated with *p*CO₂ (Fig. 6b). Similarly, excess CO₂ levels measured in the Arcachon streams, especially during summer, were

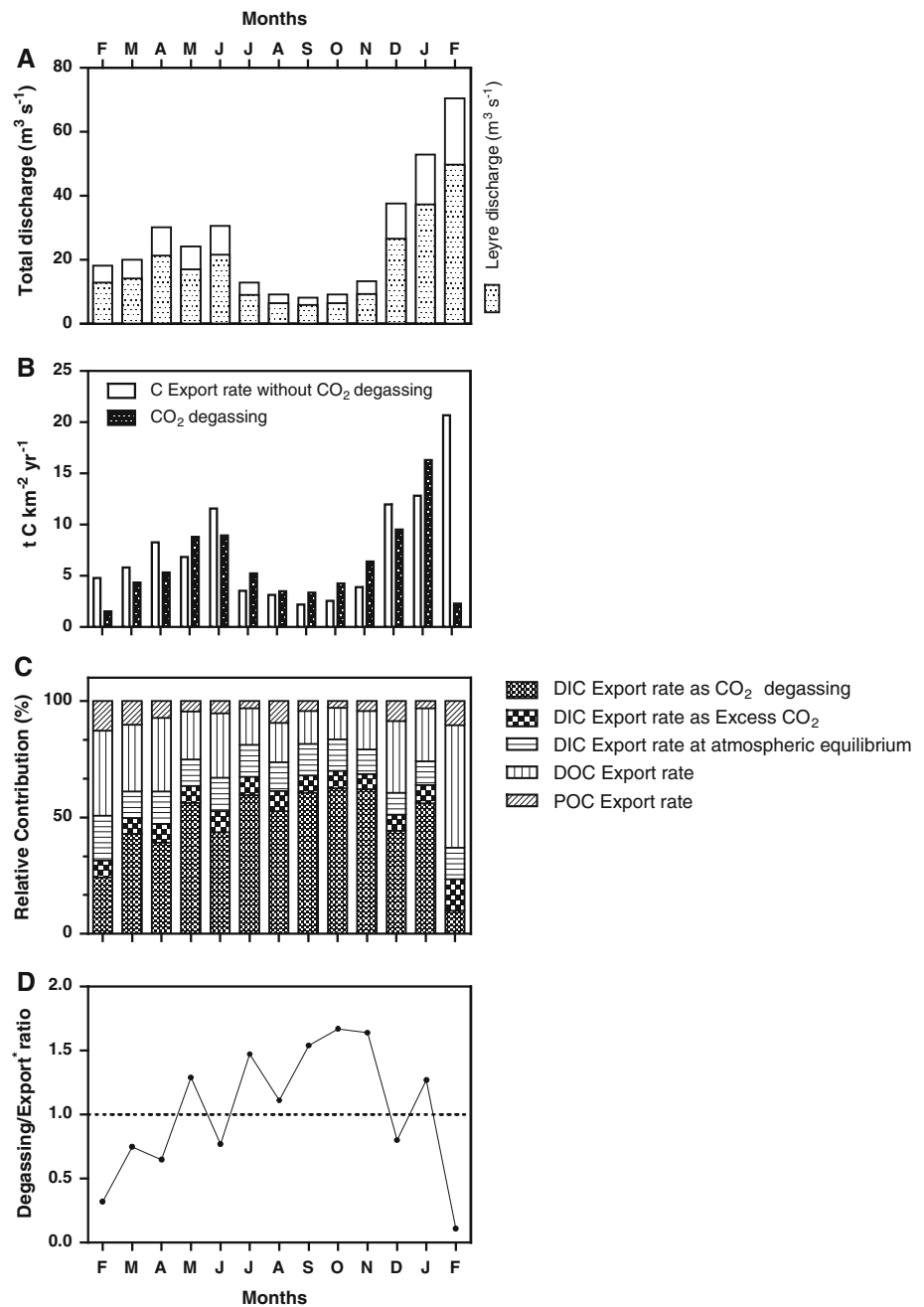
consistently larger than those measured in larger watercourses as the Leyre River. This result is in agreement with studies by Genereux and Hemond (1992) and Butman and Raymond (2011), who showed that small streams tend to emit large amounts of CO₂ per unit area. In contrast, in the winter and early spring, *p*CO₂ in these watercourses decreases due to the predominance of superficial flow, a minor contribution of groundwater to surface water and a lower water residence time in the soils and groundwater. As a consequence, this leads to lower amounts of CO₂ emitted to the atmosphere during the winter season.

Carbon export from the Arcachon lagoon watershed compared to temperate and global systems

We calculated the export of carbon from individual watersheds, including POC, DOC, DIC (at the atmospheric equilibrium and as excess CO₂) and CO₂ degassing along watercourses (Table 4), as well as the seasonal variations in the contribution of each term (Fig. 7). CO₂ degassing was calculated using an original modelling approach based on DIC isotopic equilibration with the atmosphere (Polensaere and Abril 2012). Gas transfer velocities obtained with this model ranged between 2 and 30 cm h⁻¹, consistent with those reported in other headwaters between 10 and 75 cm h⁻¹ (e.g. Butman and Raymond 2011). We observed large seasonal variations in the proportion of the different carbon species exported from the catchment throughout the year (Fig. 7). As DOC concentrations showed moderate seasonal changes, DOC export was driven by water discharge and was maximal in winter; in contrast, as DIC concentrations increased in summer, DIC export remained more stable throughout the year. As a result, the ratio between degassing and lateral transport to the Arcachon lagoon varied between 0.1 in winter and 1.6 in summer (Fig. 7).

On an annual basis, the relative proportions of each carbon species exported from the watershed of the Arcachon lagoon (Table 4) are in good agreement with those reported for temperate rivers (Meybeck 1993). A global data compilation by Alvarez-Cobelas et al. (2012) shows similar values for organic carbon export rates between 1.8 and 10.0 t C km⁻² year⁻¹ in temperate catchments; our data are also close to values reported by Abril et al. (2000) in other temperate rivers in Belgium (Table 5). However, some local specificities appeared at our study sites due to the dominance of podzols (Table 5). Indeed, organic carbon was exported predominantly in the form of DOC; this DOC export rate was higher than in a temperate forested catchment in central Japan with values ranged from 0.8 to 2.6 t C km⁻² year⁻¹ (Okazaki 2001; Kawasaki 2002). Similar DOC exports were also observed in temperate rivers of England and Wales (Worrall et al. 2007).

Fig. 7 Seasonal variations in the Arcachon lagoon catchment carbon export rates. **a** The monthly river discharges to the lagoon, with the part represented by the Leyre River, **b** comparison of the mean carbon export rate without CO₂ degassing, and the mean CO₂ degassing export rate ($t\ C\ km^{-2}\ year^{-1}$); **c** the relative contribution (%) of DIC export rates as CO₂ degassing, excess CO₂ and DIC at atmospheric equilibrium, and of dissolved organic carbon (DOC) and particulate organic carbon (POC) export rates to the mean carbon export and **d** CO₂ degassing export rate/carbon export rate without CO₂ degassing ratio (degassing/export*)



Globally, Alvarez-Cobelas et al. (2012) reported that DOC comprised on average 73 % of TOC export, close to the 80 % found in our study (Table 5). However, similar or even greater DOC export rates were measured in streams draining temperate peatlands, reaching more than 90 % of the organic carbon export rate (Billett et al. 2004; Dawson et al. 2004). This suggests a similar control on DOC export by the magnitude of organic carbon stored in the soils of peats and podzols. In the Arcachon lagoon catchment, POC export rates were typical of lowland regions, with weak erosion that leads to relatively clear waters (Meybeck 1982, 1993). These rates were slightly below the range found by

Worrall et al. (2007) in the rivers of England and Wales or by Dawson et al. (2004) in the peatland streams of Scotland (Table 5).

In our temperate podzolized catchment, DIC accounted for 58 % of the total carbon export rate. A similar dominant DIC export rate has been reported in the highly polluted Scheldt estuary (Abril et al. 2000). When compared to temperate peatlands, the Arcachon lagoon catchment has similar DIC export but lower organic carbon export rates. Also, export rates as excess CO₂ were within the range of values found in rivers of England and Wales (Worrall et al. (2007) and in peatland streams (Dawson

Table 5 Synthesis of carbon export rates from different catchment sizes and zones (temperate and global)

Site characteristics	Carbon Export rates	TOC Export	POC Export	DOC Export	DIC Export	Excess CO ₂ Export	DIC _{equilibrium} Export	CO ₂ degassing	References
Temperate lowland rivers (France)	2.0–3.7	0.8–9.3	0.1–1.6	0.7–7.8	1.2–25.6	0.1–3.1	0.5–3.1	0.5–19.4	This study
		36 %	7 %	29 %	21 %	8 %	13 %	43 %	
Temperate rivers (England and Wales)	9.5–11.4	5.3–7.2	1.9–2.6	3.4–4.6		2.1–2.9		4.2	Worrall et al. (2007)
		60 %	25 %	35 %		24 %		40 %	
Impacted temperate rivers (Belgium)	8.6–38.2	2.8–21.3	2.2–17.4	0.7–3.9	5.7–16.8	0.6–1.4	5.2–15.5		Abril et al. (2000)
		36 %	27 %	9 %	61 %	6 %	55 %		
Temperate lowland peatland streams (Scotland)	30.4 ± 5.7	28.3 ± 5.7			2.1 ± 0.5			4.6	Billett et al. (2004)
		93 %			7 %				
Temperate peatland streams (NE Scotland)	12.6–32.9	12.3–31.2	0.8–9.7	11.5–21.5		0.3–1.7			Dawson et al. (2004)
		95 %	23 %	72 %		5 %			
Temperate streams and rivers (US)								12.4 ± 3	Butman and Raymond (2011)
Temperate rivers (worldwide)		1.8–10.0	1.2–2.1	0.8–5.7					Alvarez-Cobelas et al. (2012)
Temperate rivers and streams								1.1–1.8	Aufdenkampe et al. (2011)
Global rivers and lakes		3.4						2.5	Cole et al. (2007)
								39 %	
Global with lakes								10.4	Tranvik et al. (2009)
								48 %	
Global with lakes and wetlands		3.0						24.5	Aufdenkampe et al. (2011)

The relative importance of POC export, DOC export, DIC export (DIC at equilibrium and the excess of CO₂ and CO₂ degassing) to carbon budgets is shown. Values in bold are expressed in t C km⁻² year⁻¹. The temperate (US and worldwide) and global carbon export rates have been obtained normalizing the carbon exports (in Pg C year⁻¹) found in the cited literature by the temperate (between 25°N and 50°N) and the global land surface areas, respectively (44.10⁶ and 134.10⁶ km², Aufdenkampe et al. 2011; Butman and Raymond 2011, supplementary information)

et al. 2004) (Table 5). In many studies, the portion of the DIC that is exported by river waters can largely be underestimated if the CO₂ degassing to the atmosphere is not taken into account (Cole et al. 2007; Tranvik et al. 2009; Butman and Raymond 2011). In the Arcachon lagoon catchment, export as CO₂ degassing accounts for 40–73 % of the total carbon export and was on the same order as the TOC export rate (Table 5). The range estimated in this study is also in good agreement with the CO₂ efflux value of 12.4 ± 3 t C km⁻² year⁻¹ found by Butman and Raymond (2011) in temperate streams and rivers in United States (Table 5). Finally, it is interesting to observe that the relative proportion between CO₂ degassing and TOC export in the study rivers were close to those reported at the global scale. Indeed, global TOC export by rivers to the ocean have been estimated at around

3 t C km⁻² year⁻¹ and CO₂ outgassing by rivers and lakes has been estimated at 10.4 (Tranvik et al. 2009) and at 24.5 t C km⁻² year⁻¹ when accounting for wetlands (Aufdenkampe et al. 2011).

Significance in the regional forest and lagoon carbon budgets

The total loss of carbon from the watershed of 6 g C m⁻² year⁻¹, with 2 g C m⁻² year⁻¹ as CO₂ degassing to the atmosphere, represents a very minor part of the carbon uptake by the forest inland. Indeed, the carbon fixation by the maritime pine forest of Landes Gascony is estimated to be 345 g C m⁻² year⁻¹ on average from 1996 to 2006 (EUR-OFLUX site of the Bray, 44°43′33.24″N, 0°46′33.72″W) (Loustau, personal communication). However, this total

carbon loss through the watercourses becomes more significant in some special years, like the year 2002, when the carbon uptake was only $57 \text{ g C m}^{-2} \text{ year}^{-1}$ (Jarosz et al. 2008). However, the Landes Gascony ecosystem seems to lose less carbon through the watershed compared to other similar ecosystems such as, for instance, northern peatlands (Billett et al. 2004). When considering the lagoon ecosystem, inputs from land by rivers and streams represent a flux of $10,494 \text{ t C year}^{-1}$ among which $6676 \text{ t C year}^{-1}$ is organic and $3818 \text{ t C year}^{-1}$ is inorganic. These fluxes are significant when compared, for instance, with primary production in the lagoon by the eelgrass *Zostera noltii* ($17,800 \text{ t C year}^{-1}$; Auby and Labourg 1996) and phytoplankton ($17,920 \text{ t C year}^{-1}$; Glé et al. 2008). However, Dang et al. (2009) have shown that riverine particulate organic matter ($1,142 \text{ t C year}^{-1}$, Table 4) contributes modestly (less than 15 %) to the diet of primary consumers, such as clams in the Arcachon lagoon (below 15 %). Similarly, Dubois et al. (2011) have shown that terrestrial POC contributes less than 20 % of the sediment organic matter (SOM) of the Arcachon lagoon. The riverine DOC, can potentially fuel the aquatic trophic chain through the microbial loop; however, its impact is probably limited due to the fast dilution of the freshwater with oceanic waters and the short flushing time of the lagoon with the tide. Similarly, riverine DIC inputs as excess CO_2 is probably a very minor contributor of the CO_2 degassing reported during emersion in the Arcachon lagoon (Polsenaere et al. 2012).

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