Environ Monit Assess (2016) 188:41
DOI 10.1007/s10661-015-5054-9

Using recent high-frequency surveys to reconstitute 35 years of organic carbon variations in a eutrophic lowland river

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Received: 2 June 2015 / Accepted: 10 December 2015

Abstract Concentrations of dissolved and particulate organic carbon (DOC and POC), total suspended solids (TSS), were measured daily, and phytoplankton pigments (chlorophyll-*a* and pheopigments) were measured every 3 days at three strategic stations along the eutrophic Loire River between November 2011 and November 2013 marked by a high annual and seasonal variability in hydrological regimes. This unique high-frequency dataset allowed to determine the POC origin (autochthonous or allochthonous). Some strong relationships were evidenced between POC, total pigments and TSS and were tested on a long-term database with a lower frequency (monthly data) to reconstitute unmeasured algal and detrital POC concentrations and estimate annual total organic carbon (TOC) fluxes from 1980 onwards. The results were subjected to only ≈25 % uncertainty and showed that the annual TOC fluxes at the outlet of the Loire River decreased from 520 10^3 tC year^{-1} (i.e. 4.7 t km^{-2} year^{-1}) in the early 1990s to 150 10^3 tC year^{-1} (i.e. 1.4 t km^{-2} year^{-1}) in 2012. Although DOC always dominates, the autochthonous POC represented 35 % of the TOC load at the basin outlet by the end of the 1980s and declined to finally represent 15 % only of the TOC. The control of phosphorus direct inputs and the invasion by *Corbicula* clams spp. which both occurred since the early 1990s probably highly reduced the development of phytoplankton. Consequently, the autochthonous POC contribution declined and TSS concentrations in summertime significantly decreased as well as a result of both less phytoplankton and less calcite precipitation. At the present time, at least 75 % of the POC has allochthonous origins in the upper Middle Loire but downstream, autochthonous POC dominates during summer phytoplanktonic blooms when total pigments concentrations reach up to 70 μg L^{-1} (equivalent to 75 % of the total POC).

Keywords Organic carbon · River eutrophication · Carbon speciation · Loire

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Published online: 18 December 2015

Introduction

Fluvial networks constitute a major link in the global carbon cycle, connecting together soils, groundwater, atmosphere and oceans. Large quantities of carbon are transported, transformed or stored depending on the river morphology, its hydrology and the interactions that the water body may have with the biological compartment (Hope et al. 1994; Battin et al. 2009). Among the different carbon species, organic carbon in both dissolved and particulate forms is an essential source of energy in stream ecosystems (Wetzel 1984).

In most rivers, dissolved organic carbon (DOC) dominates the particulate organic carbon (POC) exports (Hope et al. 1994; Meybeck 2005). Indeed, approximately 0.21 Gt C y^{-1} enter the oceans in the dissolved form against 0.17 Gt C y^{-1} in the particulate form (Ludwig and Probst 1996). Dissolved organic carbon in a given downstream ecosystem is the result of upstream soil leaching (Meybeck 2005) and a legacy of prior metabolic activities into the river (Battin et al. 2009). Particulate organic carbon origins are either allochthonous (i.e. "detrital", resulting from soil and litter erosion processes) or autochthonous (i.e. "algal", derived from phytoplankton, periphyton or aquatic fixed vegetation). Detrital POC usually dominates, except in rivers subjected to eutrophication where the phytoplanktonic biomass constitutes a significant source of autochthonous C because of anthropogenic pressures (Abril et al. 2002; Hein et al. 2003; Wang et al. 2004; Wysocki et al. 2006; Amann et al. 2012). For instance, "algal" POC during summer blooms contributed significantly to the TOC composition in the Mississippi (Wang et al. 2004; Wysocki et al. 2006), the Danube (Hein et al. 2003), the Elbe (Amann et al. 2012) and the Loire Rivers and estuaries (Billen et al. 1986; Etcheber et al. 2007). High contents of organic matter exported to the estuaries may produce anoxia in the estuarine turbidity maxima zone (Etcheber et al. 2007) and release large quantities of CO_2 into the atmosphere (Amann et al. 2012).

Dissolved and particulate organic carbon are subjected to a high temporal variability (Coynel et al. 2005b; Coynel et al. 2005a; Halliday et al. 2012; Némery et al. 2013). In most rivers, a large quantity of organic carbon is transported during floods which might represent a very little period of time. Additionally, hydrological and biogeochemical conditions are greatly seasonal and many rivers presented clear trends in their water quality parameters as a result of anthropogenic pressures and environmental regulations undertook to counteract or limit the human impact (Lehmann and Rode 2001; Howden et al. 2010; Bouraoui and Grizzetti 2011; Istvánovics and Honti 2012; Grimvall et al. 2014). Consequently, assessing accurately fluvial carbon loads requires high-frequency surveys at least conducted weekly and during an entire seasonal cycle (Wetzel 1984). Similarly, studying contamination trajectories or environmental policies impacts on fluvial carbon requires long-term datasets, and investigating the spatial variation of organic carbon composition along the river course demands to set up several sampling stations.

The Loire River in France is a good example of a eutrophic lowland river presenting dramatic biogeochemical long-term changes. In the 1980s, its eutrophication was severe with very high phytoplankton concentration (up to 300 μg chlorophyll-*a* L^{-1}) likely because of the high phosphorus availability (anthropogenic point sources) combined to the fact that the river morphology favours algal development. Since phosphorus inputs in the system were greatly reduced thanks to 1991 European environmental measures, the concentration of available phosphorus greatly declined (from a summer average around 110 μg P-PO4 L^{-1} in 1990 to ≈70 μg P-PO4 L^{-1} in 2010 in the Middle Loire), and the concentration of phytoplankton has decreased to lower levels (<70 μg Chl. *a* L^{-1}) (Minaudo et al. 2015).

A few previous works studied the organic carbon in the Loire System (Dessery et al. 1984; Billen et al. 1986; Etcheber et al. 2007), but these were based on a limited number of samples and remained focused on the estuarine zone. Thus, organic carbon exports into the estuary have never been properly assessed, nor have been studied the spatial variations in the TOC composition. No attention was given to the dissolved form, but it has been shown that the Loire characteristic consists in its high potential of developing autochthonous POC due to eutrophication processes. Additionally, these studies might be out of date as they were conducted in a changing ecosystem due to eutrophication mitigation. Unfortunately, POC has never been measured within the national river quality network which monthly monitors the major water quality variables since the early 1980s. However, if one evidences at the present time some strong relationships between total suspended solid (TSS), POC and algal pigments concentrations, can POC concentration of the past reasonably be estimated based only on TSS and algal pigments concentrations?

This paper attempts to answer this question based on long-term but monthly datasets recorded during the period 1980–2013 at three strategic stations located in the Middle and Lower Loire River, and high-frequency data sampled during 2 years (November 2011 to November 2013) at the same locations. The high-frequency data makes it possible to accurately compute the organic carbon fluxes, offers the ability to determine the origins of the POC and thus allows evidencing some strong links between the different key variables. Such relationships tested on the long-term dataset enable the POC estimation over 35 years at the different stations which permit an evaluation of how the total organic carbon composition has changed along the river system since 1980.

Site location and methods

Study area

The Loire River basin in France (110,000 km^2) covers 20 % of the French territory. Its hydrological regime is pluvial with some snow-melt influences because of high headwater elevation in the Upper Loire (6 % of the basin area is over 800 m above sea level). The Loire was already highly eutrophied in the 1980s (chlorophyll-*a* >250 μg L^{-1}) as a result of highly available nutrients, low river velocity and shallow waters in the summer. Since the early 1990s, the river phytoplankton biomass has considerably decreased (Floury et al. 2012; Minaudo et al. 2015).

Three strategic stations were chosen. Station 1 is located at Saint-Satur (S1), in the upper part of the Middle Loire catchment (Fig. 1), and receives 33 % of the total basin contribution (36,000 km^2, interannual discharge average $\overline{Q} = 300$ m^{3}s^{-1}). The Middle Loire is constituted by sedimentary rocks and favours algal development because of its morphological features. Indeed, the valleys becoming wider, multiple channels and islands slow down the flow velocity (Latapie et al. 2014). Consequently, average water depth can be low in the summer (≈1m), contributing to the warming and the clarity of the water column. Station 2 (S2) is located at Cinq-Mars-La-Pile and corresponds to the outlet of the Middle Loire Corridor: between S1 and S2, the river receives no significant tributaries, but some groundwater inputs from the Beauce aquifers where agricultural pressure is intense (Schnebelen et al. 2002). It receives 40 % of the total basin contribution (43,600 km^2, $\overline{Q} = 355$ m^{3}s^{-1}). Station 3 at Montjean S3 is located at the downstream of the confluence with the Maine tributary and at the upstream limit of the dynamic tide; this site is considered to be the outlet of the Loire (110,000 km^2, $\overline{Q} = 825$ m^{3}s^{-1}), and the entry point to the estuary. The intermediate catchment between stations S2 and S3 represents 60 % of the total Loire Basin as many of the major tributaries meet the Loire River in its lower section (Cher, Indre, Vienne and Maine Rivers).

Datasets

Data used in this paper is constituted by two sets: a high-frequency survey conducted during two complete years (15 November 2011 to 14 November 2013) on three strategic sites and long-term time series from the national regulatory monitoring conducted from 1980 onwards.

High-frequency survey data sets

Samples were collected using the same procedure at each station. Water was sampled from a bridge in the main river channel. Total suspended solid concentrations (TSS) were measured daily. Dissolved and particulate organic carbon (DOC and POC), chlorophyll-*a* and pheopigments concentrations were determined on a 3-day frequency. Phytoplankton samples were fixed in situ with Lugol solution, and a selection of them were analysed. This selection was decided afterwards, based on the algal pigments results. Filtrations were immediately made on site with 0.45 μm cellulose acetate membrane filters for chemical parameters and with 0.70-μm glass filter (Whatman GFF) previously ashed at 500°C during 6 h for chlorophyll-*a* and pheopigments. TSS concentrations were determined by filtration of a precise volume of each water sample through pre-weighed filters and by drying them at 105°C. After filtration, water samples and filters were stored at −80°C until analysis. Samples were unfrozen the day of the analysis. Dissolved organic carbon concentrations were measured with a carbon analyser (Shimadzu TOC-V CSH/CSN with TN unit). Chlorophyll-*a* and pheopigments were measured by fluorimetry at a wavelength >665 nm after an excitation step between 340 and 550 nm. For POC analyses, the filters were firstly treated with HCl 2N to remove carbonates, dried at 60°C for 24 h and measured with a C/S analyser (LECO C-S 200). Phytoplankton samples

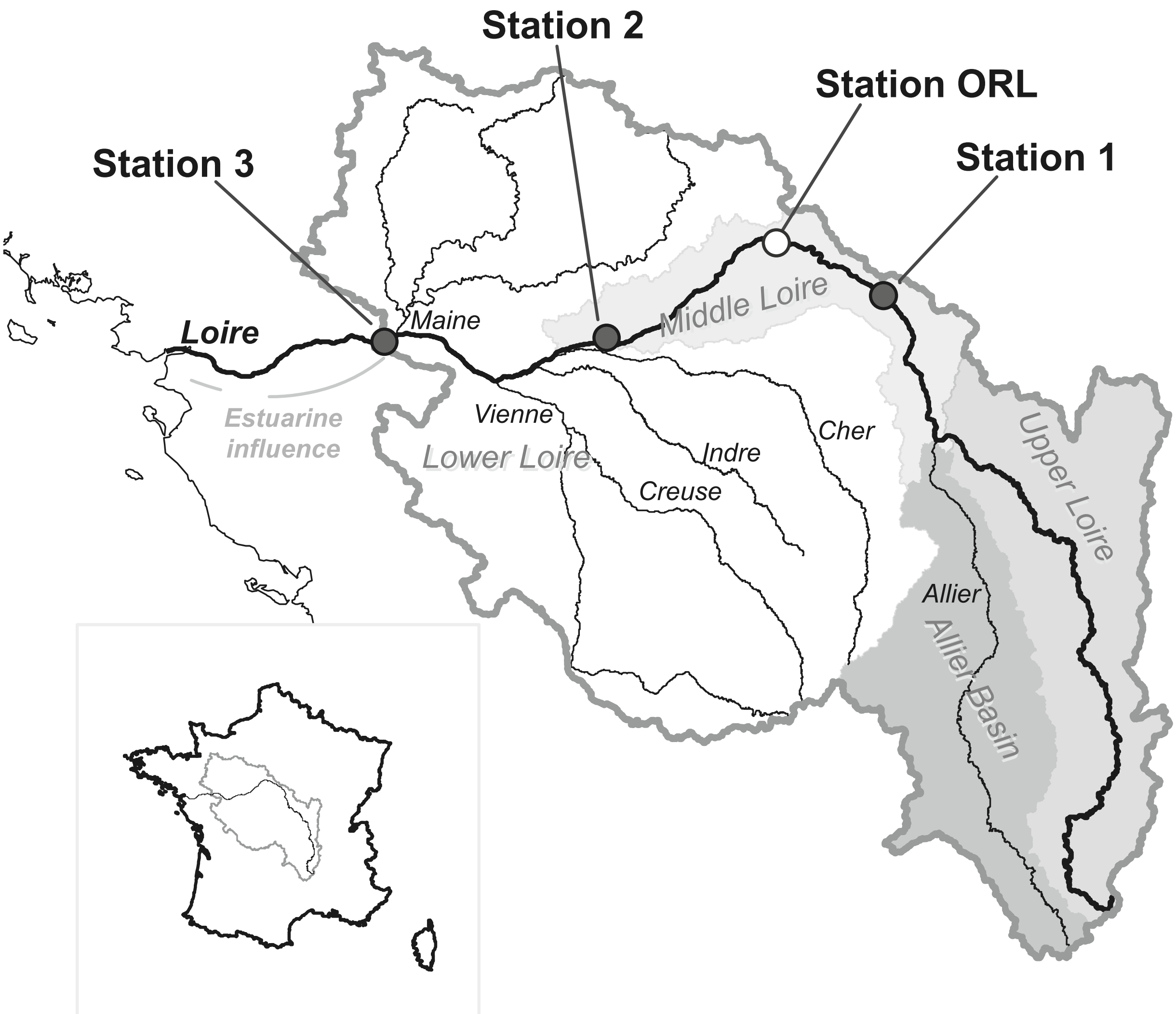

Fig. 1 Study area and sampling stations locations

were identified and counted using Utermöhl (1958) method. The phytoplankton concentration was expressed in mgC L^{-1} using specific biovolumes obtained by geometrical approximation for each identified species according to Lund and Talling (1957) and Rott (1981).

The separation of living phytoplankton biomass (characterized by chlorophyll-*a*) and algal detritus (characterized by pheopigments) depends on the protocol used. This paper considers the sum of chlorophyll-*a* and pheopigments, which increased the robustness of the data and corresponded better to the phytoplanktonic biomass as an active biomass and organic detritus (Dessery et al. 1984; Meybeck et al. 1988). Thus, for clarity further in the text, "total pigments" corresponds to the sum chlorophyll-*a* + pheopigments.

Long-term datasets

The three stations described above were sampled at least monthly between 1980 and 2012 within the national water quality monitoring. Concentrations of TSS, chlorophyll-*a*, pheopigments and DOC were downloaded from the Loire-Brittany River Basin Agency database (http://osur.eau-loire-bretagne.fr/exportosur/Accueil). Station ORL located in the Orléans city, between S1 and S2, was also added to this study in order to increase the robustness of the interpretation as its frequency was weekly and not monthly between 1987 and 2006; it was monthly the rest of the time. The DOC series were unfortunately only available since 1992.

Water discharge time series

Daily river flow time series (*Q*) at gauging stations located at the same place as the water quality stations were downloaded from the national water monitoring "Banque Hydro" database (http://www.hydro.eaufrance.fr/) and used in this paper for both the high-frequency survey and the long-term analysis. During the period 1980–2012, Q was available at S1 during 1992–2013, ORL (1980–2013), S2 (1998–2013) and S3 (1980–2013).

Partitioning organic carbon

Total organic carbon (TOC) in rivers consists of DOC and POC (Eq. 1). Allochthonous POC originates from terrestrial sources (soil erosion) and should then be strongly linked to detrital suspended sediments (e.g. Némery et al. 2013). It is of low bioavailability in contrast to the autochthonous POC mostly constituted in eutrophic rivers by phytoplankton, macrophytes and periphyton (Wetzel 1984; Hein et al. 2003).

$$TOC = DOC + POC = DOC + POC_{alloch} + POC_{autoch} \tag{1}$$

Autochthonous POC, also called "algal POC", was assessed using the relationship of the ratio POC:total pigments with total pigments concentrations (Dessery et al. 1984; Billen et al. 1986; Meybeck 2005). The value of the ratio reached for high total pigments values would then be used to assess algal POC from total pigment concentration (Eq. 2).

$$POC_{autoch} = \alpha \cdot pigments \tag{2}$$

Where POC_{autoch} represents the autochthonous POC, α is the ratio value reached for high total pigments values and *pigments* is the total pigments concentration (Fig. 2). The allochthonous POC can then be estimated by subtracting POC_{autoch} to the total POC concentration. No changes of this relationship over time are expected here as several different studies found similar α values for different rivers (Dessery et al. 1984; Billen et al. 1986; Meybeck 2005). It is then hypothesized in this study that some external changes in waste water inputs or land-use practices do not impact significantly the relationship.

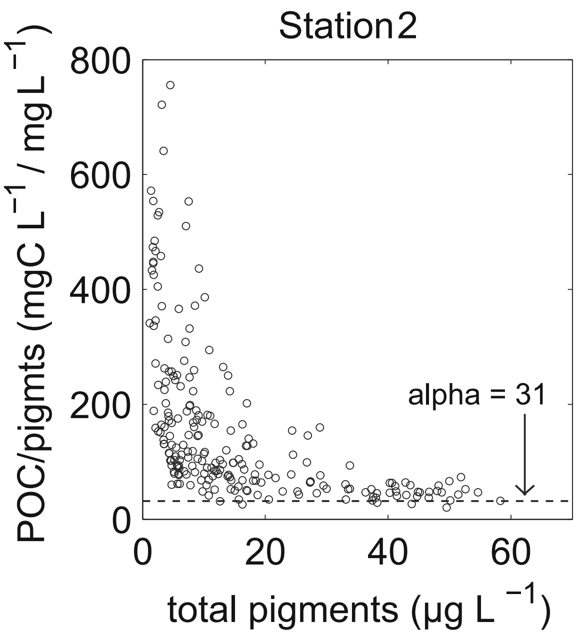

Fig. 2 Example of POC to pigments ratios at station 2 highlighting the ground-level used to calculate autochthonous POC

Estimating POC concentrations from TSS and total pigments datasets

Many studies highlighted the link existing between POC and TSS in watersheds under high erosion (Gao et al. 2002; Meybeck 2005; Coynel et al. 2005a; Némery et al. 2013). It has been shown that POC can be predicted by TSS when both POC and TSS are dominated by detrital origins (Slaets et al. 2014) via a linear relationship (Eq. 3).

$$POC_{alloch} = a \cdot TSS_{alloch} + b \tag{3}$$

Unfortunately, this equation requires that the detrital component of TSS has been isolated. In eutrophic rivers, the algal contribution to the total suspended matter can be significant (Meybeck 2005), and a great increase of algal biomass provokes a significant increase of pH via the photosynthesis activity and thus favours calcite precipitation (Grosbois et al. 2001; Neal 2001). The autochthonous suspended matter (SS_{autoch}) is in this way a combination of phytoplankton and precipitated calcite. In this paper, the allochthonous suspended matter (SS_{alloch}) was assessed indirectly based on the relationship between TSS and total pigments (Fig. 3). The lower level of the scatter plot forms a line of which the

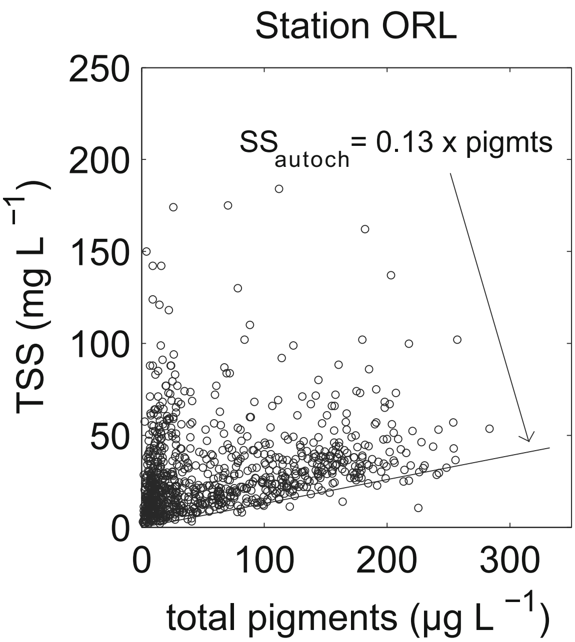

Fig. 3 Example of the autochthonous TSS assessment at station ORL based on the relationship between TSS and total pigments (1980–2012)

mathematical equation was assessed and used to estimate the SS_{autoch} concentration with the hypothesis that this line corresponded to both the suspended phytoplankton and the precipitated calcite. The detrital part was then estimated by subtracting SS_{autoch} to the TSS concentration (Eq. 4).

$$SS_{allloch} = TSS - SS_{autoch} = TSS - a' \cdot pigments \quad (4)$$

Based on Equations 2, 3 and 4, total POC time series could be calculated only from TSS and total pigment datasets. First the values of α, a', a and b were assessed on the basis of the first year of measurements (2012) and applied on the 2013 TSS and total pigments series, in order to predict the 2013 POC concentrations as a cross-validation step. Total POC concentrations being successfully estimated (see section "High-frequency survey data sets"), this method was used to estimate POC concentrations of the past based on monthly measurements (section "Water discharge time series"). The values of α, a', a and b computed at S2 were used for station ORL data processes because of the geographical proximity of the two stations.

No change over time of the TSS-pigments relationship is expected as the dominant phytoplankton species remained the same in the Loire during the period of study (Abonyi 2014).

Fluxes calculations

Time series for the different parameters sampled with a 3-day frequency (DOC, POC, total pigments) were interpolated on a daily frequency to allow daily flux calculations. Daily fluxes were computed using daily discharge (Eq. 5).

$$Flux_i = K_1 \cdot Q_i \cdot C_i \quad (5)$$

Where $Flux_i$ expressed in tons.day^{-1} is the flux on day i, K_1 is a unit conversion factor, Q_i is the daily average discharge and C_i is the instantaneous concentration measured on day i. In order to estimate the error made by computing daily fluxes from 3-days frequency data, TSS daily fluxes were assessed using Eq. 5 on both daily measured TSS and 3 days under-sampled and interpolated TSS concentrations. The errors on the two-year cumulated TSS fluxes were under 5 % when using under-sampled data. This made very consistent the DOC and POC fluxes calculations based on the 3-day frequency interpolated data.

Particulate organic carbon concentrations were not measured within the long-term national survey. Thus, POC time series were computed based on TSS and total pigments monthly concentrations (sometimes weekly) and on the method described above. Both algal and detrital POC loads (L_y) where discharge weighted (Eq. 6) since the related fluxes uncertainties were largely studied for the main water quality variables (Raymond et al. 2013; Moatar et al. 2013)

$$L_y = K_2 \cdot \frac{\sum_{i=1}^{n} (C_i \cdot Q_i)}{\sum_{i=1}^{n} Q_i} \cdot \overline{Q_y} \quad (6)$$

Where C_i and Q_i are the same as in Eq. 5, K_2 is a unit conversion factor and $\overline{Q_y}$ is the mean discharge for the period of load calculation (e.g., 1 year).

Computing loads from monthly measurements on variables subjected to significant time variability calls into question the uncertainties of such calculation. These uncertainties therefore needed to be taken into account when calculating POC and DOC loads from monthly measurements. Moatar et al. (2013) defined the percentage of flux occurring in 2 % of the time ($M_{2\%}$) as being a good indicator for bias and imprecisions of load assessment from a low-frequency sampling using Eq. 6. In the present study, the $M_{2\%}$ indicators were calculated on daily concentrations during the period November 2011 to November 2013, and the corresponding errors could then be assessed depending of the sampling frequency.

The uncertainty on the estimated total POC was composed on one side by the error made by the model estimating POC from TSS and pigments (Err_{model}), and on the other side by the error due to a low-sampling frequency ($Err_{samplFrequ}$) (Eq. 7).

$$Err = \sqrt{Err_{model}{}^2 + Err_{sampl\,Frequ}{}^2} \quad (7)$$

The variable Err_{model} corresponded to the maximum flux error occurring in the cross-validation step (see 2.4).

Results

High-frequency variability of Q, TSS, total pigments and organic C concentrations during November 2011 to November 2013

The river discharges at stations 1 and 2 were very close, with a little delay (≈2 days during floods and up to 5 days during low flows) (Fig. 4 and Table 1). On average, 84 % of discharge at S2 came directly from S1 catchment. At S3, only 43 % came from the catchment at S2. However, most of the dynamic recorded at S2 was preserved. One event only (in October 2012) originated largely from the Lower Loire catchment.

During the first year (November 2011 to November 2012), Q averaged 259, 303 and 651 $m^3\ s^{-1}$ at S1, S2 and S3, respectively. It almost doubled the next year as the averages were 415, 496 and 1163 $m^3\ s^{-1}$. During both years of observation, Q values presented successively some significant events:

1. a period of high flows during the winter 2011/2012. The maximum Q_M reached 2600 $m^3\ s^{-1}$ at S3;
2. another high flow event occurred in spring 2012 (Q_M = 2000 $m^3\ s^{-1}$ at S3) followed by a period of very low discharge during summer 2012 (minimum at S3 was 130 $m^3\ s^{-1}$);
3. a long period of high discharge composed of several events between October 2012 and July 2013. Q at S3 peaked once to 3500 $m^3\ s^{-1}$ and was followed by four well-defined events, each of them over the limit characterizing high flows with 20 % probability to be exceeded;
4. lower discharge was observed in July but remained over 200 $m^3\ s^{-1}$.

Total pigments concentrations characterized the eutrophic state of the Loire River, with values at S1 remaining low (90th percentile $pigmts_{90\%}$ was 13 μg L^{-1} throughout the period of study), contrasting with S2 and S3 where $pigmts_{90\%}$ reached respectively 40 and 44 μg L^{-1}. Two major events occurred:

1. The 2012 algal development period started early in February and lasted until the end of August (212 days, $pigmts_{90\%}$ = 49 μg L^{-1} at S3).
2. In 2013, some significant algal development could not be seen until June and ended by the end of August (96 days, $pigmts_{90\%}$ = 59 μg L^{-1} at S3).

Selection and characterization of hydrological and biological events

Among the significant variations of discharge and total pigments previously listed, four periods were selected in order to highlight the organic composition variation during hydrological versus during biological events, illustrating two opposite functioning of the Loire River, the first when most of the chemical elements are simply transferred downstream, and the other when phytoplankton blooms greatly modify the river biogeochemistry. For this purpose, the hydrological events H1 and H2 occurred in winter during a limited phytoplankton activity, and were not superimposed by the biological events B1 and B2 which occurred during the main pigments events (Fig. 4 and Table 1). The algal pigment concentrations remained very low during the selected hydrological events ($pigmts_{90\%}$<25 μg L^{-1} at S3) and on the contrary reached their highest values during B1 and B2 (respectively, 64 and 69 μg L^{-1}). Although both B1 and B2 started during relatively high levels of discharge (beginning, respectively, at 1000 and 1720 $m^3 s^{-1}$ at S3), Q quickly decreased to lower values, typical of summer low flows.

Total suspended solid concentrations presented an important variability, significantly correlated to Q (R correlation coefficients ranged between 0.61 at S3 up

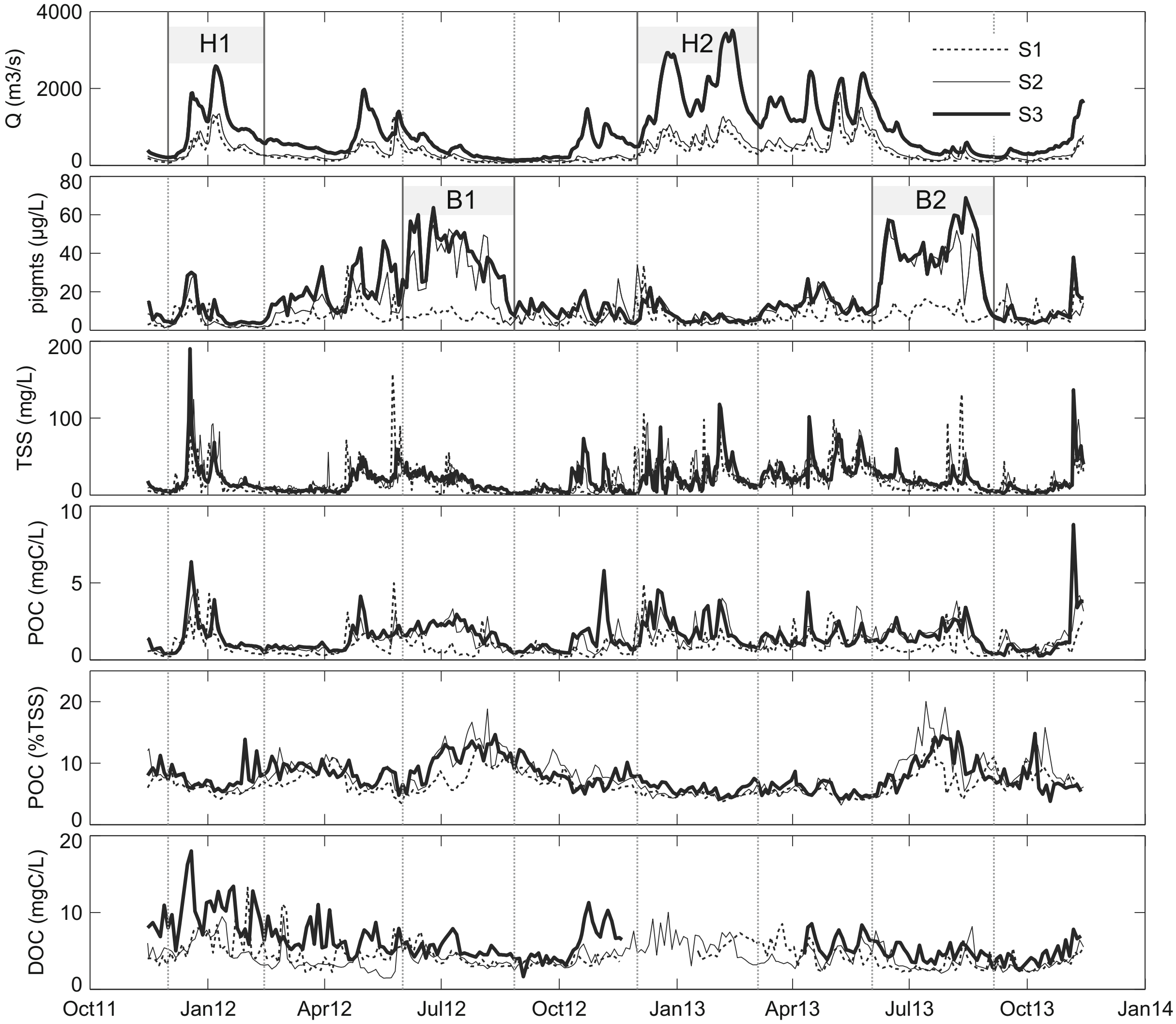

Fig. 4 High-frequency recorded data at the three stations highlighting the selected hydrological and biological events during the period of study

Table 1 Hydrological and biological characteristics (discharge min $Q_{\min}$, average $\overline{Q}$, max Q_{M} (m^3 s^{-1}) and total pigments 90th percentile pigmts$_{90\%}$ (µg L^{-1})) during the 2 years of measurements and during the selected events

Event	Beginning	End	Duration (d)	$Q_{\min}$			$\overline{Q}$			Q_{M}			pigmts$_{90\%}$		
				S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
Year 2012	15/11/11	14/11/12	365	60	73	132	259	303	651	1280	1340	2580	12	38	45
Year 2013	15/11/12	14/11/13	364	86	108	205	415	496	1163	1900	1900	3510	14	40	43
H1	01/12/11	14/02/12	75	70	113	206	473	533	1116	1260	1340	2580	13	20	23
H2	01/12/12	05/03/13	94	258	240	487	582	713	1982	1030	1270	3510	11	16	15
B1	01/06/12	27/08/12	87	60	73	132	181	233	416	457	652	1020	10	50	54
B2	02/06/13	05/09/13	95	89	111	217	220	278	573	855	929	1720	14	48	59

to 0.72 at S1 and S2). Thus, the highest values (over 100 mg L^{-1}) were reached during flood events illustrating the fact that most of TSS originates from soil erosion processes during high flow events. Most of the time, maxima were reached at the basin outlet, but for many flood events TSS concentrations decreased going downstream, spatializing which part of the Loire basin contributed to the total suspended sediment load at S3.

Particulate organic carbon concentrations were also very variable, and ranged between 0.2 and ≈6.5 mgC L^{-1}. Most of the time, POC was well correlated with TSS and peaked at 6.4 mgC L¯1 during H1 in the same time as TSS. During the whole survey, POC was increasing going downstream especially between S1 and S2 during the main biological events. The POC content in percentage of TSS (POC%) showed a seasonal distribution; its minimum occurred during winter (≈5% TSS) and its highest values were observed during summer blooms (≈15% TSS). This variable was then relatively well correlated with total pigments when algal production was significant (correlation coefficients ≈ 0.45). The POC% values were always a bit lower at station 1 compared to the two others.

Dissolved organic carbon concentrations ranged at S1 and S2 from 3 mgC L^{-1} during low flows to ≈12 mgC L^{-1} and from 3 to 20 mgC L^{-1} at S3. Dissolved organic carbon was correlated to water discharge with correlation coefficients ranging between 0.5 at S1 and 0.65 at S2. The recorded DOC concentrations in 2012 appeared lower than in 2013. Unfortunately, some of the samples were not collected during winter 2013 at S1 and S3; consequently, the only continuous records during the 2 years were at S2.

The estimated value of α (see section 1.3 and Table 2) enabled the calculation of algal POC and of detrital POC (Fig. 5) by subtraction with total POC. Algal POC concentration could reach 2 mgC L^{-1} during summer blooms at both S2 and S3. This autochthonous contribution averaged 30–35 % of the total POC concentration at S1 and S2 during the 2 years of observation, and up to 44 % at S3. This contribution could be a lot higher during summer blooms and could occasionally constitute the total POC concentration. During the selected hydrological events H1 and H2, autochthonous POC was minor (12–19 % of the total POC). During the biological events B1 and B2, it comprised around 40 % of the total POC at S1, and was largely dominating at S2 and S3 (≈70 %).

The phytoplankton concentrations were very low at S1 (<0.2 mgC L^{-1}) but reached ≈1.5 mgC L^{-1} at S2 and S3 during the main biological events. The phytoplankton concentrations were always lower than the algal POC, but its variation respected the autochthonous POC dynamic. During the B1 and B2 events, phytoplankton could comprise 60–100 % of the algal POC which supported the results of the algal POC calculation. Even if both phytoplankton and algal POC concentrations remained very low in winter, phytoplankton constituted surprisingly only 10–20 % of the algal POC.

Fluxes budget and TOC composition

The 2013 particulate loads represented twice the loads of 2012 (Table 3) which was expected regarding the hydrological conditions: the annual TSS load at the basin outlet (S3) reached only 0.6 Mt in 2012 and a little more than 1.2 Mt the next year, corresponding, respectively, to 5.1 and 11.2 t km^{-2} $year^{-1}$. This range of specific export rates agrees with what Grosbois et al. (2001) determined in the Middle Loire (8 t km^{-2} $year^{-1}$ during 1995–1997). The POC cumulated fluxes represented 38 10^3 t in 2012 at S3 and 70 10^3 t in 2013 (equivalent to 0.3 and 0.6 tC km^{-2} $year^{-1}$).

Unfortunately, due to a lack of data through winter 2013, DOC loads could not be computed at S1 and S3 during the year 2013. However, DOC loads at S2 were twice higher in 2013 and were equivalent to 1 tC km^{-2} $year^{-1}$ in 2012 against 2.2 tC km^{-2} $year^{-1}$ the next year.

Dissolved organic carbon generally dominated representing >70 % TOC. On the contrary, the composition of the particulate form differed largely depending on the period. During the hydrological events, the allochthonous matter represented 80–90 % of the total POC load. During the main biological events B1 and B2, the detrital POC remained the principal source of the total POC at S1 (≈75 %) but was dominated at S2 and S3 by autochthonous POC. In that way, the contribution of algal matter to the total POC increased from 27 up to 75 % going downstream during the periods of high algal development.

The flux duration curves of TSS, pigments, DOC and POC gave similar results from one station to another. Total suspended solid concentration was the most variable parameter as 50 % of the cumulated flux occurred in 10 % of the time (Fig. 6) against 13, 13 and 20 % of the time for DOC, POC and pigments, respectively. Similarly, 99 % of the TSS cumulated flux occurred in 80 % of the time against ≈88 % of the time for DOC, POC and pigments.

Table 2 Key coefficient values necessary for the POC estimation. As indicated, these coefficients were determined using some different period of records. The relation between detrital POC and detrital TSS was established using the 2012 year for predicting the 2013 year, and using the 2012–2013 period for assessing POC concentration since 1980

Equation	Variable assessed	Period	S1	ORL	S2	S3
POC : pigmts = α * pigmts	α	Years 2012 and 2013	32	32	31	33
autochthonousTSS = a' * pigmts	a'	1980–2012	0.13	0.13	0.15	0.15
detrital POC = a * detrital TSS + b	a	Year 2012	0.044	-	0.049	0.050
	b		0.053	-	0.109	0.004
	R^2		0.92	-	0.90	0.94
	a	Years 2012 and 2013	0.041	-	0.042	0.049
	b		0.057	-	0.160	−0.033
	R^2		0.93	-	0.86	0.91

Estimating organic carbon loads of the past (1980–2013)

Cross-validation of POC load estimation based on TSS and pigments series

The high-frequency data were split into two subsets, each corresponding to 1 year of records. The relationships between POC, TSS and total pigment concentrations were assessed and tested using 2012 data (Table 2) and the POC concentration was then estimated for the next year from TSS and pigments and eventually compared to the observations for cross-validation (Fig. 7). Both the dynamic and the levels of the predicted series were well reproduced although predicted POC concentrations were overestimated most of the time and underestimated during the main biological event. However, standard deviation errors remained under 0.35 mgC L^{-1} and the errors on the 2013 POC load using this calculation were approximately ± 10 % at S1 and S3 and ± 19 % at S2.

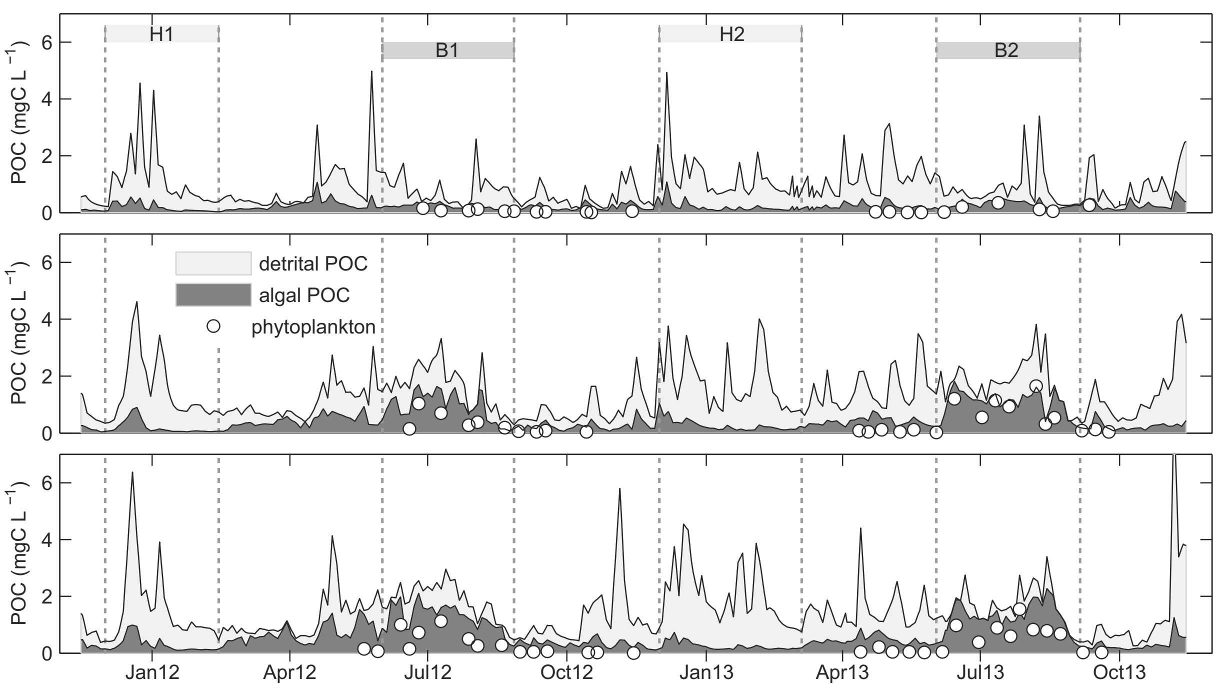

Fig. 5 Calculated POC composition at the three stations during the period of study. *Dark shades* correspond to the computed algal POC and *grey shades* to the detrital POC. *White dots* represent the observed total phytoplankton biomass

Table 3 TSS, DOC, POC, detrital POC and algal POC exports (in 10^3 t per event duration) at the three stations for a selection of hydrological and biological events

	TSS (10^3 t)			DOC (10^3 t)			POC (10^3 t)			detritalPOC (10^3 t)			algalPOC (10^3 t)		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
2011–12	199	227	557	44	45	165	10.6	15.1	38.0	8.6	11.0	25.1	2.0	4.1	12.8
2012–13	345	556	1224	-	80	-	17.2	28.5	69.6	14.0	22.0	53.2	3.2	6.5	16.5
H1	93	112	245	20	22	79	5.0	6.7	15.3	4.4	6.0	12.7	0.6	0.7	2.5
H2	136	237	647	-	35	-	6.2	11.1	35	5.2	9.7	31.2	1.0	1.4	3.9
B1	22	39	69	6.7	7.5	17	1.3	3.2	6.3	0.9	1.5	2.1	0.4	1.8	4.3
B2	34	57	105	6.1	10.1	24	1.8	4.2	8.0	1.3	1.9	2.1	0.5	2.3	5.8

Uncertainties due to sampling frequency

Uncertainties due to sampling frequency could be assessed using the flux duration in a short period of time; the $M_{2\%}$ indicator determined for TSS, total pigments, POC and DOC ranged between 7 and 20 % (Fig. 6). Such $M_{2\%}$ values are low compared to many other systems around the world with similar basin area (≈100,000 km^2). For instance, $M_{2\%}$ for TSS ranges from 15 up to 35 % (Moatar et al. 2006; Raymond et al. 2013). Therefore, the corresponding imprecision on the annual load calculation based on a monthly sampling in the Loire River are ± 10–20 %.

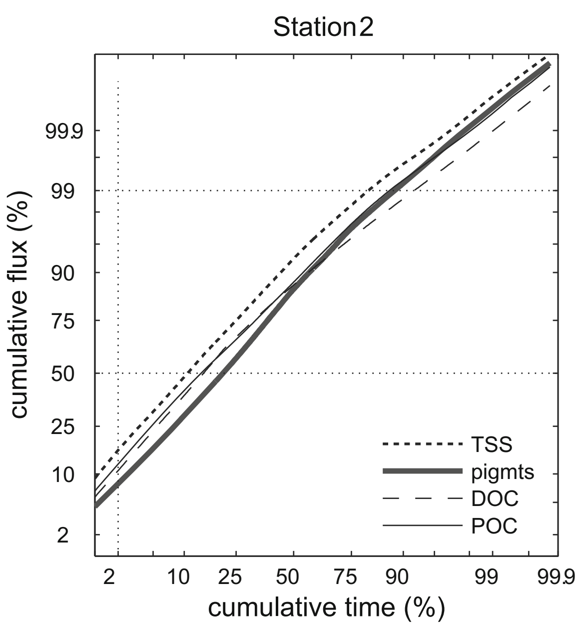

Fig. 6 Fluxes duration curves of TSS, pigments, DOC and POC at station 2

Consequently, the maximum uncertainty on estimated POC loads was 28 % as a combination of 20 and 19 % using Eq. 7. It was lower depending on the sampling frequency like at station ORL where data frequency was weekly between 1984 and 2006 and the corresponding total uncertainties on the loads did not exceed ± 21 %.

Annual TOC loads evolution since 1980

The POC concentrations and loads of the last three decades could then be assessed at stations S1, ORL, S2 and S3 depending on the availability of datasets. The model showed a positive performance as the estimated POC loads during 2012 based on the long-term monthly data slightly overestimated the POC load at S1 (error was 6 %) and significantly underestimated POC loads at S2 and S3 (errors were 27 and 28 %, respectively) but these errors remained limited and equivalent to the estimated uncertainty for this calculation. This supported both the POC calculation based on TSS and pigments series, and the method used to estimate the range of uncertainty.

The algal POC annual loads presented some great variations since 1980 (Fig. 8). The calculated values at S1 and ORL remained very close for the whole period, with a continuous decrease at ORL from ≈20 10^3 tC year^{-1} down to ≈5 10^3 tC year^{-1}. Algal POC at S2 could only be assessed during the period 1998–2012 but presented a significant decline as well. Prior to 2005, algal POC load at S2 was always twice the load estimated at ORL; the autochthonous production significantly declined at S2 over the next decade resulting in similar algal POC loads at the present time between these two stations. At the basin outlet (S3), algal POC exports into the estuary were highly variable but always over 40 10^3 tC year^{-1} during the 1980s. The next decade, it increased

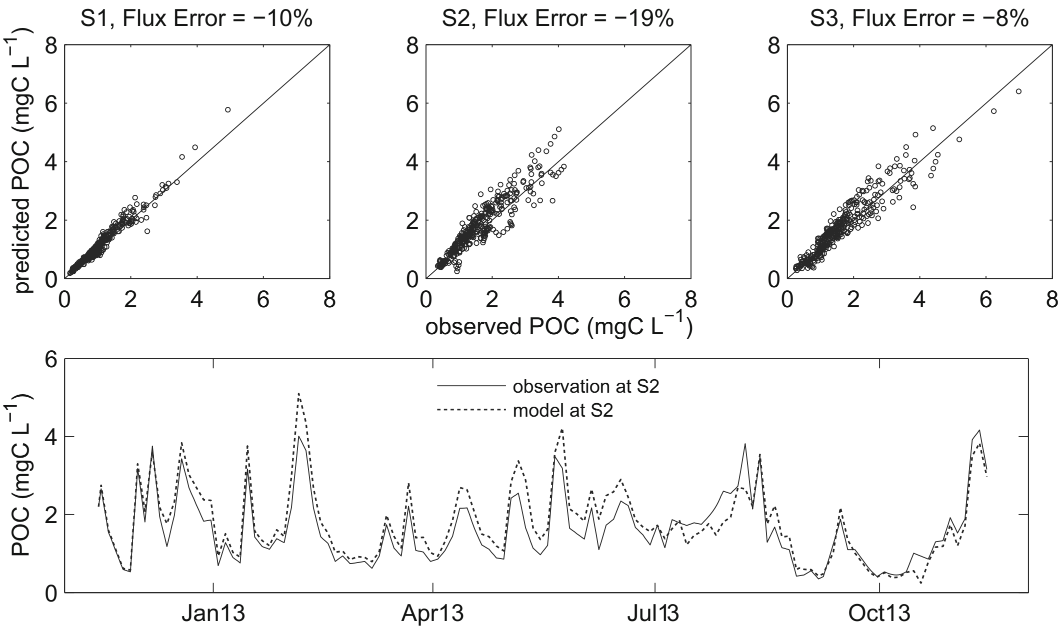

Fig. 7 Performances of the POC estimation compared to the observations at the three stations with a focus on the station 2. The total POC flux errors are also indicated for each station

first to reach the highest algal POC export recorded (in 1994, 108 10^3 tC year^{-1}) and then dramatically declined to finally reach ≈ 15 10^3 tC year^{-1} since 2010.

The detrital POC loads at stations S1, ORL and S2 ranged between ≈10 to 40 10^3 tC year^{-1} with a maximum reached in 1994. Estimated detrital POC loads declined after 1999. At station 3, the detrital POC reached its maximum value in the early 1980s (85 10^3 tC year^{-1}) and then decreased with values between 10 and 50 10^3 tC year^{-1}.

The POC loads showed high variations since the 1980s, decreasing at station 3 from ≈ 120 10^3 tC year^{-1} in 1980 down to ≈30 10^3 tC year^{-1} in 2012, with a maximum reached in 1994 (180 10^3 tC year^{-1}). At station 3, algal POC constituted on average 70 % of the total POC during the 1990s, contrasting with 50 % of it (and under) since 2005.

The DOC concentrations in the Loire River were only available during the 1992–2012 period. However, DOC loads appeared very well correlated to water fluxes and thus could be estimated for the period 1980–1991 when discharge data was available. The DOC exports were characterized by significant variations, around 20–80 10^3 tC year^{-1} at stations S1, ORL and S2 and peaked in the early 1990s. The DOC loads at S3 decreased from 400 10^3 tC year^{-1} in 1994 down to ≈ 100 10^3 tC year^{-1} in 2010–2012.

The TOC exports reached 520 10^3 tC year^{-1} at S3 in 1994 and declined to ≈150 10^3 tC year^{-1} in the early 2010s. The TOC loads variations were strongly correlated with water fluxes (Table 4). Nonetheless, most of this strong link was due to a close relationship between DOC concentration and water fluxes, plus the fact that DOC loads were dominant (60 % of TOC was composed by DOC in the 1990s, and this proportion even increased up to 75 % this last decade; the water flux explained at least 75 % of the DOC exports). Conversely, POC loads evolutions since 1980 were less explained by the water fluxes variations. This was mostly due to a poor relationship between algal POC concentration and water fluxes suggesting that the important decline in the autochthonous contribution was only partly due to decreasing hydrological conditions but more likely to some external changes.

The calculated POC concentrations presented seasonality variations throughout the whole period (Fig. 9). The algal POC maximum was reached in the summer and highly decreased from ≈ 4 mgC L^{-1} in the 1990s down to ≈1.8 mgC L^{-1} the next decade and ≈ 1.2 mgC L^{-1} for both 2012 and 2013. Conversely, detrital POC seasonality was inverted with a minimum occurring in the summer and the averaged concentration remained at the same level from 1980 onwards (0.5 mgC L^{-1} in summer and ≈ 2 mgC L^{-1} in winter). Dissolved organic carbon

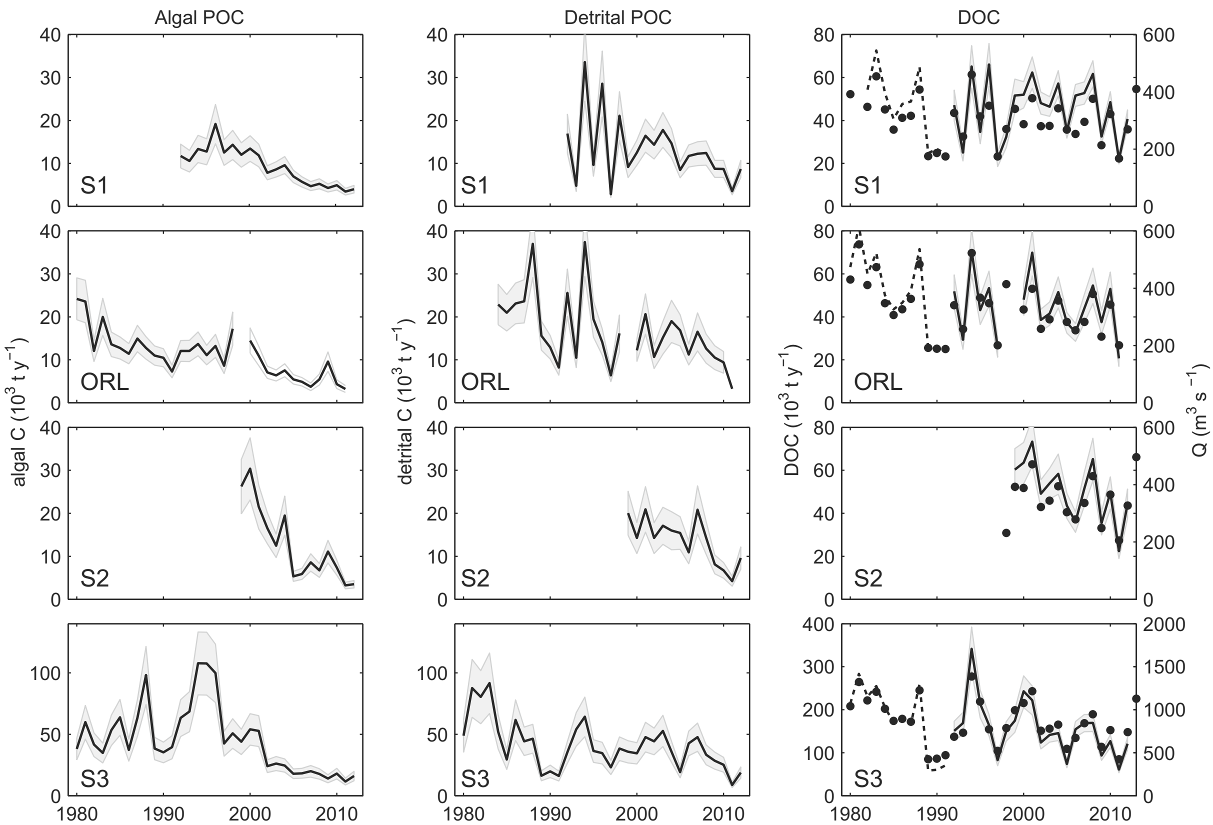

Fig. 8 Estimated algal and detrital POC loads and computed DOC loads highlighting in *grey* the uncertainties due to a varying sampling frequency at stations S1, ORL, S2 and S3 since 1980. *Black dots* represent the mean annual water discharge and *dotted lines* are the estimated DOC fluxes from the regression between DOC and Q (see Table 4)

concentration seemed to be characterized by a seasonal variation as well with a minimum occurring in summer, but its cycle was less significant. As a combination of opposed seasonal patterns, the total organic carbon concentration seasonality was unclear.

Table 4 Correlation coefficients (R) assessed from the correlation between cumulative discharge fluxes and TOC, POC, DOC, algal POC and detrital POC annual loads during the period 1980–2012

	R (*n*)			
	S1	ORL	S2	S3
TOC = f(Q)	0.87 (21)	0.94 (18)	0.89 (14)	0.93 (21)
POC = f(Q)	0.67 (21)	0.77 (27)	0.68 (15)	0.77 (33)
DOC = f(Q)	0.92 (21)	0.97 (18)	0.98 (14)	0.97 (21)
Algal POC = f(Q)	0.38 (22)	0.64 (31)	0.57 (15)	0.51 (33)
Detrital POC = f(Q)	0.73 (21)	0.79 (27)	0.66 (15)	0.76 (33)

Numbers of couples (*n*) used for each correlation are specified in brackets

Total suspended solid concentration did not present any significant seasonal variations, and seemed to have reduced from 1980 onwards mainly because of decreasing autochthonous suspended solids (SS_{autoch}) in summer (Fig. 9). A large amount of TSS in summer was autochthonous in the 1980s and 1990s and represented up to 30 mg L^{-1} at S2 when phytoplanktonic blooms were very high (chlorophyll-*a* over 200 μg L^{-1}). From 2000 onwards, SS_{autoch} greatly decreased and now remains under 10 mg L^{-1}.

Discussion

Estimated TOC evolution in a river with eutrophication mitigation

Decrease in phytoplankton development from the early 1990s onwards was observed when improvements in waste water treatment processes all over the Loire Basin

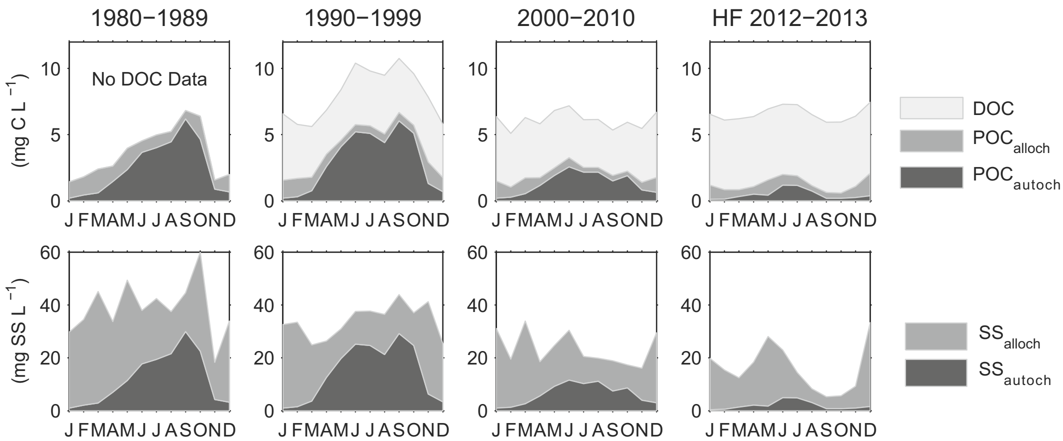

Fig. 9 Seasonal evolution from 1980 onwards at station 2 of the TOC composition (DOC, detrital and algal POC) and the TSS composition (allochthonous and autochthonous TSS). Panels on the right (2012–2013) were computed from the high-frequency datasets

limited the orthophosphate availability (Oudin et al. 2009; Floury et al. 2012; Minaudo et al. 2015). The Middle and Lower Loire Reaches were the most subjected to this regional change. On average, orthophosphate concentrations were reduced threefold between 1980 and 2012 and chlorophyll-*a* reduced 2.5 fold. Our study suggests that controlling P may also reduce POC fluxes entering into the estuary. It should be mentioned that this control on P inputs was concomitant with the invasion of *Corbicula* bivalves (Brancotte and Vincent 2002). One single clam body is able to filter up to ≈700 mL h^{-1} (Vohmann et al. 2010). This grazer may have had a significant role on the sharp decreases which were also observed in some other European rivers (Hardenbicker et al. 2014; Pigneur et al. 2014).

Most of the POC was autochthonous during the worse stage of eutrophication (70 %), and most of it was labile (Etcheber et al. 2007). The decline of particulate matter entering the estuary certainly positively impacted the estuarine and coastal zones. Considering less labile C entering the estuary, one should expect less oxygen depletion within the turbidity maxima zone, with a reduced potentiality of anoxia and fish kills, and less CO_2 released into the atmosphere. Additionally, autochthonous suspended matter greatly decreased in summer. This autochthonous suspended matter is composed by both the phytoplankton itself and precipitated calcite when conditions allowed its formation. In fact, high photosynthesis rates increase the pH value and may result in dissolved calcium losses by authigenic calcite formation. In the Loire River, pH values over 9 were frequently recorded in the summer during the period 1990–2000 (Minaudo et al. 2015) suggesting that authigenic calcite may have contributed significantly to the summer TSS concentration. This observation was described in several other studies in the Loire River such as Grosbois et al. (2001, 2012) and Meybeck (2005). Indeed, Grosbois et al. (2001) estimated that precipitated calcite represented 25 % of the TSS load in 1995–1997. Because of lower photosynthesis activity and thus lower pH in summertime since 2000 (Minaudo et al. 2015), calcite precipitation is less likely to be significant at the present time. Therefore, not only POC declined with eutrophication mitigation, but also summer TSS concentrations.

Currently, the POC specific yield of the Loire (≈0.45 tC km^{-2} $year^{-1}$) is comparable to the Rhine River's yield (0.58 tC km^{-2} $year^{-1}$, Ludwig and Probst 1996) and below the average for the world major rivers (0.85 tC km^{-2} $year^{-1}$, Coynel et al. 2005a, 2005b). Besides, the DOC specific yield of the Loire (≈1.6 tC km^{-2} $year^{-1}$) is over the Rhine River's yield (1.01 tC km^{-2} $year^{-1}$, Ludwig and Probst 1996) and close to the average for the world major rivers (2.05 tC km^{-2} $year^{-1}$, Coynel et al. 2005a, 2005b).

We should not expect significant modifications in the current organic carbon exports of the Loire River. Eutrophication declined considerably and autochthonous POC already constitutes a very little part of the total organic load. If the abundance of the invader *Corbicula* in the Loire River is confirmed, we should take into account organic carbon losses from the water to the benthic compartment and expect important releases during periods with high mortality rate. Besides, it seems reasonable to think that the decline of phytoplankton in the Loire River allowed more the development of macrophytes species: the water column being more transparent, the light would better penetrate to the river bed, enabling the growth of macrophytes. Additionally, aquatic fixed vegetation are able to extract nutrients contained in the upper sediment layer and can potentially keep growing even if phytoplankton already reached its P limitation (Carignan and Kalff 1980; Hood 2012). We unfortunately lack data and studies about macrophytes evolutions in the Loire River but one can hypothesizes that it may represent a significant storage of organic C as long as it is attached to the river bed and probably constitutes a source of autochthonous POC when plants are torn out and decay.

The rivers where eutrophication metrics are still increasing should keep recording a rising trend of POC (Verity 2002). Indeed, models predicted increasing temperature and lower discharge in summer (Moatar and Gailhard 2006; Whitehead et al. 2009; Bustillo et al. 2014) potentially intensifying the risk of eutrophication in shallow rivers (Arheimer et al. 2005; Barlocher et al. 2008; Istvánovics et al. 2014). Still, the current limitation for phytoplankton developments in the Loire River remains the phosphorus availability (Minaudo et al. 2015). The autochthonous contribution to the POC exports should then remain around 15 10^3 tC year^{-1}, leaving an annual total POC export around 50 10^3 tC year^{-1} (≈0.5 tC km^{-2} year^{-1}).

Using high-frequency surveys over an extended river course

The use of high-frequency data allowed the observation of some strong relationships between the key variables and thus enabled the estimation of POC series with satisfying results. The organic carbon fluxes could be very accurately estimated and the POC fluxes calculated from the daily survey were close to the estimation based on the established relationships and the monthly data (comparison for 2012 only, section 3.2.3). Additionally, this study permitted to quantify the uncertainties of low-frequency sampling load calculations. Moreover, this high-frequency survey allowed an accurate description of the dynamic of the different form of organic carbon. The results clearly highlighted how much TOC was composed differently depending on the type of event. The control of this composition was largely dominated by hydrology as DOC was well related to discharge and composed most of the TOC. Nevertheless, autochthonous origins controlled by biological factors are not to be ignored, especially in summer: during summer blooms (B1 and B2 events), algal POC contributed up to 80 % of POC concentrations, which represented 15 % of the total organic carbon. This proportion could be even more significant especially in eutrophic conditions. In the Loire during the 1990s when eutrophication was severe, POC could represent almost 40 % of the total organic carbon (Figs. 8 and 9). However, the biological control only lasts as long as hydrological conditions remain stable. Discharge variations are impacting turbidity, water residence time, and irradiance fluctuations. These parameters are key factors as they are conditioning, limiting and selecting successful phytoplankton species in rivers (Reynolds and Descy 1996; Istvánovics and Honti 2012). Thus, one can consider that the biological control on the composition of TOC depends on hydrological conditions as long as nutrient supplies are not exhausted. In this way, hydrology is ruling the repartition of TOC by determining good or bad conditions for algae growth.

The results also indicated how much the organic carbon dynamic and composition differ widely from one station to another. For instance, a large quantity of autochthonous POC was formed within the Middle Loire “corridor” (from S1 to S2). Thus, the POC estimation method could be tested on two different dynamics, S1 beeing detrital-like and S2 and S3 a combination of detrital and autochthonous origins. The results appeared correct in every case, confirming the consistency of the method used to assess POC.

Conclusion

The different forms of POC could be estimated with some reasonable uncertainties which valued the regular monthly survey carried out by the national water authorities. These results highlighted the large anthropogenic impact on the fluvial organic carbon composition and fluxes. In particular, controlling phosphorus inputs strongly reduced the exports of autochthonous POC into the estuarine zone. This autochthonous contribution now represents a small part of the total export, even if algal POC can still be significant in summer.

Such simple methods to estimate detrital and algal POC provided satisfying results for the long-term estimation based on low-frequency data sets although it still has to be tested on some other lowland rivers. Indeed, most of the uncertainty originated from the sampling frequency and, in the Loire River, temporal variability is lesser compared to some other rivers. A more dynamic system may necessitate high-frequency surveys to allow reasonably the POC assessment. This could change the sampling and analytical procedure that researchers may have: after surveying POC concentration every three days for 2 years, do we still need to analyse it so frequently if we are able to predict it satisfactorily with TSS and pigments only? Slaets et al. (2014) developed a method to continuously monitor particulate organic carbon with a single turbidity sensor in headwaters catchments. Similarly, the combination of a turbidity sensor with a chlorophyll sensor would certainly allow continuous POC assessments in large rivers even with significant phytoplankton blooms, offering accurate carbon fluxes calculations, with a limited error.

Acknowledgments Data used in this study was funded by the French electricity company "Electricité de France", "l'Etablissement Public Loire", FEDER European funds and by the Loire River Basin Agency (AELB). This study would not have been possible without the great efforts made by the different persons who sampled the Loire every day (Yannick Bennet, André Dubois, Hervé Couet, Laurence Lanctin, Didier Louvel), and those who made the countless analysis (Laureline Gorse, Eric Imbert, Andras Abonyi, Anne-Marie Lançon and Maria Leitao).

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