Biogeosciences Discuss., 8, 11165–11213, 2011
www.biogeosciences-discuss.net/8/11165/2011/
doi:10.5194/bgd-8-11165-2011

Biogeosciences
Discussions

The composition and flux of particulate and dissolved carbohydrates from the Rhône River into the Mediterranean Sea

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Received: 27 September 2011 – Accepted: 6 October 2011 – Published: 22 November 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Carbohydrates are important components of the carbon cycle and may be used as indicators of the origin and the diagenetic status of marine and terrestrial organic matter. Nevertheless, comprehensive studies of both particulate (PCHO) and dissolved (DCHO) carbohydrates in rivers are scarce, and the seasonal and interannual variability of these compounds in relationship to the bulk particulate (POM) and dissolved organic matter (DOM) is largely unknown. For the period 2007–2009, we sampled once per month POM and DOM and measured the total suspended matter (TSM), POM, DOM, PCHO, and DCHO for the Rhône River, which flows into the Mediterranean Sea. Using these measurements, we estimated for the above parameters annual fluxes for the period 2001–2010. The estimated carbohydrate fluxes averaged $0.061 \pm 0.043 \times 10^{10}$ moles C y^{-1} for PCHO and $0.041 \pm 0.0062 \times 10^{10}$ moles C y^{-1} DCHO, representing 8 % and 7 % of the annual flux of POC and DOC, respectively. During flood and low-water periods, POM variations were reflected into the PCHO pool, whereas this was not observed for DOC and DCHO, indicating a decoupling between particulate and dissolved organic matter. Our results also showed that flood and low-water periods may be differentiated using the ratios PCHO/DCHO and POC/DOC, which had a significant linear relationship.

Based on the carbohydrate abundances in both the PCHO and DCHO pools, we conclude that this material mainly derives from allochthonous sources (vascular plants, bacteria and soils). Moreover, during flood events, an enrichment in mannose in POM was observed, probably reflecting an angiosperm source (leaves or grasses). By expanding our results to the northwestern Mediterranean Sea (Gulf of Lions), we found that the total organic carbon (TOC) fluxes of the Rhône River accounted for ~1 % of the standing stock of seawater TOC. Considering that glucose is the most abundant carbohydrate in both particulate and dissolved organic matter pools (~33 %), its annual flux in the northwestern Mediterranean Sea was estimated to 19.2×10^8 moles glucose-C.

1 Introduction

Particulate and dissolved organic matter (POM and DOM) in river systems constitute a small pool of organic carbon (~0.02 Gt C, assuming an average riverine freshwater volume of 2000 km^3 and an average POM and DOM value of 5 $mg\,C\,l^{-1}$ ea.) nevertheless, it affects the global carbon budget not only because it serves as an important substrate for various organisms, including bacteria (Vannote et al., 1980; Sempéré et al., 2000; Bergfeld et al., 2009), but also because it constitutes a major source of reduced carbon to the world's oceans, with an annual flux of ~0.4 $GT\,y^{-1}$ (Meybeck, 1982, 1983; Aufdenkampe et al., 2011). Moreover, riverine POM and DOM play a key role in several physical (e.g. erosion, sediment transport and accumulation, floods) and chemical processes (e.g. weathering of rocks, adsorption and desorption reactions, coagulation, UV transformations) occurring within the drainage basin and the river itself (Vigier et al., 2001; Mopper and Kieber, 2002 and references therein; Dagg et al., 2004; McKee et al., 2004; Mallin et al., 2006).

Increasing attention is now being given to the dynamics and sources of POM and DOM in rivers because they significantly influence fisheries production and water quality (e.g. transport of pollutants, metal complexation) and also provide a record of natural and anthropogenic activities within the drainage basin (e.g. landscape sustainability, water clogging, river flow redistribution) (Kao and Liu, 1996, 1997; Ripl and Hildmann, 2000; Solomon et al., 2000). Nevertheless, the chemical composition and processing of riverine organic substances is not well known because it is a complex function of diverse physical, chemical, and biological processes; therefore, comprehensive analyses across dissolved and particulate forms are limited. In general, characterizations of riverine POM and DOM concern analyses of bulk chemical properties (e.g. elemental composition and stable carbon isotope analyses) or measurements of broad compound classes (e.g. total carbohydrates or total amino acids). Analyses of individual compounds are scarce and typically involve components of only a family of compounds (e.g. lipids). However, previous investigations in rivers have suggested that POM and

DOM are derived from decaying terrestrial plants (Opsahl and Benner, 1999) or in situ algal production (Kendall et al., 2001) and are thus rich in carbohydrates. Other minor compounds include nitrogen-free biomacromolecules such as terpenoids, humics, alkanes, phenols, tannins, and lignins (Degens et al., 1991; de Leeuw and Largeau, 1993; Kujawinski et al., 2002). Compared with carbohydrates, these nitrogen-free biomacromolecules are highly resistant to microbial degradation; however, photochemistry appears to control the decomposition of these biorefractory substances (Opsahl et al., 1999; Mopper and Kieber, 2002 and references therein; Benner et al., 2004). Because rivers are dynamic ecosystems, it is also important to study the composition of POM and DOM throughout the seasons to estimate the watershed mass transport (i.e. flux) of the organic matter. Again, most of the previous studies in rivers have been confined to seasonal bulk measurements of the concentrations of POM and DOM, stable radiogenic isotopes (e.g. $\delta^{15}N$, $\delta^{13}C$, $\Delta^{14}C$; Alin et al., 2008), lignin biomarkers (Hedges et al., 1986; Spencer et al., 2010) and very little is known about the temporal variability of other labile biochemicals (e.g. carbohydrates, amino acids; Hedges et al.,1994; Aufdenkampe et al., 2007). Freshwater inputs from rivers play a major role in the Mediterranean Sea because they significantly enhance the primary productivity through the transport of carbon and nutrients (Moutin et al., 1998; Sempéré et al., 2000), and they contribute to the balance of water inputs through the Strait of Gibraltar (Copin-Montégut, 1993; Bray et al., 1995). Since the damming of the Nile, the Rhône River is the main contributor of freshwater to the Mediterranean Sea, accounting for approximately 50 % of the total freshwater discharge into the sea (Margat, 1992; Bethoux and Gentili, 1999).

For the last decade, the Climate and Human-induced Alterations in Carbon Cycling at the River-seA connection (CHACCRA) group has been investigating the cycling and fluxes of bioactive elements, their potential impact on the climate, and the effects of hydrology changes on the Rhône River. However, these investigations focused on measurements of POM, DOM, nutrients, dissolved inorganic carbon (DIC), chromophoric dissolved organic matter (CDOM), total suspended matter (TSM) fluxes, and freshwater discharges (Coste and Raimbault, 1993; Sempéré et al., 2000; Pont et al., 2002; Para et al., 2010); therefore, little information regarding labile biochemicals (e.g. carbohydrates) in both particulate and dissolved fractions is currently available. In addition, previous data on the export of labile organic material and its relationship with the bacterial carbon demand, as previously assessed by Sempéré et al. (2000) for the Rhône River, cannot be validated if the relationships of organic chemical compositions to biological sources and the biodegradation mechanisms are not taken into account.

Here we report the first analyses of individual particulate and dissolved carbohydrates over a period of two years (2007–2009) along with DOM and POM measurements for the Rhône River. The organic material was collected during contrasting discharge conditions at a gauging station located approximately 50 km above the river mouth (see sampling site for details). Using these data, we estimated the carbohydrate fluxes from the Rhône River into the Mediterranean Sea over the period 2001–2010 and evaluated the major organic matter sources and degradation mechanisms occurring in the area. In this study, the objectives were the following:

1. to give an estimate of the annual fluxes of particulate and dissolved carbohydrates into the Mediterranean Sea;
2. to contrast the carbohydrate composition of POM and DOM collected during floods and low water discharge periods; and
3. to examine the distribution of the carbohydrates and determine whether carbohydrates can be used as tracers of organic matter sources and biological activities.

2 Study area and sampling

The Rhône River is 816 km long, drains an area of 100×10^3 km^2, and has average annual discharge of 53×10^9 m^3 of water and 10 ± 5 Mt of sediment (Ibanez et al., 1997; Sempéré et al., 2000; Pont et al., 2002; de Madron et al., 2003; Rabouille et al., 2008).

The river stage fluctuates by 2 to 6 m annually, with a peak discharge in early spring and late autumn and a minimum in summer (Pont et al., 2002). The main tributaries of the Rhône River include the Saône River (433 m^3 s^{-1}) that has an oceanic pluvial regime (highest discharge in winter), the Isère River (336 m^3 s^{-1}), and the Durance River (173 m^3 s^{-1}). Inundation events are not observed due to the excessive canalization (with rare exceptions occurring near the delta in the Camargues area); therefore, extensive interaction of river water with the surrounding floodplain and its vegetation is small.

The Rhône Delta is divided into two outlets, the Petit Rhône and the Grand Rhône, corresponding to 20 % and 80 % of the water flow, respectively (Ibanez et al., 1997). The water samples analyzed in this study were collected between May 2007 and June 2009 at the town of Arles, which is located on the Grand Rhône (47.5 km upstream of the Mediterranean Sea). The collection site is among those routinely studied over the last two decades by the French scientific community (Moutin et al., 1998; Sempéré et al., 2000; Pont et al., 2002; Sicre et al., 2008; Ollivier et al., 2010). Water samples were collected at the SORA observatory station near the Compagnie Nationale du Rhône (CNR; http://www.cnr.tm.fr/fr/) gauging station in Arles at a distance of 7 m from the right bank and 0.5 m under the surface (Eyrolle et al., 2011). The sampling site has a rectangular cross section (width of the river ~150 m) and previous studies have shown that the vertical and horizontal distribution of suspended matter generally remains uniform (Pont et al., 2002).

3 Methods

River water (1–2 l) was collected once per month in glass bottles that were cleaned with 2 % of HCl. The bottles were closed with Teflon-lined screw caps and kept in the dark at 4 °C before filtration. The samples were brought to the lab in dry ice (<24 h) and filtered through 0.7 µm retention-size filters (GF/F-47 mm; $P < 50$ mm Hg) to separate the particulate and dissolved fraction. Prior to filtration, the 0.7 µm GF/F filters were flushed with Milli-Q water and a small volume of the sample to minimize contamination (Yoro et al., 1999). Depending on the content of the organic matter in the samples, 200 to 500 ml of water was filtered for subsequent particulate carbon and carbohydrate measurements. In general, for each water sample, two filters were obtained, unless more sample was available ($n = 4$). Immediately after filtration, the filters were rinsed with a few ml of Milli-Q water to eliminate salts and then freeze dried. After lyophilization, the filters were dried in a desiccator for 24 h and then stored in the dark at −20 °C until analysis. All glassware (i.e. bottles, vials, ampoules, and pipets) used in this study, including GF/F filters and quartz wool, were combusted at 450 °C for 6 h prior to use.

For the dissolved carbon studies, the 0.7 µm-filtrates were re-filtered through 0.2 µm retention-size filter (polycarbonate filter-47 mm) previously rinsed with 5 % HCl, Milli-Q water, and 50 ml of the sample. Triplicate sub-samples were collected for DOC analyses and transferred into 10 ml-glass ampoules (Wheaton®), which were previously rinsed 3 times with sample. Then, 20 µl of H_3PO_4 acid was added as a preservative, and the ampoules were flame-sealed. The ampoules were stored in the dark at 4 °C until further analyses. The remaining sample was used for dissolved carbohydrate analyses and stored in polycarbonate bottles in the dark at −20 °C. Similarly, for the dissolved carbohydrate analyses, two sub-samples of the same water sample were analyzed, unless more sample was available ($n = 4$).

3.1 Particulate and dissolved organic carbon (POC & DOC) determination

To remove inorganic carbon, the GF/F filters with collected particles were covered with 100 µl of 0.5 N H_2SO_4 and then dried at 60 °C. The POC analyses on the filters were carried out using high temperature combustion (900 °C) performed on a CN Integra mass spectrometer (Raimbault et al., 2008). Analytical errors based on duplicate analysis were approximately 5 %.

DOC concentration was measured by high temperature combustion on a Shimadzu TOC 5000 analyzer, as described in Sohrin and Sempéré (2005). A four-point

calibration curve was constructed daily with standards prepared by diluting a stock solution of potassium hydrogen phthalate in Milli-Q water. To avoid random errors associated with day-to-day instrument variability, all of the samples from a given experiment were analyzed in a single day. The procedural blanks (runs with Milli-Q water) ranged from 1 to 2 µM C and were subtracted from the values presented here. Deep seawater reference samples (provided by D. Hansell; Univ. Miami) were run daily (43.5 µMC, CV = 2–3 %, $n = 4$) to check the accuracy of the DOC analysis. Total organic carbon (TOC) concentrations were estimated by summing POC and DOC.

3.2 Particulate and dissolved carbohydrates (PCHO & DCHO) determination

3.2.1 Carbohydrate extraction and isolation

Filters for the PCHO analysis were cut out with clean scissors and transferred to 40 ml glass tubes with Teflon-lined screw caps. A few ml of 12 M H_2SO_4 were added using a pipette, and the samples were allowed to sit for 2 h at room temperature, after which the acid was diluted to 1.2 M with Milli-Q water. Then, the samples were sparged with N_2 and hydrolyzed in a sand bath for 3 h at 100 °C (Mopper, 1977; Cowie and Hedges, 1984; Skoog and Benner, 1997). The hydrolysis was stopped by placing the tubes in an ice bath for 5–10 min.

Aliquots of 7 ml were neutralized with $CaCO_3$ (precombusted at 450 °C for 6 h) in 10 ml glass tubes. Prior to neutralization, adonitol, at a final concentration of 1 µM, was added to the sample as an internal standard to estimate the losses during the neutralization steps. After neutralization, the samples were centrifuged 3–4 times at 4000 rpm for 5 min, and the supernatant was filtered through quartz wool and pipetted into scintillation vials. The vials were frozen at 4 °C until time of analysis (this never exceeded 24 h).

For the DCHO analysis, two aliquots each 9 ml of the 0.2 µm-filtered sample were freeze dried, and the obtained powder was treated using the above procedure (i.e.

hydrolysis, and neutralization). Because of the low salinity (<1 ‰) of the sampling site, our water samples did not require any further treatment (e.g. desalination steps).

3.2.2 Liquid chromatography

A Dionex ICS-3000 anion exchange chromatograph fitted with a pulsed amperometric detector (HPAEC-PAD) was used for all carbohydrate analyses. The sample injection was performed with an AS 50 (Dionex) autosampler equipped with a 250 µl sample loop. The separation of the carbohydrates was performed on a Dionex CarboPac PA-1 analytical column (250 × 4 mm I.D.; anion exchange capacity 100 µequiv.) and a Dionex CarboPac PA-1 guard column (50 × 4 mm I.D.). An amino trap (30 × 3 mm I.D.) was placed before the guard column to retain amino acids and similar compounds, which may interfere with the carbohydrate analysis. The analytical column, the guard column, and the amino trap were placed into a thermal compartment. The temperature of the compartment was set at 17 °C, which was found to be optimal for the separation of the monosaccharides in previous studies (Panagiotopoulos et al., 2001; Panagiotopoulos and Sempéré, 2005a). Sugars were detected by an electrochemical detector (ED40-Dionex) set in the pulsed amperometric mode. The detector was equipped with a flow cell containing a gold working electrode and an Ag/AgCl reference electrode. The waveform used in this study was standard quadruple-potential and the settings were as follows: $E_1 = 0.1$ V ($T_1 = 0.4$ s), $E_2 = -2$ V ($T_2 = 0.01$ s), $E_3 = 0.6$ V ($T_3 = 0.01$ s) and $E_4 = -0.1$ V ($T_4 = 0.6$ s). Data acquisition and processing were performed using the Dionex software Chromeleon.

3.2.3 Analytical conditions

Eleven individual monosaccharides were detected in the hydrolysates of the particulate and dissolved organic material, including deoxysugars (fucose, and rhamnose), pentoses (arabinose, ribose, and xylose), one amino sugar (glucosamine), hexoses (galactose, glucose, and mannose), and acidic sugars (galacturonic, and glucuronic acids).

Neutral and amino sugars were separated with an isocratic 19 mM NaOH elution at 17 °C (eluent A: 20 mM NaOH; eluent B: Milli-Q water) following Panagiotopoulos et al. (2001). Acidic sugars (i.e. uronic acids) were detected in a separate analysis using a gradient of two mobile phases (eluent C: 1 M NaOH; eluent D; 0.5 M CH_3COONa). The gradient program used for this chromatographic separation was as follows:

1. 0–12 min 62.5 % eluent B, 7.5 % eluent C, 30 % eluent D
2. 12–13 min 80 % eluent B, 20 % eluent C (ramp 5)
3. 13–20 min 80 % eluent B, 20 % eluent C (end of the analysis).

At the end of each analysis (neutral and/or acid sugars) the column was regenerated with 1 M NaOH for 35 min and then equilibrated (~20 min) with the initial eluent conditions of the analysis. The flow rate was set at 0.7 ml min^{-1} for both neutral and acidic sugars analyses.

3.2.4 Calibration, precision, detection limit, blanks, and recoveries

The calibration range we used in this study varied from 50 nM to 10 µM to cover the entire range of concentrations found in the dissolved and particulate samples. Therefore, we constructed two calibration curves: one ranging from 50–1000 nM and the other from 1 to 10 µM. The response was linear for all sugars, as shown by the high correlation coefficients ($r > 0.99$), suggesting that their quantitative determination was feasible within this concentration range.

The precisions, as shown by the coefficient of variation (CV), were 5–10 % and 0.9–2.0 % ($n = 6$) for the peak area and retention time, respectively, for repeated injections of a standard solution of 50 nM per sugar. Repeated injections ($n = 6$) of a typical particulate sample resulted in a CV of 4–6 % and 0.03–0.21 % for the peak area and retention time, respectively, for all sugars. The detection limit of the method (S/N = 3) was approximately 10 nM for neutral and amino sugars, whereas for acidic sugars it was 20 nM.

The procedural blank consisted of Milli-Q hydrolyzed in the same manner as the samples (see above). Sugars were not detected in the blank. The only contaminant detected was eluted as a relatively large peak immediately after the xylose (>30 min) and probably corresponds to the neutralization product of H_2SO_4 and $CaCO_3$ (i.e. SO_4^{2-}). This peak also appeared in the analysis of the acidic sugars and was eluted at 10.9 min just after the galacturonic acid. Adonitol was recovered at a percentage of 80–95 %; however, we have chosen not to correct our original data.

3.3 Statistics

Principal components analysis (PCA) was used to reduce the multidimensional nature of the data set and to evaluate the interrelationships among the carbohydrates (variables). PCA has been successfully used in previous studies to assess the origin or the degradation status of organic matter (Ingalls et al., 2003; Wakeham et al., 2002; Panagiotopoulos and Sempéré, 2005b; He et al., 2010). The number of observations in this study was 250 (10 sugars × 25 samples), which clearly permitted the use of this statistical approach. PCA was performed using the individual carbohydrate concentrations (i.e. glucose, and mannose) as well as the POC and DOC data (Table 1). The PCA statistics were performed using the statistical package XLSTAT 2010.2 (Microsoft Excel add-in program).

4 Results

4.1 Bulk parameters

4.1.1 Water discharge (*Q*), total suspended matter (TSM), organic carbon content of particles (OC %), POC, and DOC concentrations

The Rhône River exhibits two periods of peak discharge: a spring peak related to snowmelt in the Alpine and Massif Central watersheds and a fall peak related to storm

events originating from humid air masses over the Mediterranean Sea. During the sampling period (May 2007–June 2009), discharge fluctuated from 1233 to 4800 $m^3 s^{-1}$, whereas TSM concentrations varied between 6 and 1044 $mg\,l^{-1}$, with peak values occurring during the flood of February 2009 (Table 1). Less intense flood episodes occurred in April, May, September and October 2008. The flood event observed in late May 2008 was due to artificial releases of water from the Serre-Ponçon dam located approximately 250 km north of the sampling station (Eyrolle et al., 2011). During the flood events of 2008, discharge varied from 2983 to 3822 $m^3 s^{-1}$, corresponding to TSM concentrations of 88–1044 $mg\,l^{-1}$ (Table 1).

The organic carbon content (OC % wt) of the particles ranged from 1.8 to 6.4 % (Table 1) and was similar to that reported in previous studies in the Rhône (Cauwet et al., 1990; Sempéré et al., 2000) and other riverine systems (Ittekkot, 1988; Hedges et al., 1994). The POC concentrations ranged from 16 to 2334 µM C, with the highest values recorded during the flood events (Table 1; Fig. 1a). In agreement with previous investigations, the OC % correlated well with TSM, according to the formula $OC\,\% = -0.005 \ln TSM + 0.054$ ($r = 0.71$, $n = 24$, $p < 0.0001$), and likely results from the combination of autochthonous organic particles with land-derived material and resuspended particles (Meybeck et al., 1982; Thurman, 1985; Ittekkot, 1988; Sempéré et al., 2000).

Finally, DOC concentrations averaged 134 ± 30.6 µM C, which was lower but in the same order of magnitude as seen in previous studies in the Rhône (Cauwet et al., 1990; Sempéré et al., 2000). The DOC/POC ratios reached minimum values (0.1–0.6) during flood episodes, which indicates a higher POC transport compared with DOC during these events (Table 1).

4.1.2 Particulate and dissolved carbohydrate concentrations (PCHO & DCHO) and their contribution to the organic carbon pool

PCHO concentrations ranged from 0.22 to 11 µM and, similar to POC, were higher during the flood episodes (2.4–11 µM; Table 1). The particulate sugars represented 3 to 18 % of POC (PCHO-C/POC %); however, the maximum observed values did not coincide with the flood episodes (Table 2). Our results are within the expected range of values measured in other riverine systems in Europe (Danube and Tech rivers; da Cunha et al., 2002; Reschke et al., 2002), America (Amazon, Paraná, and São Francisco rivers; Depetris and Kempe, 1993; Hedges et al., 1994; Jennerjahn and Ittekkot, 1999), Africa (Niger and Orange rivers; Thurman, 1985), and Asia (Ganges and Indus rivers; Ittekkot et al., 1982; Thurman, 1985;).

The DCHO concentrations averaged 1.5 ± 0.53 µM and accounted for 4 to 13 % of DOC (Tables 1 and 3). Our results are similar to previous values reported from the Parana (4–25 %, Depetris and Kempe, 1993), Williamson (2 %, Sweet and Perdue, 1982), Niger (0.3–21 %, Thurman, 1985) and Mackenzie (2.7–21 %, Thurman, 1985) rivers, and in ultrafiltrated organic matter collected from Arctic rivers (2–4 %, Amon and Benner, 2003) or the Amazon (3–5 % Hedges et al., 1994). Similar to the DOC/POC ratios, DCHO/PCHO reached minimum values (0.1–0.8) during flood episodes, which indicated higher particulate carbohydrate transport than dissolved carbohydrates during these events (Table 1).

4.1.3 Relations between water discharge and TSM, POC, DOC, PCHO and DCHO

Daily TSM, POC, DOC, PCHO and DCHO loadings were calculated by multiplying their concentrations by the daily water discharge (Q) during the sampling period. The discharge rate correlated very well with TSM, POC and PCHO fluxes as shown by the correlation coefficients:

$$\text{Log (TSM)} = 3.3\log(Q) - 9.22\ (n = 25, r = 0.90, p < 0.0001)$$

$$\text{Log (POC)} = 2.63\log(Q) - 6.65\ (n = 25, r = 0.86, p < 0.0001)$$

$$\text{Log (PCHO)} = 2.14\log(Q) - 6.93\ (n = 25, r = 0.86, p < 0.0001)$$

$$\text{Log (DOC)} = 0.23\log(Q) + 1.34\ (n = 24, r = 0.44, p < 0.05)$$

Similar linear relationships between TSM, POC and DOC and Q have already been reported for the Rhône (Sempéré et al., 2000; Pont et al., 2002; Eyrolle et al., 2011)

and other riverine systems (Meybeck et al., 1982; Ittekkot and Arain, 1986; Hedges et al., 1994), indicating that the concentrations of these parameters are controlled by the water discharge. In our study, Q did not correlate with DCHO. As the log/log relationship was found not to be significant, DCHO transport (see below) was estimated by multiplying the average concentration (Table 1) by the corresponding river discharge. The DCHO error is given by the standard deviation found for the average DCHO concentration. The same approach has already been used by Sempéré et al. (2000) to estimate annual dissolved inorganic carbon (DIC) fluxes.

4.1.4 Annual fluxes of TSM, POC, DOC, PCHO and DCHO

In this study, we estimated the annual fluxes of carbohydrates along with POC and DOC to evaluate the exported amount of "labile" organic matter to the Mediterranean Sea in particulate and dissolved forms. We used the above equations and calculated TSM, POC, DOC, PCHO and DOC fluxes for each day from 2001 to 2010 (Fig. 2; Table 4). Then these fluxes were corrected by the factor given by Ferguson (1987), which gives a better estimate of the river loads (Smith et al., 1996).

From January 2001 to December 2010, the average total discharge was estimated to be $46 \pm 8.5\,\text{km}^3\,\text{y}^{-1}$, whereas $9.21 \pm 8.5 \times 10^6\,\text{t}\,\text{y}^{-1}$ of suspended solids reached the Mediterranean Sea (Table 2). These values are similar to those reported by Sempéré et al. (2000) (period 1987–1996; $54 \pm 12\,\text{km}^3\,\text{y}^{-1}$; $9.90 \pm 6.53 \times 10^6\,\text{t}\,\text{y}^{-1}$) or Pont et al. (2002) (period 1967–1996; $53.6\,\text{km}^3\,\text{y}^{-1}$; $7.4 \times 10^6\,\text{t}\,\text{y}^{-1}$), which were also estimated after extrapolation from log/log relationships. Our results are lower than those that Eyrolle et al. (2011) estimated from 2001–2003, which is due to the fact that the latter authors also included in their measurements the contribution of the "petit" Rhône, which carries approximately 20 % of the total liquid flux.

The calculated average POC and DOC fluxes were 0.784 ± 0.530 and $0.61 \pm 0.13 \times 10^{10}$ moles C y^{-1}, respectively (Table 2). These values are approximately twofold lower than those estimated by Sempéré et al. (2000) (period 1987–1996; $\text{POC} = 1.62 \pm 0.92 \times 10^{10}$ moles C y^{-1}; $\text{DOC} = 1.08 \pm 0.30 \times 10^{10}$ moles C y^{-1}), but similar to those reported by Cauwet et al. (1990) (period 1986; DOC = 0.8–1.1 × 10^{10} moles C y^{-1}).

Finally, the PCHO-C fluxes (0.061 ± 0.043 × 10^{10} moles C y^{-1}) were higher than those of their dissolved counterparts, DCHO-C (0.043 ± 0.019 × 10^{10} moles C y^{-1}), indicating that carbohydrates are primarily exported to the Mediterranean Sea in the particulate form.

4.2 Molecular composition of carbohydrates

4.2.1 Distribution of carbohydrates in POM and DOM

Aldohexoses were the most abundant compound class (0.3–6 µM) of carbohydrates in POM and accounted for approximately half of the PCHO (54 ± 6 %). Aldopentoses were second in abundance (29 ± 7 %), followed by deoxysugars (13 ± 2 %), amino sugars (4 ± 1 %) and uronic acids (1 ± 1 %). Glucose was by far the most abundant sugar, averaging 33 ± 7 % of the PCHO, followed by galactose (16 ± 4 %), xylose (12 ± 2 %), and arabinose (12 ± 6 %) (Table 2). Mannose was next in abundance (8 ± 2 %) followed by fucose and rhamnose with equivalent contributions (6–7 %) to the PCHO pool. Finally, glucosamine, ribose, and galacturonic acid were the least abundant carbohydrates accounting for <5 % of the PCHO (Table 3). Ribose is a fragile monosaccharide and generally is destroyed during acid hydrolysis. Therefore, the results presented here should be looked as minimum ribose concentrations.

Similar to POM, aldohexoses were the most abundant compound class in DOM, accounting for approximately half of the DCHO (53 ± 7 %). Aldopentoses contributed 21 ± 5 % to the DCHO pool, followed by deoxysugars (14 ± 4 %), uronic acids (6 ± 3 %), and amino sugars (6 ± 2 %). Glucose was again the most abundant sugar, averaging 33 ± 7 % of the DCHO, followed by mannose (11 ± 3 %), galactose (11 ± 4 %), and arabinose (9 ± 4 %) (Table 3). Xylose, rhamnose and fucose accounted for ~7–7.5 % of the DCHO. Ribose was generally below the detection limit, whereas galacturonic acid was higher in abundance (6 ± 3 %) in the DCHO pool than the PCHO (Tables 2 and 3).

5 Discussion

5.1 Fluxes and lability of organic matter in the Rhône River

Previous investigations assessed POM lability after the classification of TSM into nine groups of a specific range (0–15, 15–50, 50–150 mg l^{-1}, etc.) (Meybeck, 1982). This classification was based on the carbohydrate and amino acid measurements in POM, which are generally considered to be labile compounds (susceptible to bacterial degradation), and because of their quantitative significance in POM (Moran and Hodson, 1989; Smith and Hollibaugh, 1993; Ittekkot 1988; Wakeham et al., 1997; Panagiotopoulos and Sempéré, 2005b and references therein; He et al., 2010). We used the same classifications and estimated the labile POC (LPOC) fluxes into the Gulf of Lions over the period 2001–2010 from the calculated TSM concentrations.

Our results showed that LPOC was mainly distributed between TSM concentrations of 0–15 mgl $^{-1}$ (57 % of the data) and 15–50 mg l^{-1} (22 % of the data). Over the 10 yr estimation, the LPOC fluxes ranged from 0.05 to 0.26 × 10^{10} moles C y^{-1} (average 0.14 × 10^{10} moles C y^{-1}) and were approximately six fold lower than those of the POC fluxes, but two fold higher than those of the PCHO-C fluxes (Table 4). The LPOC fluxes accounted for 11–28 % (av. 18 %) of the bulk POC. The latter average value is approximately two fold higher than the average value of the PCHO-C fluxes/POC fluxes (~8 %; Table 4) over the period 2001–2010. This difference may be attributed to the presence of other labile compounds (e.g. amino acids, nucleic acids) in POM, which are included in the LPOC estimates.

During the sampling period, we found two significant relationships between PCHO-C and POC, and PCHO-C and LPOC (Fig. 3a, b). This result is in agreement with previous studies highlighting the role of carbohydrates as active labile components of the riverine POM pool (Ittekkot and Arain, 1986; Ittekkot, 1988; Depetris and Kempe, 1993; Hedges et al., 1994, Bergamaschi et al., 1999). Although our data cover only a two year period, this is the first time these relationships have been established in a riverine system; thus, it might be useful to evaluate the carbohydrate content of POC or the amount of LPOC in riverine particles and *vice versa*. Further measurements of amino acids or other labile compounds in POM in rivers may also help to improve or establish similar relationships.

The refractory particulate organic carbon (RPOC) fluxes were calculated after the subtraction of the LPOC fluxes from the bulk POC fluxes. Our results showed that the RPOC fluxes ranged from 0.17 to 1.69×10^{10} moles C y^{-1} (average 0.64×10^{10} moles C y^{-1} or 0.08 Tg C y^{-1}), representing 72 to 89 % of the bulk POC (av. 80 %). The RPOC contribution to the bulk POC falls into the range of 55–95 % reported for several world rivers (Ittekkot, 1988) and matches well with the RPOC found in the Orinoco (~80 %), Zaire (~80 %), Indus (~80 %), and Brahmaputra (~80 %) rivers. RPOC survives microbial degradation and is mostly lost in estuaries, although a small fraction is incorporated into coastal marine sediments (Hedges and Keil, 1995; Prahl et al., 1994; Hedges et al., 1997; Keil et al., 1998).

Similar to POM, riverine DOM is composed of old and young material (i.e. labile DOC; LDOC); nevertheless, the young component of DOM predominates, as shown by radiocarbon measurements (Raymond and Bauer, 2001). Biodegradable riverine DOM originates mainly from autochthonous in situ production, whereas refractory DOM results from POM solubilization and/or the weathering of sedimentary rocks and soils (Smith and Hollibaugh, 1993; Hedges and Keil, 1995; Kao and Liu, 1996; Keil et al., 1997; Prahl et al., 1998; Schillawski and Petsch, 2008).

In contrast to LPOC, which can be estimated by the TSM particle range (see above), literature data for LDOC in rivers do not exist. Nevertheless, if we assume that sugars constitute the major fraction of the LDOC (DCHO-C/DOC = 7 %; Table 3), the average flux of LDOC would average 0.043×10^{10} moles C y^{-1}, which is in agreement with the annual flux of DCHO (0.041×10^{10} moles C y^{-1}; Table 4). The remaining refractory-DOC (RDOC) can be calculated as the difference between DOC and LDOC and equals 0.57×10^{10} moles C y^{-1}.

Our LDOC fluxes are approximately four times lower than that of 0.16×10^{10} moles C y^{-1} reported by Sempéré et al. (2000); however, it is important to

note that the latter authors estimated LDOC fluxes using literature data by applying a mean of LDOC/DOC = 15 % (Spitzy and Ittekkot 1991; Volk et al., 1997). In contrast, our LDOC fluxes are likely underestimated because no amino acids were measured in this study. Unfortunately, no amino acid data are available for the Rhône River; nevertheless, previous investigations have suggested that amino acids generally account for 1–3 % of DOC in rivers (Lara et al., 1998; Amon and Meon, 2004; Duan and Bianchi, 2007). Applying a LDOC/DOC ratio of 10 % (DCHO-C/DOC + DAA-C/DOC), the LDOC flux in the Rhône River would average 0.061×10^{10} moles C y^{-1}, which is good agreement with the average value reported by Sempéré et al. (2000).

5.2 Seasonal and interannual variability of bulk carbohydrates

The high PCHO-C/POC values (>9 %) observed in the spring of 2008 (11, 25 March; April 2008) and 2009 (3, 10 March; 7 April) along with the low TSM concentrations (6–27 mg l^{-1}) suggest a predominantly autochthonous input of POM such as in situ primary production (Fig. 4). This is in agreement with previous investigations in which LPOC is generally associated with low TSM concentrations (Meybeck, 1982; Ittekkot and Arain, 1986; Ittekkot, 1988; Sempéré et al., 2000). Although chlorophyll data were not available during the sampling period, previous chlorophyll measurements over a period of 20 yr (1980–1999) showed that fresh organic matter is regularly produced in spring and summer. In agreement with these observations, Harmelin et al. (2010) reported that the low C/N ratios (C/N < 8) associated with the high organic carbon content (% C ~ 4 %) in POM are mainly observed in the spring and summer, coinciding with higher growth of diatoms and chlorophytes. In contrast, in the fall and winter, the C/N ratios were higher (>8) and were associated with low % C (~2 %), suggesting the predominance of allochthonous terrestrial material in POM (Harmelin et al., 2010).

The lowest OC % content and PCHO-C/POC ratios were observed during flood episodes and were associated with higher TSM concentrations (Tables 1, 2; Fig. 4), which further indicates that POM is mainly derived from allochthonous material originating from soils or litter in the drainage area. The sugars in this allochthonous POM are probably associated with humic substances (Koivula and Hänninen, 2001; Fischer et al., 2007) or derived from highly degraded cellulosic material (Moran and Hodson, 1989). Although high phytoplanktonic production occurs in the spring, the flood events observed in this period generally diminish the production of autochthonous material because of the reduced light penetration to the river (Thurman, 1985).

The PCA was further used to assess the differences in the carbohydrate content of the particulate samples. Two principal components were identified that accounted for almost 98 % of the total variance in POM (Fig. 5a). Our results showed that, during flood events, carbohydrates exhibited a distinct molecular composition, which is typical of each flood event and clearly differs from that of low-water periods. Figure 5a also indicates that, in low-water periods, carbohydrates exhibit compositional similarities to POM (the points cluster in the middle of the figure), which probably suggests a common source.

Earlier investigations in the Rhône River suggested that phytoplankton contributes only 10 % to the annual POC, whereas soil organic matter, an allochthonous material, is the major source of POC (Harmelin et al., 2010). Therefore, it appears that POM at the sampling site has an allochthonous signature, which makes imperceptible the organic matter produced within the river (autochthonous source). In agreement with these findings, other studies based on the δ^{13}C measurements of fatty acids indicated that POM consists of a mixture of different sources with a strong contribution from terrestrial plants (allochthonous source) and a smaller input from freshwater microalgae, mostly diatoms (Bourgeois et al., 2011).

In contrast to PCHO, the DCHO concentrations did not exhibit large variations between flood and low-water events, which further indicates that flood episodes mainly affect the PCHO pool rather than DCHO pool (Fig. 1b; Table 3). In accordance with that, our PCA results showed that the DCHO concentrations during flood events were generally similar to the DCHO concentrations measured during low-water events (Fig. 5c). The PCA also showed that the DCHO concentrations could explain only 55 % (PC1 + PC2) of the variability in the DOM pool, which probably indicates different DCHO sources (Fig. 5c; see later discussion).

Over the two-year period of study, DCHO dominated over PCHO throughout low water events (DCHO/PCHO > 1), indicating a higher DCHO transport during the low discharge periods (Table 1). A significant positive relationship between DOC/POC and DCHO/PCHO was established in this study (Fig. 6), further suggesting that the carbohydrate pool (PCHO + DCHO) covaries with the bulk of organic matter (TOC = POC + DOC), although total carbohydrates make up on average a small percentage of TOC (15 %; Tables 2 and 3).

5.3 Carbohydrate compositional patterns

The patterns of occurrence of the individual carbohydrates over the period studied indicated that glucose was the dominant sugar in PCHO and DCHO (~33 % in average; Tables 3, 4). Glucose was also found to be the dominant carbohydrate in the Parana (PCHO 30–45 %; DCHO 35–45 %; Depetris and Kempe, 1993), Caroni (DCHO 50 %; Ittekkot et al., 1982), Niger (DCHO 45 %; Ittekkot et al., 1982), Orinico (DCHO 28 %; Ittekkot et al., 1982), Amazon (PCHO 35–50 %, DCHO 25 %; Hedges et al., 1994), and São Franscisco rivers (PCHO 35–60 %; Jennerjahn and Ittekkot, 1999). With a few exceptions, glucose generally accounted for >35 % of the DCHO during flood events compared to the low-water discharge periods (Table 3). This enrichment of glucose in the DCHO pool is probably due to the weathering of soils or the transport of carbohydrate polymers (e.g. cellulose) from vascular plants (Cowie and Hedges, 1984; Fischer et al., 2007).

Galactose was the second most abundant carbohydrate in PCHO, whereas mannose and galactose contributed approximately equally (~11 %) to the DCHO pool (Tables 3 and 4). A survey of several world rivers revealed that the second most abundant carbohydrate in the DCHO and PCHO pools was fructose (Ittekkot, 1982; Depetris and Kempe, 1993). In our study, we did not detect fructose in either the dissolved or particulate carbohydrate pools. Nevertheless, these studies showed that galactose accounted for 8–10 % of DCHO, which is in agreement with our results.

In a terrestrial environment, galactose may derive from various sources, such as non-woody plant tissues, phytoplanktonic cell walls and bacteria in soils (Hecky et al., 1973; Cowie and Hedges, 1984; da Cuhna et al., 2002). The higher abundances of galactose in the PCHO pool (av. 16 %) than in the DCHO pool (av. 11 %) most likely suggest a phytoplanktonic influence in POM (see also the previous discussion). Other studies have found an enrichment of galactose in the particulate material in a coastal environment and/or sediments where primary productivity is generally high (Cowie and Hedges, 1984; Bergamaschi et al., 1999; He et al., 2010).

Although mannose was not among the most abundant carbohydrates in the PCHO pool, its contribution to the PCHO reached maximum values during flood events (except 22 April 2008; Table 2). Figure 7a shows a significant correlation between mannose in POM and discharge. This relationship indicates an enrichment in mannose of the particulate carbohydrate pool during high discharge periods, which probably reflects a local temporal influence by angiosperms (i.e. flowering plants). The reported percentages of mannose for angiosperms (leaves or grasses) fall into the range of 8–20 % and are similar to our results (Cowie and Hedges, 1984).

Arabinose and xylose were more abundant in the PCHO pool than in the DCHO pool (Tables 2, and 3) indicating the presence of structural heteropolysaccharides in both the POM and DOM compartments (i.e. arabinogalactans or arabinoxylans). The lower abundances of arabinose and xylose in the DCHO pool compared with the PCHO pool may reflect their different potential hydrolysis rates by extracellular enzymes as suggested by Arnosti (2000).

Fucose and rhamnose contributed approximately equally to both the PCHO and DCHO pools (6–7 %; Tables 2 and 3). These two carbohydrates were strongly associated in both POM and DOM, as shown by the strong correlations coefficients (POM: Fuc (µMC) = 1.62, Rha (µMC)–0.14, $r = 0.98$, $n = 25$, $p < 0.0001$ and DOM: Fuc (µMC) = 1.19, Rha (μMC)–0.08, $r = 0.94$, $n = 21$, $p < 0.0001$). Although fucose and rhamnose may have various sources, such as vascular plants, planktons and bacteria, their strong association and their high abundance in POM and DOM pools (av. 18–21 %, calculated on a glucose-free basis) clearly suggest a bacterial contribution

(Cowie and Hedges, 1984, Bergamaschi et al., 1999; Ogier et al., 2001) (Fig. 5d). Moreover, the high abundances of deoxysugars strongly point toward an advanced decomposition status of the organic material (see later discussion). Amino sugars and ribose are not the major structural components of vascular plants; they generally are components of the microbial biomass in plant detritus, particularly in more highly degraded material (Hicks et al., 1994). Glucosamine and ribose formed a cluster close to fucose and rhamnose, which further reinforces the idea that these carbohydrates probably have a common bacterial origin and are typical of highly degraded organic material in POM and DOM (Fig. 5d).

In contrast to DOM, all carbohydrates in POM formed a compact cluster (except galacturonic acid, Fig. 5c). This result may suggest a common origin or a mixture of different origins; nevertheless, as indicated above, the allochthonous signature appears to dominate.

5.4 Carbohydrate origins in the Rhône River

The origins of carbohydrates in both the POM and DOM pools were further assessed using the carbohydrate compositional patterns, similarly to previous investigations (Cowie and Hedges, 1984; da Cunha et al., 2002; Guggenberger et al., 1994; He et al., 2010). Because glucose composition may vary with sources, the following calculations were performed on a glucose-free basis.

Figure 7b displays a spectrum between (Fuc + Rha)/(Ara + Xyl) and Ara + Gal + GalUA % for both POM and DOM. The (Fuc + Rha)/(Ara + Xyl) ratio has been used as an indicator of soil and/or bacterial-derived organic matter (when >0.5) and of plant derived carbohydrates (when <0.5) (Guggenberger et al., 1994). Our results showed that most of the DOM carbohydrate data, including the flood episodes, exhibit values higher than 0.5, which further suggests a soil or bacterial origin. In contrast, more than the half of the POM carbohydrate data exhibited values <0.5, pointing to a vascular plant origin.

Wood may be differentiated from non-woody vascular plant tissues (e.g. leaves, grasses), because the latter contain higher amounts of pectin (a carbohydrate polymer containing mainly galacturonic acid and smaller amounts of arabinose and galactose) (Sjöström, 1981). Cowie and Hedges (1984) used the formula (Ara+Gal) % as an indicator of non-woody vascular tissues and grasses (when 20–50 %) or woody origin (<15 %). Because our study measured galacturonic acid, we also included this compound in the above calculation (i.e. Ara + Gal + GalUA %). Our results showed that the sum of these carbohydrates ranged from 28–60 %, which further suggests that POM and DOM in the sampling site have a non-woody vascular plant signature (e.g. angiosperms leaves/grasses, gymnosperms tissues). This result corroborates the PCA, where Ara, Gal, and DOC formed a compact cluster in the upper right quadrant (Fig. 5d). The above results clearly indicate that DOM at the sampling site exhibits vascular plant, soil, and bacterial signatures, whereas POM has a more pronounced terrestrial influence from vascular plants, with a small a contribution of in situ phytoplanktonic production (see above).

The fact that galacturonic acid did not fall into the cluster of arabinose, galactose and DOC may indicate various sources for this compound. Galacturonic acid can derive from vascular plants, bacteria, or phytoplankton and is an important constituent of mucopolysaccharides and soil organic matter (Fazio et al., 1982; Kenne and Lindberg, 1983; Bergamaschi et al., 1999; Fischer et al., 2007). Our results showed that galacturonic acid accounted for 3–12 % (Table 2) of our DOM samples. These values are higher than those reported for plankton (0.7–0.9 %) or sediment trap material (0.4–1.8 %; Bergamaschi et al., 1999), but similar to that found in wood, leaves, needles (4–18 %; Bergamaschi et al., 1999) and soils (17 %; Fischer et al., 2007). These results reinforce the previous conclusions that the molecular abundance of galacturonic acid in riverine DOM most likely reflects the weathering of soils and/or vascular plant signatures.

The different vascular plant sources (angiosperms leaves/grasses vs. gymnosperms tissues) in POM and DOM were further assessed using Xyl % and Man/Xyl ratios. Our results showed that xylose accounted for 15–27 % and 8–16 % of the PCHO and

DCHO, respectively. Xylose is produced in higher amounts by angiosperms than gymnosperms, whereas gymnosperms produce more mannose than xylose (Cowie and Hedges, 1984). Therefore, the higher abundances of xylose in PCHO probably suggest an angiosperm source (i.e. angiosperm leaves or grasses), whereas the lower abundances in DCHO suggest a gymnosperm source (i.e. non-woody gymnosperm tissues) (Cowie and Hedges, 1984; Bergamaschi et al., 1999; Jia et al., 2008). In agreement with this, the Man/Xyl ratios were >1 in DOM than in POM which is typical of gymnosperm source. Therefore, it appears that DOM at the sampling site exhibits an allochthonous influence of gymnosperms, which probably has its origin from the northern part of the Rhône (the Alps, Lake Geneva), where conifers dominate.

Alternatively, the low abundances of xylose in DOM may originate from selective degradation of the glucose and xylose in POM. Indeed, Opsahl and Benner (1999) showed a decrease in the xylose and glucose of different plant tissues, including leaves, wood, cypress needles and cord grass, over a four-year decomposition experiment. It is worth noticing that a similar relative abundance of xylose (11–16 %, recalculated on a glucose-free basis) was also reported in the surface sediments in the Gulf of Lions (the northwestern Mediterranean Sea) into which the Rhône River flows (Kerhervé et al., 2002).

Our results also showed the presence of various compounds that eluted within the uronic acid pool. With the exception of glucuronic and guluronic acids, which were detected in trace amounts, authentic standards for other uronic acids (e.g. methylated uronic acids) are not commercially available and therefore their identification was not possible. Bergamaschi et al. (1999) reported a plethora of uronic acids and methylated sugars in coastal sediment trap material, sediments, and vascular plants using GC-MS; other studies using global measurements suggested that uronic acids make up an important fraction of the total carbohydrates in coastal (8–12 %; Hung and Santschi, 2001) and riverine DOM (1–5 %; Hung et al., 2005). In estuarine sediments, uronic acids account for 15–36 % of the total carbohydrates (Khodse et al., 2008). Future applications using anion exchange chromatography coupled with mass spectroscopy

(HPAEC-MS; Bruggink et al., 2005; Panagiotopoulos and Wurl, 2009) will provide crucial structural information about these compounds and help us to understand their role and distribution in the terrestrial and marine environments.

5.5 Carbohydrates as indicators of the diagenetic status of riverine DOM and POM

The ubiquitous character of carbohydrates in terrestrial ecosystems allows not only the identification of their sources but also the evaluation of the biogeochemical processes (fates, metabolic pathways) occuring in the environment (Cowie and Hedges, 1984; Ittekkot and Arain, 1986; Hedges et al., 1994; Opsahl and Benner, 1999; Ogier et al., 2001; Benner and Opsahl, 2001; He et al., 2010). For example, high hexoses/pentoses (Hex/Pen) ratios are indicative of labile organic matter originating mainly from plants, whereas low ratios indicate degraded material reflecting a soil origin (Ittekkot and Arain, 1986; da Cunha et al., 2002). Our results showed that the Hex/Pen ratios varied from 0.8 to 4.0 (av. 2.2) and from 1.4 to 6 (av. 2.9) for POM and DOM, respectively. Similar values have been reported for the Parana River (POM: 2.5–3.4; DOM: 6.3; Depetris and Kempe, 1993). These findings may imply that POM is more degraded than DOM in the sampling site. However, if we conduct the same calculation on a glucose-free basis (Hex/Pen = Gal + Man/Ara + Xyl) the Hex/Pen ratio will range from 0.5 to 1.3 (av. 0.9) for POM and 0.6 to 1.9 (av. 1.1) for DOM. This result further indicates that POM and DOM exhibit similar diagenetic alteration.

The observed differences are probably due to the apparent dominance of glucose among the carbohydrates in highly degraded material (e.g. soils, vascular plants; Opsahl and Benner, 1999; Fischer et al., 2007) and in fresh material as well (e.g. plankton; Cowie and Hedges, 1984; Hama and Yanagi, 2001; Biersmith and Benner, 1998). The reported mole percentages of glucose in highly degraded vascular plant tissues ranged from 30–50 % (Opsahl and Benner, 1999) and are similar to those found in this study (~33 %; Tables 2 and 3) or other riverine systems (Ittekkot and Arain, 1986; Depetris and Kempe, 1993; Hedges et al., 1994). Although the processes that control

the degradation of organic matter are not well known, growing evidence shows that the apparent degraded signature of riverine DOM can actually attributed to processes of leaching and sorption with respect to amino acids (Aufdenkampe et al., 2001) and lignin phenols (Hernes et al., 2007). However, very little is known regarding the behavior of carbohydrates.

Our results demonstrate that POM and DOM at the sampling site have already undergone extensive transformation, which is further supported by the relative abundances of deoxysugars. (Fuc + Rha) % values calculated on a glucose-free basis ranged from 14 to 26 % (av. 18 %) and from 14 to 23 % (av. 21 %) for POM and DOM, respectively. Our values are similar to those reported for ultrafiltrated DOM and fine (<63 µm) POM in the Amazon river (Hedges et al., 1994) and agree as well with the deoxysugar values recorded at the end of decomposition experiments of vascular plants (Opsahl and Benner, 1999). Alternatively, the elevated deoxy sugar levels may arise from contributions from external sources (see above), such as microbial biomass (Cowie and Hedges, 1984; Ogier et al., 2001; Panagiotopoulos and Sempéré, 2007). Regardless of the exact mechanism, our results clearly suggest that POM and DOM at the Arles station had undergone considerable degradation within the river and/or before entering the river.

5.6 Export of terrestrial organic carbon of the Rhône River into the Gulf of Lions

Rivers discharge POC at a rate that is similar to the global accumulation rate of organic carbon in all marine sediments (Berner, 1989). Previous studies indicated that the annual deposition of POC in the proximal Rhône prodelta and the distal Rhône prodelta were $8.0 \pm 5.0 \times 10^{10}\,\mathrm{g\,y^{-1}}$ and $2.9 \pm 1.2 \times 10^{10}\,\mathrm{g\,y^{-1}}$, respectively (De Madron et al., 2000). If we assume that only RPOC accumulates on the adjacent shelf or slopes (although a portion of RPOC may undergo extensive alteration through photochemistry or other biotic processes when exiting the river), our results suggest that the RPOC annual fluxes were on average $7.7 \times 10^{10}\,\mathrm{g\,C\,y^{-1}}$ and are in agreement with previous observations.

Considering a surface area of 23 000 km^2 and assuming that DOC comprises most of the TOC, with concentrations of approximately 70 µM C in surface (0–200 m) and 40 µM below 500 m (Santinelli et al.,, 2010 and references therein), the standing stock of TOC in the Gulf of Lions is ~145 × 10^{10} moles C. The annual TOC input from the Rhône is 1.4 × 10^{10} moles C (Table 4) and represents only ~1 % of the standing stock of TOC in the Gulf of Lions. Expanding our results to the entire Mediterranean Sea, the annual TOC input of the Rhône River accounts for ~0.006 % of the Mediterranean standing stock of TOC and is in agreement with previous estimations (~0.01 %; Sempéré et al., 2000).

Our results also showed that carbohydrates accounted for ~7 % of TOC, whereas glucose represented ~33 % of the total carbohydrates (Tables 2 and 3). This corresponds to annual flux of 3.2 × 10^8 moles glucose (or 19.2 × 10^8 moles glucose-C) and highlights the important contribution of the Rhône River to the Gulf of Lions and in Mediterranean Sea in general.

6 Conclusions

The conclusions of this seasonal investigation of the carbohydrate species and related chemical parameters (POC and DOC) and their fluxes estimated for the Rhône River are summarized below:

1. Carbohydrates contributed approximately equally (av. 7–8 %) to both POM and DOM. PCHO followed the variations of POM and peaked during flood events, whereas DCHO and DOC did not show any specific trend between low and high discharge periods. Moreover, DOC and consequently DCHO concentrations were not correlated with the water discharge, suggesting a decoupling between particulate and dissolved organic matter.

2. The information on the concentration and composition of carbohydrates provided important indications of organic matter sources and the degree of diagenesis.

Our results showed that, during flood events, PCHO exhibited a distinct molecular composition (Fig. 4a), rich in mannose, which is typical of each flood event. This enrichment in mannose probably reflects an allochthonous origin, most likely from angiosperms (leaves or grasses). In low-water periods, PCHO exhibited compositional similarities to POM, which indicates a terrestrial origin (again an allochthonous source), which conceals the organic matter produced within the river (autochthonous source). Based on the (Fuc + Rha)/(Ara + Xyl), Man/Xyl ratios, Xyl % and (Ara + Gal + GlcUA) %, with the relative abundances calculated on a glucose-free basis, our results showed that DCHO had different terrestrial origins (gymnosperms tissues and soils), including bacteria (Figs. 5d, 7b). Galactose and arabinose cluster together with DOC in the PCA, indicating that the origins of these sugars are probably reflected in DOC. The Hex/Pen ratios and (Fuc + Rha) % relative abundances, both calculated on a glucose-free basis, indicated that POM and DOM had undergone considerable degradation within the river and/or before entering the river.

3. Galacturonic acid abundances in riverine organic matter showed that this compound has a good potential for tracking terrestrial organic matter origins. Similar compounds (methylated uronic acids) were also detected, but they were not identified within the uronic acid pool. As such, additional information was lost about the origins of these carbohydrates; therefore, further studies are needed to better understand their roles and distributions in the terrestrial and marine environments.

4. The estimated carbohydrate fluxes from the Rhone River into the Mediterranean Sea over the period 2001–2010 averaged 0.061 ± 0.043 × 10^{10} moles C y^{-1} of PCHO and 0.028 ± 0.0062 × 10^{10} moles C y^{-1} of DCHO, representing 8 % and 5 % of the annual flux of POC and DOC, respectively. These results are in accordance with previous flux estimates for bulk POC and DOC over the period 1987 and 1996 (Sempéré et al., 2000). Finally, by expanding our results to the Gulf of Lions (the northwestern Mediterranean Sea), we found that TOC fluxes accounted

for ~2 % of the standing stock of seawater TOC. Glucose is the most abundant carbohydrate in both the particulate and dissolved organic matter pools, and its annual flux into the Gulf of Lion was estimated to be 19.2 × 10^8 moles glucose-C.

Acknowledgements. This research was funded by the French National Research Agency, program "Vulnérabilités: Milieux et Climat" under the grant CHACCRA (contract number ANR-VULN-06-001-01), the French INSU-EC2CO program RiOMar.fr, and the MANDARINE project (region Provence Alpes Côte d'Azur). The manuscript benefited from advice and comments from W. Ludwig and M. Tedetti. Liquid discharges values in Arles were made available thanks to the CNR. The authors gratefully acknowledge M. Fournier and M. Thaust for analytical and field assistance.

The publication of this article is financed by CNRS-INSU.

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Table 1. Water discharge (Q), total suspended matter (TSM), weight percentage of organic carbon, particulate and dissolved organic carbon (POC, DOC), DOC/POC ratios, particulate and dissolved carbohydrates (PCHO, DCHO) and DCHO/ PCHO ratios measured in the Rhône River during the period May 2007 to June 2009.

Date	Q ($\mathrm{m^3\,s^{-1}}$)	TSM ($\mathrm{mg\,l^{-1}}$)	OC (%)	POC (µM)	DOC (µM)	DOC/POC	PCHO (µM)	DCHO (µM)	DCHO/PCHO
21 May 2007	1570	22.7	3.7	60.5	144	2.4	0.68	3.1	4.5
26 Jun 2007	1910	115	3.7	141	117	0.83	1.7	–	–
27 Jul 2007	1300	17.3	3.1	45.2	123	2.7	0.32	1.2	3.9
11 Dec 2007	2660	91.3	2.5	135	168	1.2	2.1	1.7	0.81
17 Jan 2008	2823	47.5	2.9	120	199	1.7	1.6	1.6	1.0
5 Feb 2008	1835	22.6	4.6	201	135	0.67	1.1	–	–
11 Mar 2008	1233	6.1	5.2	16.0	120	7.5	0.42	1.2	2.9
25 Mar 2008	1853	20.8	3.5	77.0	124	1.6	1.3	1.5	1.2
8 Apr 2008	1458	8.0	4.9	31.4	127	4.0	0.54	1.8	3.3
22 Apr 2008 (flood)	3244	88.1	2.4	288	169	0.59	2.4	1.9	0.79
13 May 2008	1156	6.2	6.4	20.6	122	5.9	0.22	1.6	7.1
27 May 2008	2669	124	2.4	124	95.7	0.77	1.1	1.1	1.0
30 May 2008 (flood)	3822	920	2.3	2334	120	0.05	14.2	1.4	0.10
18 Jun 2008	2399	72.6	3.2	286	117	0.41	1.6	1.0	0.64
1 Jul 2008	1366	14.9	4.4	53.7	80.0	1.5	0.44	1.2	2.7
8 Sep 2008 (flood)	2983	285	2.8	1311	216	0.16	11.0	2.5	0.23
22 Oct 2008 (flood)	3817	388	3.0	412	128	0.31	4.0	1.3	0.32
18 Nov 2008	1342	13.3	4.8	76.1	141	1.8	0.88	1.5	1.7
3 Dec 2008	1445	17.2	3.6	53.9	137	2.5	1.3	2.2	1.7
7 Feb 2009 (flood)	4800	1044	1.8	408	164	0.40	5.1	1.0	0.20
3 Mar 2009	1950	23.4	3.0	111	122	1.1	1.9	1.2	0.62
10 Mar 2009	1400	10.4	2.6	25.4	120	4.7	0.82	–	–
7 Apr 2009	1600	27.1	3.0	52.7	116	2.2	0.93	1.4	1.4
22 Apr 2009	1600	134	2.8	40.4	107	2.6	0.69	1.2	1.7
9 Jun 2009	1450	14.2	3.2	35.5	–	–	0.92	–	–
Average	2147	141	3.4	258	134	1.9	2.3	1.5	1.8
SD	971	270	1.1	506	30.6	1.9	3.3	0.53	1.7

Table 2. Relative abundance of particulate sugars (PCHO in mol %) and their contribution to the POC pool during the sampling period.

Date	Fuc	Rha	Ara	GlcN	Gal	Glc	Man	Xyl	Rib	GalUA	PCHO (µM-C)	PCHO-C/POC (%)
21 May 2007	7.1	6.3	9.8	5.1	16.5	34.3	7.9	11.3	1.0	0.5	3.9	6.5
26 Jun 2007	5.5	3.7	7.4	7.2	23.5	32.7	6.5	11.3	1.6	0.7	9.8	7.0
27 Jul 2007	6.4	5.5	7.0	4.4	17.1	41.2	3.6	11.2	2.3	1.4	1.8	4.1
11 Dec 2007	6.8	8.8	10.1	3.7	16.2	28.5	8.9	13.2	2.7	1.2	12.1	9.0
17 Jan 2008	7.8	9.0	11.5	3.2	16.4	26.6	7.7	14.9	2.4	0.6	9.2	7.6
5 Feb 2008	6.1	7.7	11.4	4.8	14.3	29.5	9.7	13.2	2.8	0.5	6.0	3.0
11 Mar 2008	9.4	6.3	15.5	3.9	14.7	28.1	4.7	14.5	2.6	0.3	2.4	14.8
25 Mar 2008	7.1	5.5	9.7	4.4	16.7	34.0	6.0	14.3	2.0	0.2	7.1	9.3
8 Apr 2008	6.0	6.4	7.9	4.9	13.2	42.4	5.6	13.2	0.0	3.1	3.1	9.9
22 Apr 2008 (flood)	5.8	5.5	8.6	3.4	17.8	35.2	7.9	13.9	1.6	0.4	13.8	4.8
13 May 2008	5.9	5.7	5.3	6.9	13.3	42.6	9.3	8.0	2.2	0.8	1.3	6.2
27 May 2008	7.4	5.8	10.4	3.0	19.8	26.1	7.0	14.9	5.6		6.1	4.9
30 May 2008 (flood)	4.2	6.1	9.2	3.0	17.1	32.1	10.6	16.5	1.1	0.2	80.5	3.4
18 Jun 2008	5.0	7.8	11.7	2.9	17.3	30.9	8.1	13.9	1.8	0.5	9.1	3.2
1 Jul 2008	4.8	11.0	7.0	3.9	7.9	43.6	7.1	10.1	3.1	1.6	2.5	4.7
8 Sep 2008 (flood)	4.6	8.4	10.8	4.5	18.2	28.8	12.4	9.8	2.1	0.6	63.2	4.8
22 Oct 2008 (flood)	6.1	8.2	11.0	3.5	15.7	32.0	9.9	11.8	1.4	0.5	22.9	5.6
18 Nov 2008	3.9	9.8	7.6	3.3	7.2	45.3	8.7	9.9	1.8	2.5	5.1	6.7
3 Dec 2008	3.5	8.0	33.3	1.7	8.3	25.6	6.0	10.5	1.8	1.5	7.3	13.6
7 Feb 2009 (flood)	5.2	7.8	15.0	4.5	16.7	25.7	12.8	9.8	1.7	1.5	28.8	7.1
3 Mar 2009	5.7	9.1	11.3	2.7	17.1	27.0	9.0	15.0	2.5	0.6	10.7	9.6
10 Mar 2009	6.6	9.0	20.1	2.1	14.5	23.4	7.2	13.8	1.9	1.4	4.6	18.0
7 Apr 2009	6.7	9.1	10.8	4.0	18.6	29.8	8.9	9.5	1.8	0.9	5.4	10.2
22 Apr 2009	6.0	8.5	6.0	4.2	13.9	42.4	6.8	9.5	1.9	0.9	4.0	10.0
9 Jun 2009	4.8	5.4	21.2	3.9	17.0	29.4	6.9	9.5	1.3	0.6	5.2	14.6
Average	5.9	7.4	11.6	4.0	15.6	32.7	8.0	12.1	2.0	0.8	13.0	7.9
SD	1.3	1.8	6.0	1.2	3.6	6.6	2.2	2.3	1.0	0.6	19.0	4.0

A blank indicates that this compound was below detection.

Abbreviations: Fuc., Fucose; Rha., Rhamnose; Ara., Arabinose; GlcN., Glucosamine; Gal., Galactose; Glc., Glucose; Man., Mannose; Xyl., Xylose; Rib., Ribose; GalUA., Galacturonic Acid.

Table 3. Relative abundance of dissolved sugars (DCHO in mol %) and their contribution to the DOC pool during the sampling period.

Date	Fuc	Rha	Ara	GlcN	Gal	Glc	Man	Xyl	Rib	GalUA	DCHO (µM-C)	DCHO-C/DOC (%)
21 May 2007	3.6	3.6	6.6	3.1	18.6	52.3	5.1	3.8		3.3	18.2	12.6
26 Jun 2007	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
27 Jul 2007	5.5	6.0	23.4	7.3	9.5	27.6	9.2	5.1		6.2	7.1	5.7
11 Dec 2007	5.6	5.8	5.1	4.8	12.5	30.9	15.8	11.7		7.8	10.0	5.9
17 Jan 2008	5.8	5.4	7.8	4.1	5.2	47.3	8.4	3.5		12.5	9.3	4.7
5 Feb 2008	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11 Mar 2008	9.4	8.6	8.5	7.7	11.0	25.2	14.7	6.7		8.1	7.1	5.9
25 Mar 2008	9.9	10.6	9.3	4.9	10.9	26.7	11.2	10.4		6.1	8.5	6.9
8 Apr 2008	5.4	4.9	12.3	4.8	19.0	32.1	8.4	7.3		5.8	10.0	7.9
22 Apr 2008 (flood)	8.4	9.3	9.6	4.5	9.3	34.7	10.2	8.8		5.2	11.1	6.6
13 May 2008	6.4	8.1	11.1	5.5	7.3	28.8	14.6	10.0	3.2	4.9	8.9	7.3
27 May 2008	9.6	12.3	6.6	8.2	13.5	27.6	12.2	10.0		0.0	6.3	6.6
30 May 2008 (flood)	8.1	9.2	8.1	6.6	9.0	36.1	10.0	6.0		7.0	8.3	6.9
18 Jun 2008	7.0	5.9	8.9	7.5	4.9	37.6	12.1	5.3		10.9	6.0	5.1
1 Jul 2008	6.0	7.6	5.1	7.5	9.3	32.8	11.9	5.8	7.0	7.0	6.9	8.7
8 Sep 2008 (flood)	7.4	8.8	9.9	4.2	7.7	36.1	9.4	7.6	5.2	3.6	14.6	6.7
22 Oct 2008 (flood)	9.8	11.6	6.6	6.7	9.9	24.0	11.6	10.5	3.7	5.6	7.3	5.7
18 Nov 2008	8.1	7.5	13.9	5.9	13.5	29.2	9.0	8.1		4.7	8.4	6.0
3 Dec 2008	5.1	4.7	11.4	3.1	7.3	46.2	10.7	7.9		3.5	12.7	9.3
7 Feb 2009 (flood)	6.5	6.7	6.4	9.8	5.6	39.6	9.9	5.6		9.7	6.0	3.7
3 Mar 2009	6.0	6.8	5.6	6.4	14.2	28.8	15.2	10.0		7.0	6.8	5.5
10 Mar 2009	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7 Apr 2009	7.6	7.4	11.2	7.2	12.2	27.7	13.4	7.1		6.2	7.8	6.7
22 Apr 2009	7.3	7.1	8.6	7.5	11.5	29.1	14.6	7.9		6.5	6.7	6.3
9 Jun 2009	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Average	7.1	7.5	9.3	6.1	10.6	33.4	11.3	7.6	0.9	6.3	8.9	6.7
SD	1.7	2.3	4.0	1.8	3.8	7.7	2.7	2.3	2.0	2.7	3.1	1.8

N/A: No available data A blank indicates that this compound was below detection.

Table 4. Annual Rhône River Discharge and fluxes of Total Suspended Matter (TSM), Particulate Organic Carbon (POC), Dissolved Organic.

Year	Discharges	TSM Fluxes	POC Fluxes	DOC Fluxes	PCHO-C* Fluxes	DCHO-C* Fluxes
	Km^3 yr^{-1}	10^6 t yr^{-1}	10^{10} moles C yr^{-1}	10^{10} moles C yr^{-1}	10^{10} moles C yr^{-1}	10^{10} moles C yr^{-1}
2001	57	14.7 ± 9.44	1.40 ± 0.697	0.80 ± 0.11	0.11 ± 0.049	0.052 ± 0.0027
2002	50	34.7 ± 22.3	1.89 ± 0.941	0.69 ± 0.10	0.15 ± 0.067	0.045 ± 0.037
2003	38	15.3 ± 9.83	0.800 ± 0.398	0.49 ± 0.071	0.064 ± 0.028	0.035 ± 0.025
2004	39	2.93 ± 1.88	0.410 ± 0.204	0.50 ± 0.072	0.033 ± 0.015	0.035 ± 0.020
2005	32	1.30 ± 0.835	0.220 ± 0.110	0.38 ± 0.055	0.018 ± 0.008	0.029 ± 0.017
2006	49	4.40 ± 2.83	0.650 ± 0.324	0.66 ± 0.096	0.052 ± 0.023	0.043 ± 0.023
2007	43	2.20 ± 1.41	0.400 ± 0.199	0.57 ± 0.083	0.032 ± 0.014	0.039 ± 0.0018
2008	58	10.7 ± 6.87	1.11 ± 0.553	0.77 ± 0.11	0.091 ± 0.040	0.049 ± 0.027
2009	40	2.70 ± 1.73	0.410 ± 0.204	0.54 ± 0.078	0.032 ± 0.014	0.037 ± 0.019
2010**	48	3.21 ± 0.802	0.550 ± 0.240	0.66 ± 0.096	0.026 ± 0.012	0.043 ± 0.018
10 yr average	46	9.21	0.784	0.61	0.061	0.041
Standard deviation	8.5	10.4	0.530	0.13	0.043	0.019

Carbon (DOC), Particulate (PCHO-C) and Dissolved (DCHO-C) carbohydrates during the period 2001–2010.
TSM, POC, DOC, and PCHO fluxes were calculated from the log/log relationships between the daily discharge and the corresponding loads based on 25 points between May 2007 and June 2009.
The fluxes were then corrected by the Ferguson (1987) factor C. C values were 1.231, 1.269, 1.020 and 1.143 for TSM, POC, DOC and PCHO-C, respectively.
DCHO-C fluxes were obtained by multiplying an average DCHO concentration by daily discharge rate.
* Carbon content of carbohydrates considering that 1 mol of carbohydrates contains 6 mol of carbon.

** 2010 water discharges were available from 1 January till 6 December.

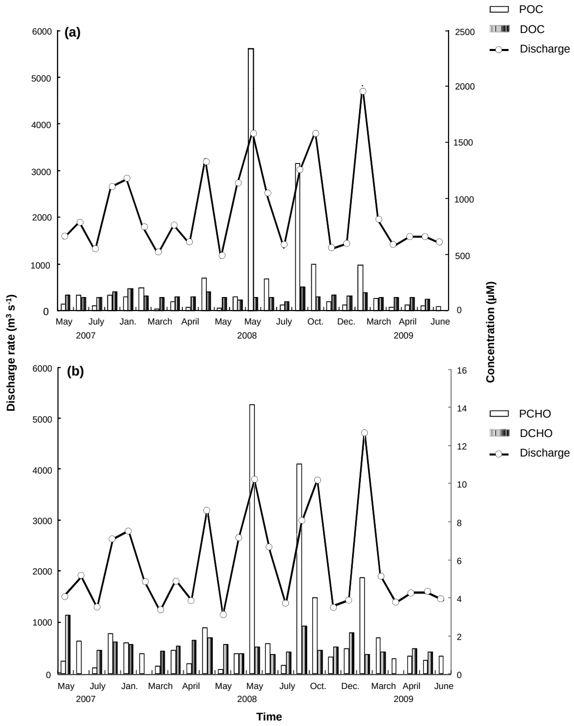

Fig. 1. Daily discharge of the Rhône River (in m^3 s^{-1}) between May 2007 and June 2009 as a function of **(a)** POC and DOC concentrations (in µM C) and **(b)** PCHO and DCHO concentrations (in µM).

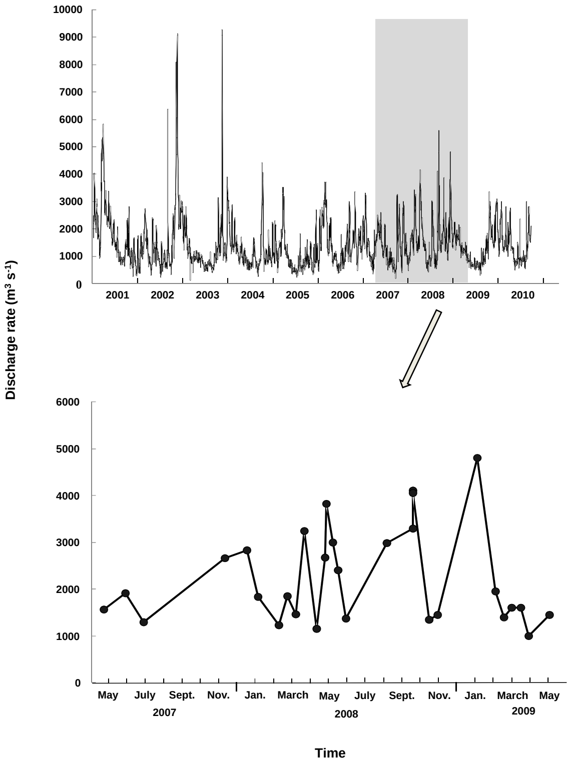

Fig. 2. Daily discharge (in m^3 s^{-1}) at the sampling station between January 2001 and December 2010.

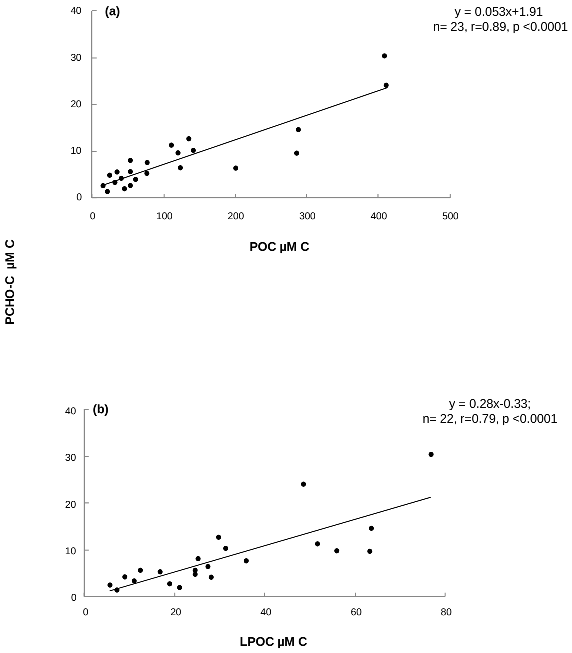

Fig. 3. The correlations between PCHO-C and **(a)** POC; **(b)** LPOC during the sampling period (May 2007–June 2009).

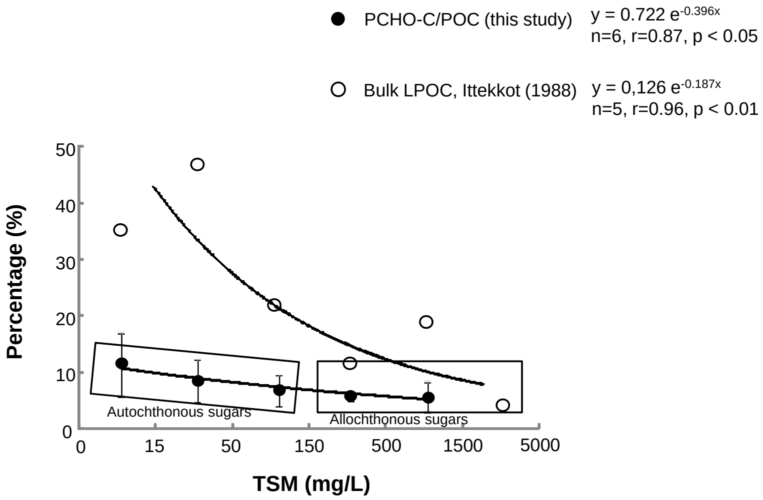

Fig. 4. The percentage of labile POC as a function of the TSM concentrations. In our study, the Rhône River TSM concentrations ranged between 6 and 1044 mg l^{-1}; therefore, TSM >1500 mg l^{-1} are not available. The error bars represent the standard deviation of the TSM concentrations for the range of 0–15, 15–50, 50–150, 150–500, and 500–1500 mg l^{-1}, as established by Meybeck (1982).

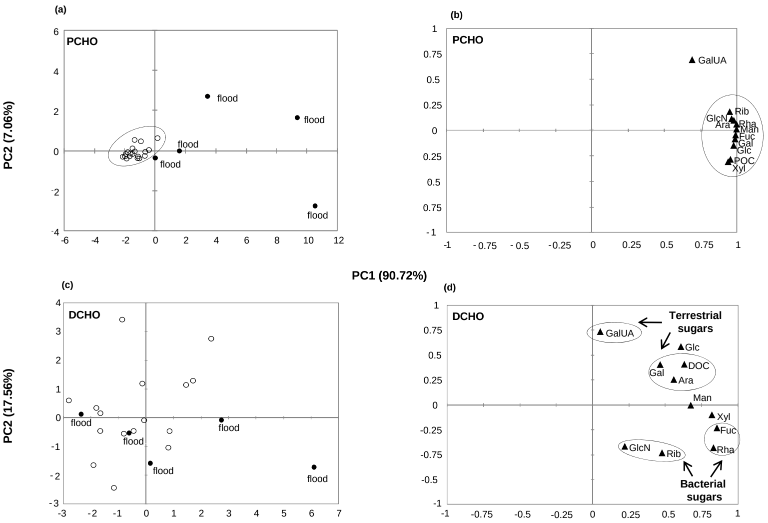

Fig. 5. Principal components analysis for particulate and dissolved carbohydrates, including POC and DOC. **(a)** and **(c)** are the sample scores, whereas **(b)** and **(d)** are the sample loadings of the PCA. The variance accounted for by each principal component is shown in parentheses after the axis label. The abbreviations of the sugars are given in Table 3.

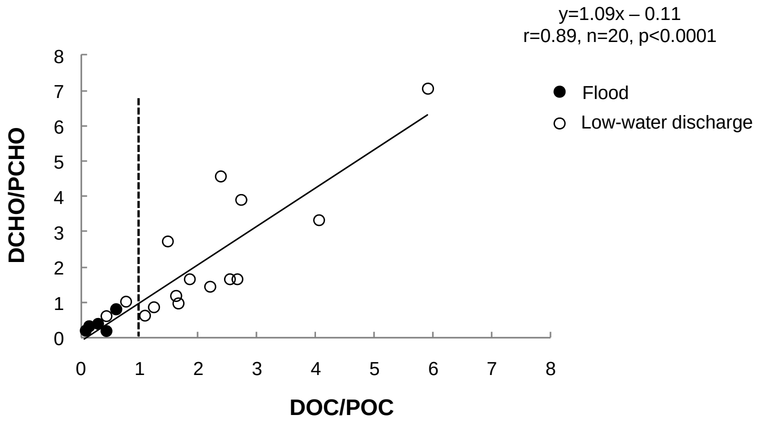

Fig. 6. Correlations between the ratios DCHO/PCHO and DOC/POC during the sampling period. We considered a flood event to occur when $Q > 3000\,\mathrm{m^3\,s^{-1}}$. This value roughly corresponded with two times the average annual flow recorded in the Rhône River ($Q = \sim 1500\,\mathrm{m^3\,s^{-1}}$).

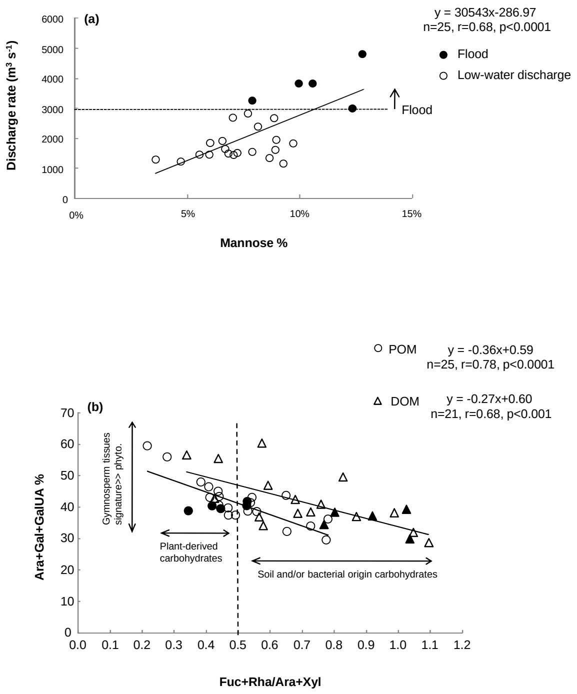

Fig. 7. (a) Correlations between mannose and discharge in POM and **(b)** Correlations between the ratio Fuc + Rha/Ara + Xyl and Ara + Gal + GalUa (%) in POM and DOM over the sampling period. Flood events are indicated as bold circles and the triangle symbols represent POM and DOM, respectively.