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Key Points:

- Hydrosedimentary processes control POC export to the estuary
- Benthic respiration is significant in total river metabolism
- Large urban effluent has an important effect on low-flow river functioning

Correspondence to:

L. Vilmin,
l.m.vilmin@uu.nl

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Carbon fate in a large temperate human-impacted river system: Focus on benthic dynamics

Lauriane Vilmin^{1,2}, Nicolas Flipo¹, Nicolas Escoffier^{3,4}, Vincent Rocher⁵, and Alexis Groleau³

¹Geosciences Department, MINES ParisTech, PSL Research University, Fontainebleau, France, ²Now at Department of Earth Sciences-Geochemistry, Faculty of Geosciences, Utrecht University, Utrecht, Netherlands, ³IPGP, Sorbonne Paris Cité, Univ Paris Diderot, Paris, France, ⁴Now at EPFL, Stream Biofilm and Ecosystem Research Laboratory, Lausanne, Switzerland, ⁵SIAAP, Direction du Développement et de la Prospective, Colombes, France

Abstract Fluvial networks play an important role in regional and global carbon (C) budgets. The Seine River, from the Paris urban area to the entrance of its estuary (220 km), is studied here as an example of a large human-impacted river system subject to temperate climatic conditions. We assess organic C (OC) budgets upstream and downstream from one of the world's largest wastewater treatment plants and for different hydrological conditions using a hydrobiogeochemical model. The fine representation of sediment accumulation on the river bed allows for the quantification of pelagic and benthic effects on OC export toward the estuary and on river metabolism (i.e., net CO₂ production). OC export is significantly affected by benthic dynamics during the driest periods, when 25% of the inputs to the system is transformed or stored in the sediment layer. Benthic processes also substantially affect river metabolism under any hydrological condition. On average, benthic respiration accounts for one third of the total river respiration along the studied stretch (0.27 out of 0.86 g C m⁻² d⁻¹). Even though the importance of benthic processes was already acknowledged by the scientific community for headwater streams, these results stress the major influence of benthic dynamics, and thus of physical processes such as sedimentation and resuspension, on C cycling in downstream river systems. It opens the door to new developments in the quantification of C emissions by global models, whereby biogeochemical processing and benthic dynamics should be taken into account.

1. Introduction

Fluvial networks occupy a relatively small area of the Earth's surface. However, they are active players in the carbon (C) cycle and can affect regional and global C balances [Cole *et al.*, 2007; Battin *et al.*, 2008, 2009; Trimmer *et al.*, 2012]. Fluvial networks process large amounts of organic C (OC). In fact, out of the 2 Pg of terrestrial OC reaching the world's streams and rivers each year [Battin *et al.*, 2008], only 0.38 to 0.53 Pg are exported to the seas [Degens *et al.*, 1991; Stallard, 1998]. Fluvial networks, from headwaters to estuaries, have an estimated global net heterotrophic rate of 0.32 Pg C yr⁻¹ [Battin *et al.*, 2008]. They hence contribute to the global carbon efflux to the atmosphere [Aufdenkampe *et al.*, 2011; Raymond *et al.*, 2013]. Based on these estimates, over one half of the terrestrial OC that reaches aquatic bodies is transformed or stored within these systems. In the scope of C cycle management to mitigate anthropogenic emissions, it is therefore essential to quantify the proportions of terrestrial OC entering river networks, which are exported to the seas, transformed, or stored in inland waters [Battin *et al.*, 2009]. In this goal, river OC biogeochemical transformation rates and exchanges at the sediment-water interface need to be quantified.

Soil erosion has a strong impact on the global C cycle [Lal, 2003]. River physical processes can have a significant impact on C cycling as well. Hydrodynamic conditions, such as natural flood events, exert an important control over sediment and OC export by rivers [Oeurng *et al.*, 2011; Némery *et al.*, 2013; Ford and Fox, 2014]. Hydrosedimentary fluxes also play a major role in the biogeochemical functioning of aquatic systems [Golterman *et al.*, 1983; Walling, 2005; Bilotta and Brazier, 2008; Hartwig *et al.*, 2012]. Their effect on C cycling should thus be accounted for. In-stream sediment concentrations can for example influence photosynthesis by impacting light radiation in the water column [Kirk, 1985]. Zahraeifard and Deng [2012] showed that sediment resuspension could affect organic matter mineralization. Finally, hydrosedimentary processes control sediment and OC accumulation in the benthic layer [Marttila and Kløve, 2014], where important biogeochemical activities take place [Brunke and Gonser, 1997; Findlay, 1995; Fellows *et al.*, 2006; Clapcott and Barmuta, 2010a].

Ecosystem metabolism, which corresponds to the balance between the ecosystem's primary production and respiration rates, is an integrative indicator of the processes affecting OC dynamics in streams [Tank *et al.*, 2010]. The development of high-frequency dissolved oxygen monitoring has led to numerous stream metabolism studies, performed, for the most part, in small streams [Atkinson *et al.*, 2008; Clapcott and Barmuta, 2010b; Demars *et al.*, 2011; Beaulieu *et al.*, 2013]. The significant role of the benthic compartment in stream metabolism has been extensively acknowledged for headwater streams. Some authors have quantified the contribution of this compartment to the total stream respiration [Naegeli and Uehlinger, 1997; Fellows *et al.*, 2001; Battin *et al.*, 2003; Flipo *et al.*, 2007; Ingendahl *et al.*, 2009]. For example, Ingendahl *et al.* [2009] showed that 6 to 14% of the total stream respiration could be attributed to the hyporheic zone in a small human-impacted river. For a small mountain stream, Naegeli and Uehlinger [1997] even found that up to 96% of the total respiration was due to the hyporheic zone. Flipo *et al.* [2007] found that benthic respiration accounted for 84% of the total stream respiration in a small headwater stream of the Seine River basin during low-flow periods. However, the relative importance of benthic and pelagic transformations in river C cycling has almost never been quantified for large rivers [Fauvet *et al.*, 2001; Trinh *et al.*, 2012].

In urbanized areas, human activities modify both hydrosedimentary processes, affecting suspended sediment (SS) distribution and benthic accumulation, and organic matter and nutrient inputs, which affect river C cycling. Urban areas can constitute important sources of river bed pollution, notably through combined sewer overflows (CSOs) [Even *et al.*, 2004, 2007; David *et al.*, 2013]. Taking the role of the sediment compartment into account is thus crucial to study the impact of urban effluents on water quality [Borchardt and Reichert, 2001]. In order to assess C cycling in human-impacted fluvial networks, it is therefore essential to acquire a sound understanding of physical processes, such as sediment accumulation and reentrainment, and biogeochemical transformations, together with the effects of the perturbations induced by human activities.

Due to the high pressure exerted by the Paris urban area through large urban effluents, the Seine River constitutes a pertinent example of a large human-impacted river system with a temperate climate [Billen *et al.*, 2007]. We study C cycling along a 220 km reach, from the Paris urban area to its estuary, at a pluriannual time scale. A recent study of hydrosedimentary processes indicated that at a pluriannual time scale, sediments tend to accumulate on the river bed at a low rate [Vilmin *et al.*, 2015a]. Net sediment accumulation occurs during low-flow periods, when biogeochemical processes are the most intense, while bed sediments are resuspended during high-flow events. In the present study, we specifically focus on the influence of these hydrosedimentary processes on the fate of OC (dissolved and particulate). OC fluxes are calculated upstream and downstream from one of the world's largest wastewater treatment plants (WWTPs), for low- and high-flow periods. We assess the effect of this major effluent on C cycling. The explicit simulation of a benthic compartment allows for the estimation of the pelagic and benthic flux contributions to (i) OC export to the estuary and (ii) total river metabolism. Besides the effect of large effluents on C cycling, this work highlights the importance of hydrosedimentary processes in the biogeochemical functioning of large human-impacted rivers subject to temperate climatic conditions.

2. Material and Methods

2.1. Study Area and Period: The Seine River From the Paris Urban Area to the Estuary (2007–2012)

The Seine River's functioning is studied here from the Paris urban area to the entrance of its estuary (Figure 1) over a 6 year period (January 2007 to December 2012; see Figure 2a).

The Seine River basin covers an area of 67,500 km², without accounting for its estuary. Along the studied stretch, the Seine River is a lowland river, with a Strahler stream order ranging from 7 to 8 [Strahler, 1957]. This 220 km stretch of the Seine River is highly impacted by human activities. The upstream part of the study area is constituted by the Paris urban area, which applies a constant pressure on the environment, notably by the importance of its WWTP effluents and CSOs. The Paris urban area represents 18% of the total French population concentrated on less than 3% of the territory. Five major WWTPs managed by the sewage public company of the Greater Paris (Syndicat interdépartemental pour l'assainissement de l'agglomération parisienne, noted (SIAAP)) are localized in the urban area. The largest, Seine Aval (SAV), treats the effluents of over 5 million equivalent inhabitants [Rocher *et al.*, 2011], which makes it the largest in Europe. During large rain events, the combined sewer system can overflow at many points [Even *et al.*, 2004, 2007].

The study area is located in a temperate climatic zone, with oceanic influence. Hydrological years start in September, and minimum and maximum discharges are usually observed in August and January, respectively.

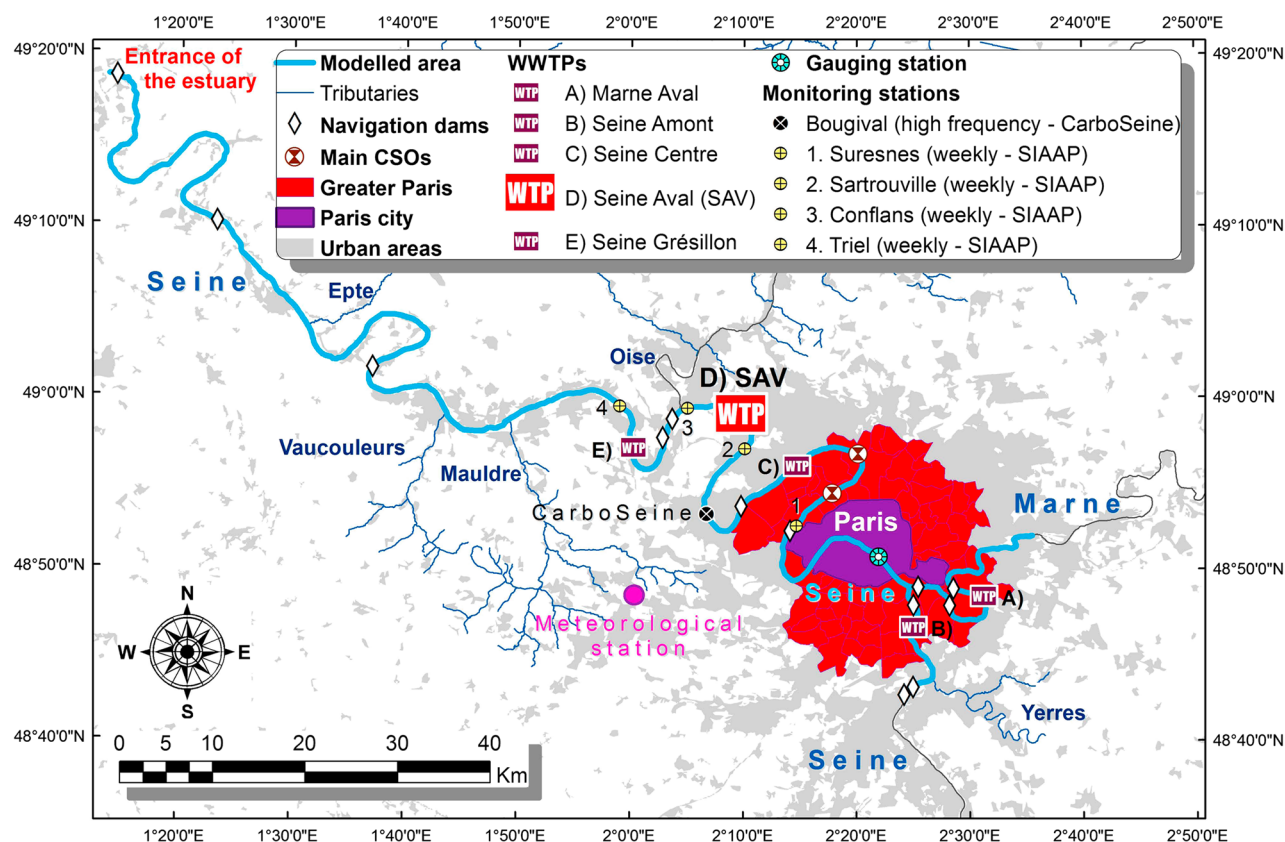


Figure 1. Study area, modeled river stretch, main tributaries and anthropogenic effluents, and locations of the monitoring stations.

Massei *et al.* [2010] showed that in addition to its annual periodicity, the Seine River's hydrology displays a periodic variability of 17 years, which is linked to the North Atlantic Oscillation. The observed mean discharge at the Paris gauging station is $310 \text{ m}^3 \text{ s}^{-1}$. Based on the distribution of daily discharges at the Paris gauging station (Figure 2b), the hydrology of the 6 year study period is representative of the last two hydrological cycles of the Seine River (1979–2012).

2.2. Simulation of Carbon Cycling in River Networks: The ProSe Model

The hydrobiogeochemical functioning of the Seine River is simulated with the ProSe model [Even, 1995; Even *et al.*, 1998, 2004, 2007; Flipo *et al.*, 2004, 2007], which has already been validated for many applications on the Seine River [Even *et al.*, 1998, 2004, 2007; Vilmin *et al.*, 2015b; Raimonet *et al.*, 2015] and its tributaries [Flipo *et al.*, 2004, 2007]. ProSe is composed of three modules (Figure 3a): (i) a hydrodynamic module that solves the 1-D shallow water equations with a finite difference scheme, using the Manning-Strickler formulation for friction, (ii) a transport module that simulates advection and dispersion of dissolved and particulate compounds with an upwind discretization scheme, and (iii) a biogeochemical module that simulates various transformation processes in the water column and the benthic layer and the exchanges between these compartments with an explicit numerical scheme.

Simulated biogeochemical processes are based on the RIVE model [Billen *et al.*, 1994; Garnier *et al.*, 1995]. RIVE simulates the cycling of carbon, O_2 , and major nutrients, with an explicit representation of the involved living species (phytoplankton, heterotrophic bacteria, and nitrifying microorganisms). This description is based on the study of these species since the late 1980s [Servais *et al.*, 1987; Servais, 1989; Garnier *et al.*, 1995; Cébron *et al.*, 2005; Raimonet *et al.*, 2015], which limits the number of parameters needing calibration and allows for the study of the effect of anthropogenic pressures on these living communities. Biogeochemical processes are simulated in the water column and in the benthic layer [Flipo *et al.*, 2004]. At the sediment-water interface, dissolved compounds exchange occurs by diffusion. Particulate compounds can settle on the river bed and be resuspended by the energy transferred from the water flow and river navigation [Martin, 2001; Vilmin *et al.*, 2015a].

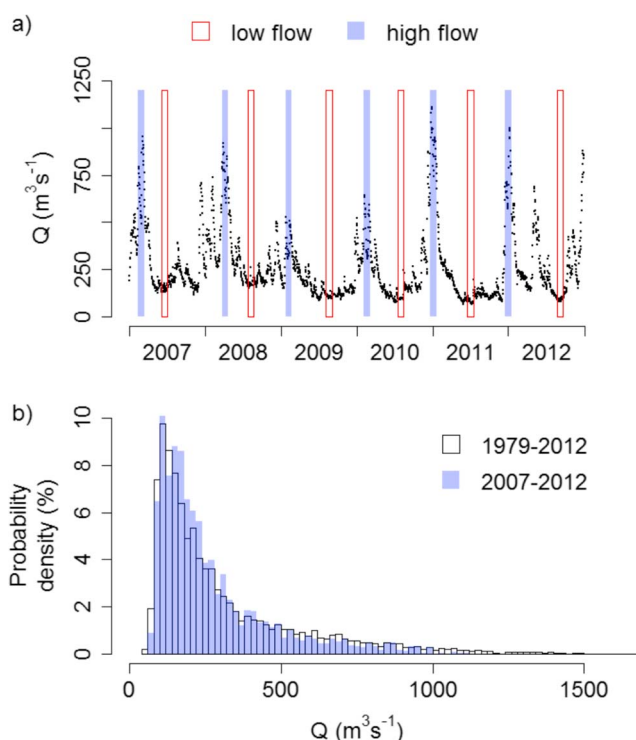


Figure 2. Hydrology of the study period (2007–2012). (a) Seine River discharge at the Paris gauging station; (b) comparison of the hydrology of the study period to the hydrology of the last two climatic cycles.

In the present paper, we focus on the biogeochemical transformations and physical processes affecting OC (Figure 3 and Tables 1 and 2). Two types of detritic OC are represented: dissolved OC (DOC) and detritic particulate OC (POC). Both of these pools are composed of a refractory fraction, a moderately biodegradable fraction, and a highly biodegradable fraction, characterized by their biodegradation rates [Servais *et al.*, 1998]. Phytoplanktonic species, heterotrophic bacteria, and nitrifying biomasses are explicitly represented and constitute living particulate OC pools.

By summing up the different fluxes linked to OC transformations (Table 2), the total OC (TOC) mass balance (MT^{-1}) of the water column can be expressed as

$$\frac{\Delta \text{TOC}}{\Delta t} = P \cdot [F_{\text{PP}}] + \mu_{\text{NB}} \cdot [\text{NB}] - R \cdot [F_{\text{PP}}] - \frac{1 - Y_{\text{HB}}}{Y_{\text{HB}}} \cdot \mu_{\text{HB}} \cdot [\text{HB}] + \Phi_{\text{sed}} \quad (1)$$

where $[F_{\text{PP}}]$, $[\text{NB}]$, and $[\text{HB}]$ are the concentrations of functional macromolecules of primary producers and nitrifying and heterotrophic biomasses, respectively (Table 1). P and R indicate the photosynthesis and respiration rates of primary producers, μ_{NB} and μ_{HB} are the growth rates of nitrifiers and heterotrophic bacteria, and Y_{HB} is the growth yield of heterotrophic bacteria (Table 1). Φ_{sed} (MT^{-1}) is the flux of TOC involved in exchanges (sedimentary processes or diffusion) between the water column and the benthic layer.

$P \cdot [F_{\text{PP}}] + \mu_{\text{NB}} \cdot [\text{NB}]$ corresponds to the water column's production term. It expresses OC production by the fixing of mineral C during photosynthesis and nitrification processes. $R \cdot [F_{\text{PP}}] + \frac{1 - Y_{\text{HB}}}{Y_{\text{HB}}} \cdot \mu_{\text{HB}} \cdot [\text{HB}]$ represents the water column respiration, which corresponds to the consumption of OC by phytoplankton and heterotrophic bacteria respirations, respectively, and its release as CO_2 in the water column.

2.3. Application of the ProSe Model to the Seine River

2.3.1. Model Setup and Boundary Conditions

In the model, a 220 km stretch of the Seine River and a 17 km stretch of the Marne River, which flows into the Seine River in Paris, are simulated (Figure 1). Four other major tributaries are taken into account as lateral boundary conditions, among them the Oise River, which flows into the Seine River 62 km downstream from Paris and represents one fourth of the total discharge at the entrance of the estuary. In addition to tributaries, 13 navigation dams are also represented. In the model, the rivers are represented by 500 m cells. Processes are simulated for the whole 2007–2012 period at a 10 min time step.

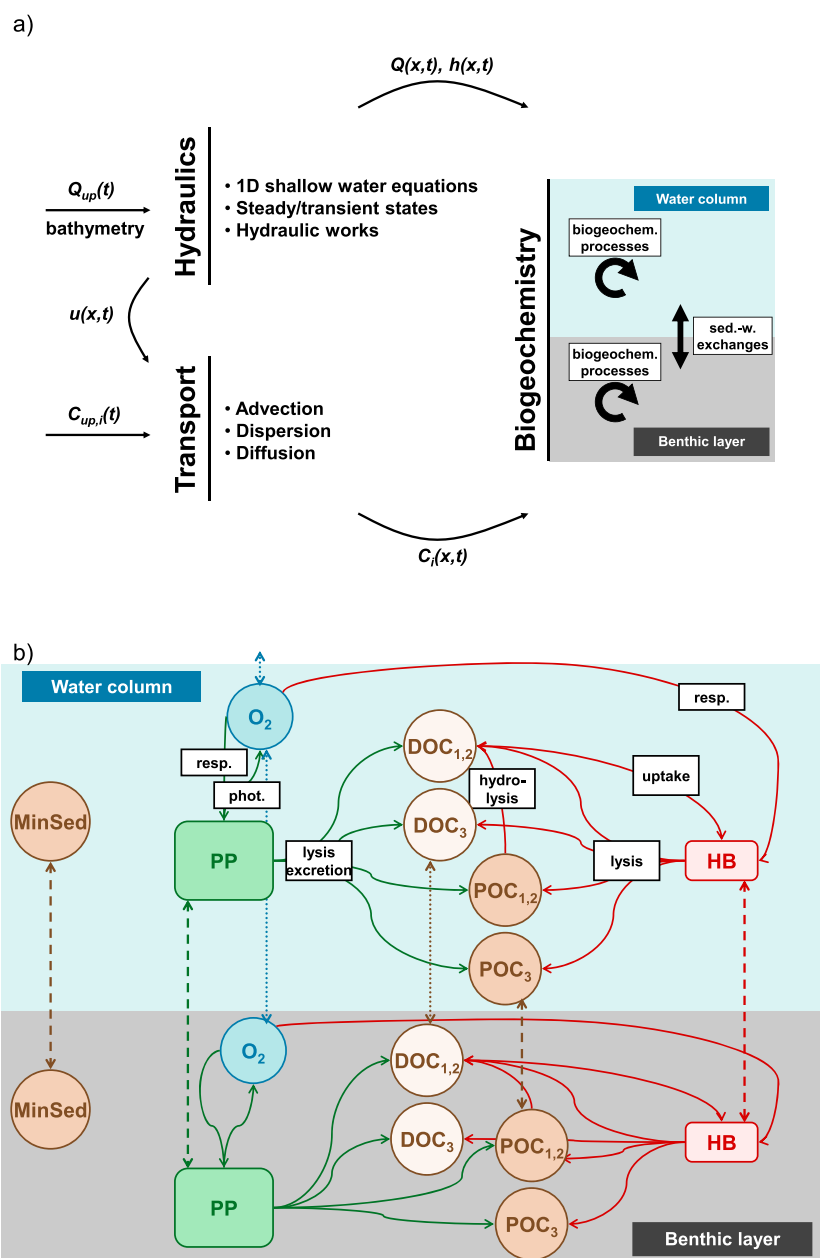


Figure 3. Schematic description of the ProSe model: (a) modules of the model and (b) simplified flowchart of the biogeochemical module. Dotted lines = diffusive exchanges; dashed lines = sedimentation/erosion exchanges. Please refer to Table 1 for notations; subscripts 1, 2, and 3 refer to the highly, moderately, and nonbiodegradable fractions of OC, respectively. For readability, NB is not represented.

The inflows of the different OC forms to the system are estimated based on TOC or 5 day biochemical oxygen demand (BOD5), SS, and chlorophyll *a* concentration measurements [Servais *et al.*, 1987, 1998; Tusseau-Vuillemin *et al.*, 2002; Servais and Billen, 2009]. Daily TOC and SS and weekly chlorophyll *a* concentrations, acquired by the Greater Paris public drinking water service (SEDIF) and the SIAAP are available close to the upstream limits of the simulated stretches of the Seine and Marne rivers (13 km and 25 km upstream from the Seine-Marne confluence, respectively) and in the Oise River upstream from its confluence with the Seine River. Monthly concentrations of BOD5, SS, and chlorophyll *a* are monitored in smaller tributaries by the national river monitoring network (RCS). All river discharges are extracted at a daily time step from the Banque HYDRO national database (www.hydro.eaufrance.fr). Data from the stations closest to the upstream boundary

Table 1. Variables and Parameters Used in ProSe for the Simulation of Biogeochemical Processes Related to the C Cycle

Notation	Description	Dimension
[PP]	Concentration of primary producers	[ML ⁻³]
[F _{pp}]	Concentration of primary producers' functional macromolecules	[ML ⁻³]
[HB]	Concentration of heterotrophic biomass	[ML ⁻³]
[NB]	Concentration of nitrifying biomass	[ML ⁻³]
[POC]	Concentration of detritic particulate organic C	[ML ⁻³]
[DOC]	Concentration of dissolved organic C	[ML ⁻³]
<i>P</i>	Photosynthesis rate of primary producers	[T ⁻¹]
<i>E</i>	Excretion rate of primary producers	[T ⁻¹]
<i>R</i>	Respiration rate of primary producers	[T ⁻¹]
<i>K_{i,PP}</i>	Mortality rate of primary producers (constant)	[T ⁻¹]
<i>μ_{HB}</i>	Growth rate of heterotrophic bacteria	[T ⁻¹]
<i>Y_{HB}</i>	Growth yield of heterotrophic bacteria (constant)	adimensional
<i>K_{i,HB}</i>	Mortality rate of heterotrophic bacteria (constant)	[T ⁻¹]
<i>μ_{NB}</i>	Growth rate of nitrifiers	[T ⁻¹]
<i>K_{i,NB}</i>	Mortality rate of nitrifiers (constant)	[T ⁻¹]

conditions is used for the Seine and Marne Rivers (1 km and 30 km upstream from the Seine-Marne confluence, respectively). For the simulated tributaries, discharge is forced with the measurements at the station closest to their confluence with the Seine River. Concentrations (notably BOD5 and SS) and water discharge of the five WWTP effluents of the Paris urban area are provided at a daily time step by the SIAAP. One hundred fifty-one CSOs are accounted for in the model as lateral boundary conditions. The SIAAP provides measurements/estimates of the effluents' water discharges at a daily time step, together with BOD5 and SS concentrations. The concentrations of 34 large CSO effluents are informed daily; the other 117 CSOs are described by their average annual water quality. The urban runoff that is not collected in the sewer system is neglected [Némery *et al.*, 2005].

2.3.2. Validation of the Simulation of OC Cycling

Simulated dissolved O₂ concentrations and chlorophyll *a* dynamics were recently compared with high-frequency data at the Bougival CarboSeine monitoring station (56 km downstream from the Seine-Marne confluence, left river branch; see Figure 1) [Vilmin *et al.*, 2016]. The model was shown to be able to reproduce algal dynamics properly. Moreover, increases in O₂ concentrations during algal blooms matched the measurements, and O₂ drops (mostly due to CSO events) were synchronized with observed drops. These O₂ peaks and drops are linked to the system's primary production and respiration. We therefore assume that the model is able to provide good estimates of the river metabolism.

Table 2. Biogeochemical Processes Related to the C Cycle Simulated With ProSe^a

Process	[PP]	[HB]	[NB]	[POC]	[DOC]
Photosynthesis	+ <i>P</i> · [F _{pp}]				
Growth		+ <i>μ_{HB}</i> · [HB]	+ <i>μ_{NB}</i> · [NB]		− $\frac{\mu_{HB}}{Y_{HB}}$ · [HB]
Excretion	− <i>E</i> · [F _{pp}]				+ <i>E</i> · [F _{pp}]
Respiration	− <i>R</i> · [F _{pp}]				
Mortality	− <i>K_{i,PP}</i> · [PP]	− <i>K_{i,HB}</i> · [HB]	− <i>K_{i,NB}</i> · [NB]	+ $\frac{1}{2}$ · <i>K_{i,PP}</i> · [PP] + $\frac{1}{2}$ · <i>K_{i,HB}</i> · [HB] + $\frac{1}{2}$ · <i>K_{i,NB}</i> · [NB]	+ $\frac{1}{2}$ · <i>K_{i,PP}</i> · [PP] + $\frac{1}{2}$ · <i>K_{i,HB}</i> · [HB] + $\frac{1}{2}$ · <i>K_{i,NB}</i> · [NB]
Hydrolysis				− <i>K_{b,POC}</i> · [POC]	+ <i>K_{b,POC}</i> · [POC]

^aNotations are given in Table 1. For more details on the calculation of the different terms, please see Even [1995], Even *et al.* [1998], Billen *et al.* [1994], Garnier *et al.* [1995], and Raimonet *et al.* [2015].

Table 3. Statistics Calculated on Observed and Simulated DOC and POC Concentrations at the Monitoring Stations: Mean Values (\bar{C}_{obs} , \bar{C}_{sim}) and Standard Deviations (σ_{obs} , σ_{sim}) of Observed and Simulated Concentrations, Correlation, Bias, and RMSE

Station	Variable	\bar{C}_{obs} (mg C L ⁻¹)	\bar{C}_{sim} (mg C L ⁻¹)	σ_{obs} (mg C L ⁻¹)	σ_{sim} (mg C L ⁻¹)	ρ	Bias (mg C L ⁻¹)	RMSE (mg C L ⁻¹)
Suresnes SIAAP (KP 24)	DOC	2.50	2.57	0.58	0.58	0.50	0.07	0.58
Sartrouville SIAAP (KP 65)	DOC	2.62	2.72	0.74	0.47	0.68	0.10	0.55
Conflans SIAAP (KP 78)	DOC	3.33	3.43	0.84	0.44	0.62	0.09	0.67
Triel SIAAP (KP 92)	DOC	3.36	3.27	0.83	0.48	0.46	-0.09	0.75
Bougival CarboSeine (KP 56 LB)	DOC	3.38	2.62	1.00	0.29	-0.01	-0.75	1.27
Bougival CarboSeine (KP 56 LB)	POC	1.16	1.14	0.54	0.83	0.18	-0.02	0.89

In order to further validate the ProSe model in terms of OC simulation, model outputs are compared to DOC and POC measurements. Weekly DOC measurements are provided by the SIAAP at four monitoring stations for the 2010–2012 period. The location of each monitoring station is indicated by its kilometer point (KP), which corresponds to its distance in kilometers from the Seine-Marne confluence. DOC and POC measurements were also performed on grab samples at 24 dates in 2011 and 2012 at Bougival [Escoffier *et al.*, 2016]. Mean concentrations and standard deviations of the time series at the sampling dates, correlation between simulated and measured concentrations, bias, and root-mean-square error (RMSE) are calculated at each of these stations to assess the model's accuracy (Table 3).

2.4. Assessment of the Sediment Composition and of the Carbon Mass Balance for Different Hydrological Conditions

Meybeck and Moatar [2012] highlighted differences in river functioning between low-flow and high-flow periods. Moreover, as the effects of human pressures may differ depending on flow characteristics [Vilmin *et al.*, 2015b; Raimonet *et al.*, 2015], amounts of mineral sediments and OC, inflows and fluxes linked to the different biogeochemical transformations and to the exchanges between the water column and the benthic layer are (i) spatially integrated along two distinct stretches—upstream from SAV (78 km, river bed area of $1.00 \cdot 10^7 \text{ m}^2$) and downstream from SAV (142 km, river bed area of $2.56 \cdot 10^7 \text{ m}^2$) and (ii) averaged for the whole 6 year period and for low-flow and high-flow periods only.

The proportion of organic matter in the SS and in the accumulated bed sediments is thereby assessed (Table 4). A conversion factor from C weight of organic matter to dry weight of sediments of 2.5 g gC^{-1} is used.

This integration also provides information on OC circulation and cycling in the different compartments (water column and benthic layer). The relative contribution of these compartments to OC export to the estuary and

Table 4. Average Flow and Meteorological Conditions and Computed Sediment Composition and Export for Different Hydrological Conditions

	Unit	2007–2012	Low Flow	High Flow
Flow and meteorological conditions				
\bar{Q}_{Paris}	$\text{m}^3 \text{ s}^{-1}$	269	118	675
\bar{V}_{Paris}	m s^{-1}	0.41	0.21	0.86
\bar{T}_{water}	$^{\circ}\text{C}$	14	22	7
\bar{I}_{max}	J cm^{-2}	187	253	135
Simulated amount of organic matter in sediments				
Upstream SAV - Water column	%	12	30	4.4
Upstream SAV - Benthic layer	%	7.3	7.6	6.5
Downstream SAV - Water column	%	15	46	6.1
Downstream SAV - Benthic layer	%	8.0	8.0	7.6
Simulated export of SS				
With sedimentation	t d^{-1}	916	138	4814
Without sedimentation	t d^{-1}	1024	235	4798

Table 5. OC Inflows and Outflows (t C d^{-1}) and Fluxes Linked to Pelagic Processes and Sediment-Water Exchanges Upstream and Downstream From SAV^a

Flux	2007–2012					Low Flow					High Flow				
	DOC	POC	PP	HB	NB	DOC	POC	PP	HB	NB	DOC	POC	PP	HB	NB
Inflows															
Seine River	43.49	10.87	0.77	0.24	0.14	14.96	3.74	0.43	0.08	0.06	143.93	35.98	1.81	0.81	0.34
Marne River	19.09	5.48	0.43	0.21	0.07	6.93	1.06	0.42	0.10	0.02	58.79	17.27	0.80	0.47	0.17
Other up. inflows	4.85	6.69	0.00	0.45	0.06	4.40	5.29	0.00	0.36	0.05	5.05	8.99	0.00	0.60	0.08
SAV	20.16	8.88	0.00	1.44	0.06	16.99	5.51	0.00	0.89	0.05	22.78	13.99	0.00	2.17	0.06
Oise River	33.96	8.49	0.58	0.19	0.08	10.23	2.56	0.19	0.06	0.03	103.16	25.79	0.93	0.58	0.18
Other down. inflows	2.61	0.54	0.02	0.06	0.01	1.46	0.41	0.00	0.06	0.01	4.53	0.83	0.07	0.06	0.02
Σ inflows	124.15	40.95	1.79	2.60	0.41	54.97	18.57	1.04	1.55	0.23	338.24	102.85	3.62	4.70	0.86
Calculated fluxes with sedimentation															
Outflow (estuary)	111.42	30.74	9.52	1.96	0.36	49.10	6.84	26.18	0.45	0.12	320.01	126.94	3.18	6.73	0.88
$\Delta\Phi$	−12.72	−10.21	7.73	−0.63	−0.04	−5.87	−11.72	25.14	−1.09	−0.11	−18.23	24.08	−0.44	2.03	0.02
Up. pela. proc.	−2.55	0.34	1.38	−0.03	−0.05	−2.59	0.90	4.00	−0.26	−0.06	−1.53	0.05	−0.09	0.17	−0.02
Up. sed.-w. exch.	0.21	−2.42	−0.01	−0.01	−0.01	0.56	−4.98	−0.06	−0.02	−0.02	−0.16	2.76	0.00	0.01	0.00
Down. pela. proc.	−10.21	3.12	6.46	−0.40	0.03	−5.44	8.13	24.15	−0.47	−0.01	−12.98	0.75	−0.23	1.14	−0.02
Down. sed.-w. exch.	−0.15	−11.32	−0.10	−0.21	−0.02	2.08	−15.90	−0.37	−0.31	−0.05	−5.27	15.10	−0.01	0.27	0.04
Calculated fluxes without sedimentation															
Outflow (estuary)	110.88	42.29	7.59	2.10	0.41	46.31	23.64	17.89	0.42	0.19	325.33	106.98	3.17	6.61	0.84
$\Delta\Phi$	−13.27	1.33	5.80	−0.50	0.00	−8.66	5.07	16.86	−1.13	−0.03	−12.91	4.12	−0.45	1.91	−0.02
Up. pela. proc.	−2.49	0.09	1.16	−0.03	−0.05	−2.43	0.21	3.14	−0.27	−0.07	−1.51	0.05	−0.09	0.17	−0.02
Down. pela. proc.	−10.78	1.15	4.65	−0.49	0.05	−5.84	2.71	15.98	−0.84	0.01	−13.24	0.58	−0.24	1.30	−0.02

^aDOC = dissolved organic C, POC = detritic particulate organic C, PP = primary producers, HB = heterotrophic bacteria, NB = nitrifying biomass, $\Delta\Phi$ = (Outflow − Σ inflows), up. = upstream (from SAV), down. = downstream (from SAV), pela. proc. = pelagic processes, sed.-w. exch. = sediment-water exchanges.

to river metabolism is estimated. Moreover, the explicit representation of different living species in the model allows for the estimation of their relative involvement in the total river metabolism.

OC budgets are given in t C d^{-1} . For comparison with other estimates from the literature, export yields (i.e., export fluxes per surface area of water basin) are provided in $\text{kg C km}^{-2} \text{ yr}^{-1}$ in the text. Likewise, biogeochemical transformation fluxes and exchanges at the sediment-water interface are divided by the surface area of the river bed and are provided in $\text{g C m}^{-2} \text{ d}^{-1}$ or $\text{g C m}^{-2} \text{ yr}^{-1}$.

To study the river during hydrological extremes, we define low-flow periods as the 30 consecutive driest days (based on moving average of daily discharge at the Paris gauging station) of each calendar year. Likewise, high-flow periods correspond to the wettest consecutive 30 days of each hydrological year (Figure 2a). The average measured discharge ($\overline{Q_{\text{Paris}}}$) and computed velocity ($\overline{V_{\text{Paris}}}$) at the Paris gauging station are provided for the whole 2007–2012 period and for low- and high-flow periods only in Table 4. For discussion purposes, the mean maximum daily solar radiation ($\overline{I_{\text{max}}}$) at the Trappes meteorological station (see Figure 1) and the average daily water temperature of the Seine River ($\overline{T_{\text{water}}}$) at the upstream boundary condition are also given.

The integrated OC inflows and outflows are displayed in Table 5. Inflows and outflows and OC transformation fluxes upstream and downstream from SAV for 2007–2012, low flows, and high flows are displayed in Figures 5–7, respectively.

2.5. Sensitivity of River Carbon Cycling to Hydrosedimentary Processes

In order to quantify the effect of hydrosedimentary processes (particle settling and resuspension processes) on river C cycling, an additional simulation without sedimentation processes is performed. In this simulation, no benthic compartment is constituted and OC transformations occur only in the water column. In other words, no benthic retention and transformations are simulated in this specific simulation.

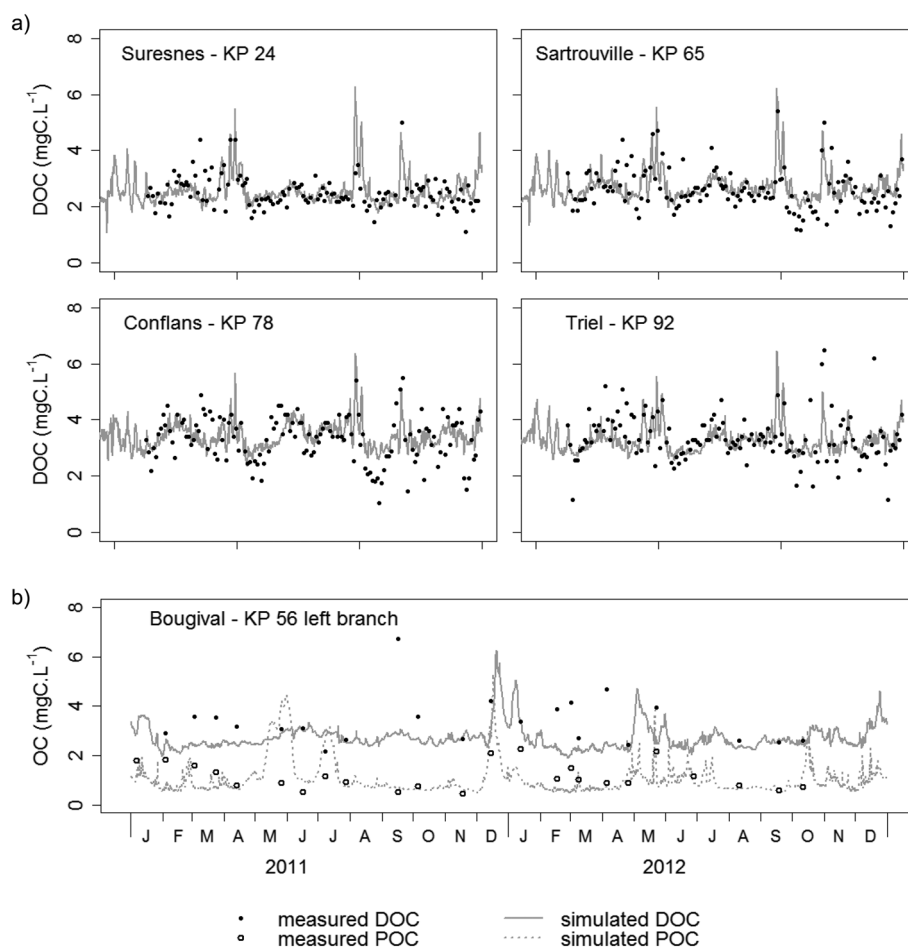


Figure 4. Measured and simulated (a) DOC concentrations at the four SIAAP stations and (b) DOC and POC concentrations at the CarboSeine station of Bougival.

3. Results

3.1. Simulation of OC Dynamics From the Paris Urban Area to the Estuary

DOC concentrations are well assessed by the model at the SIAAP monitoring stations (Figure 4a and Table 3). The biases between simulated and observed concentrations range from -2.7% at Triel (KP 92) to $+3.8\%$ at Sartrouville (KP 65). Even though DOC variability is slightly underestimated by the model at all stations except Suresnes (KP 24), the simulated time series are rather well correlated to the observed ones, with correlation coefficients of 0.46 – 0.68 .

POC concentration measurements are only available at the CarboSeine Bougival station (KP 56, left river branch) in 2011 and 2012. The simulated concentrations match the observed ones (Figure 4e), with an average difference of -1.7% . The model seems to overestimate POC variations. For the 2011–2012 period at Bougival, this is notably due to the simulation of two summer POC concentration peaks that do not appear on the measurements.

The POC data available in the study area is very scarce. However, Vilmin *et al.* [2015a] showed that the model is very efficient in representing total SS concentrations, which have been extensively measured. We can therefore assume that the particle exchanges between the benthic layer and the water column are well characterized by the model. Moreover, since ProSe reproduces DOC and POC dynamics in a realistic way, and also algal blooms and O_2 variations [Vilmin *et al.*, 2016], we henceforth consider that the model provides relevant estimates of the OC export fluxes and of the different terms of the river metabolism.

3.2. Impact of the Paris Urban Area's Effluents on Sediment Composition

A large effluent, such as SAV, can induce changes in the total sediment composition especially during low-flow periods, when the river's natural specific load is low (Table 4). On average, the percentage of organic matter

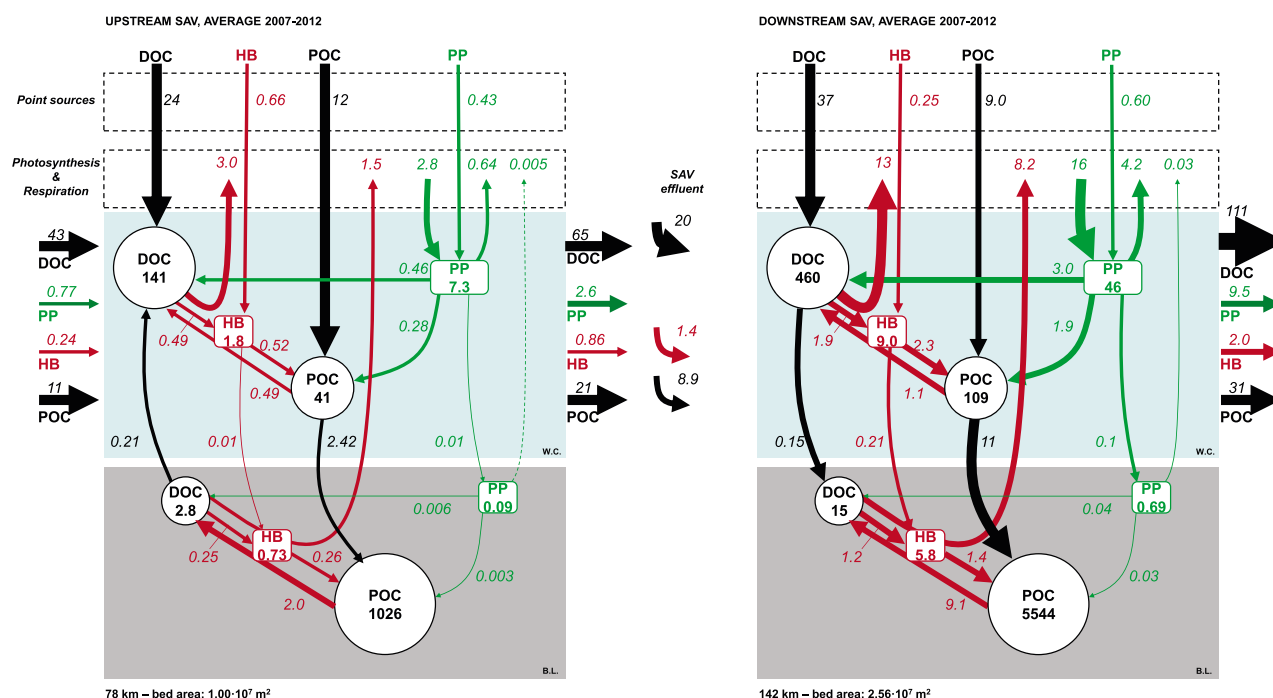


Figure 5. C weight (t C) and fluxes (t C d⁻¹) in the water column and the sediment layer, upstream and downstream from SAV, for the whole 2007–2012 period.

in SS in the water column increases downstream from SAV from 12 to 15%. This increase is even more pronounced during low-flow periods, when the proportion of organic matter in SS is high, equal to 30% upstream from SAV and to 46% downstream. The composition of benthic sediments along the studied stretch is rather constant, whatever the hydrological conditions, with 92–93.5% of mineral particles. Yet the organic matter content of benthic sediments is 10% higher downstream than upstream from SAV.

3.3. Carbon Inflows and Export to the Estuary

On average, 154 t of TOC are exported daily by the Seine River to its estuary (Table 5). TOC inputs from the SAV effluent account for 20% of this export flux. OC in the Seine River is mainly dissolved. In fact, DOC export at the estuary represents over 70% of the TOC export (Table 5). At a pluriannual time scale, primary producers constitute only a small proportion of the TOC export (6%). The heterotrophic biomass accounts for less than 2% of the exported OC for all hydrological conditions. About one half of the heterotrophic bacteria enters the river within the SAV effluent. Even though heterotrophic bacteria represent a very small fraction of the TOC in the Seine River, they have a significant impact on C cycling through their involvement in detritic C mineralization and respiration. The nitrifying biomass accounts for less than 0.25% of the TOC export of the Seine River. Its contribution to C cycling in the Seine River is negligible and is thus not represented in Figures 5–7.

During low-flow periods, the SAV effluent constitutes a large proportion of the TOC sources to the system (31%; see Table 5). The proportion of DOC in the TOC export of the Seine River is lower than the average pluriannual proportion (60%). This is notably due to the significant export of primary producer biomass, which constitutes 78% of the particulate OC flux at the entrance of the Seine River's estuary (Table 5). The biomass of primary producers accounts for almost one third of the TOC export, even though inflows from upstream catchments and tributaries are small.

A large proportion of the river's TOC export occurs during the high-flow periods. In fact, high-flow daily TOC export (458 t C d⁻¹) is 3 times higher than the average daily export for the 2007–2012 period (Table 5). A quarter of the DOC export and one third of the POC export occur during the 30 wettest days of the year. During high flow, exported OC originates mostly from the upstream river basins and SAV represents only 8.7% of the TOC sources to the system.

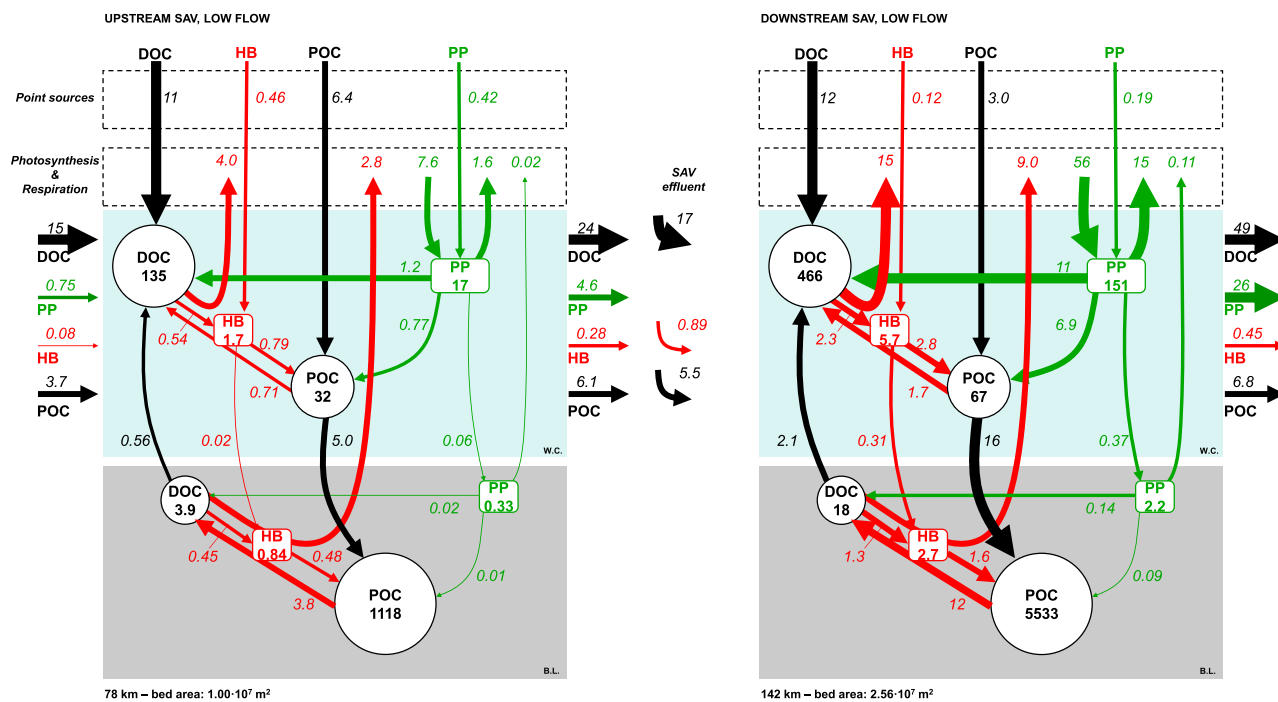


Figure 6. C weight (t C) and fluxes (t C d⁻¹) in the water column and the sediment layer, upstream and downstream from SAV, during low-flow periods.

3.4. Processes Affecting River Carbon Cycling: Production, Respiration, Biodegradation, and Sediment-Water Exchanges

The Seine River acts either as a sink (the export at the estuary is inferior to the sum of inflows) or a source (the export at the estuary is superior to the sum of inflows) for the different forms of OC in the system. The discrepancies between export fluxes at the estuary and inflows to the system ($\Delta\Phi$; see Table 5) can be explained by

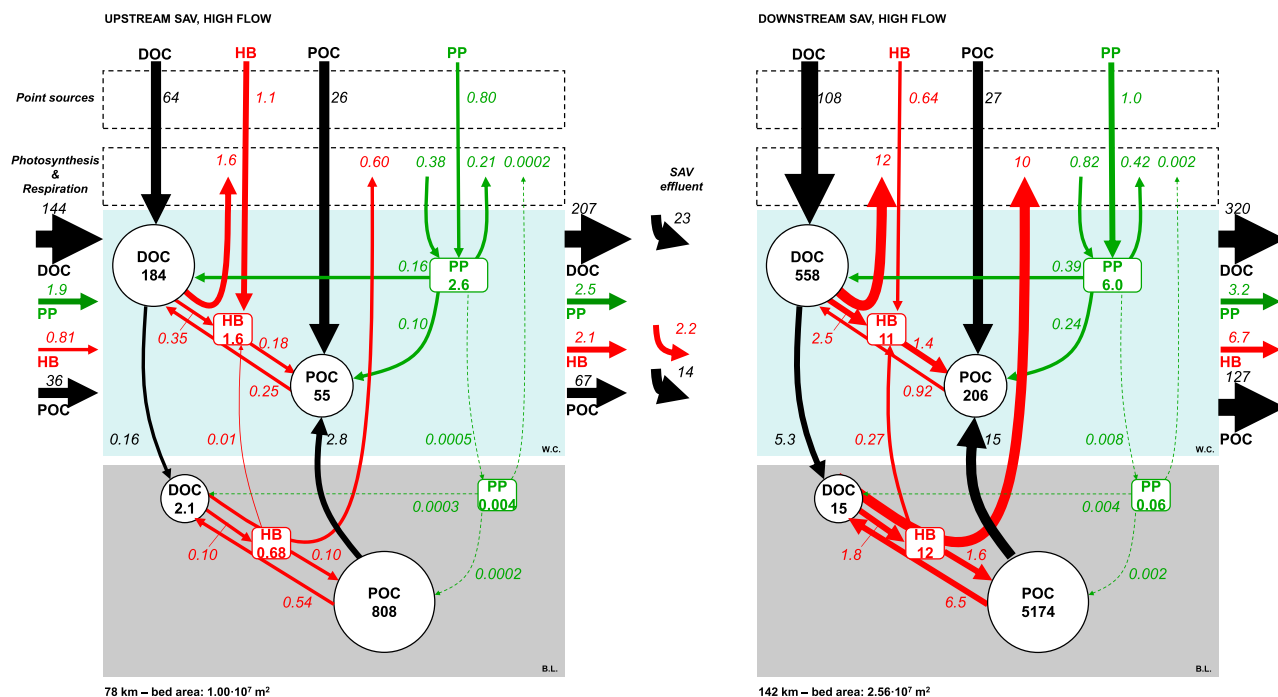


Figure 7. C weight (t C) and fluxes (t C d⁻¹) in the water column and the sediment layer, upstream and downstream from SAV, during high-flow periods.

the biogeochemical processes occurring in the water column and in the benthic compartment (production, respiration, and OC biodegradation) and by the sediment-water exchange processes (Figures 5–7). On average for the 2007–2012 period, the Seine River constitutes a sink of DOC, POC, and heterotrophic bacteria. Each year, 13 t of DOC (10% of all inflows) and 10 t of POC (25% of all inflows) entering the system are not exported to the estuary (Table 5). On the contrary, the system is on average a source of primary producers, since around 8 t C of primary producer biomass is produced along the study stretch yearly. The trends remain the same—but are even more pronounced—for low-flow periods, when only 37% of the entering POC is exported to the estuary (Table 5). The functioning is different for high-flow periods: the Seine River becomes a source of POC and heterotrophic bacteria and a sink of primary producers.

3.4.1. Average Pluriannual Functioning

At a pluriannual time scale, the Seine River is on average a heterotrophic system, with a net production of CO_2 of $0.23 \text{ g C m}^{-2} \text{ d}^{-1}$ upstream from SAV and of $0.37 \text{ g C m}^{-2} \text{ d}^{-1}$ downstream from SAV (Figure 5). It can therefore constitute a significant source of greenhouse gas to the atmosphere. This is mostly due to heterotrophic activity, which explains 84% of the total daily respiration flux of 31 t C d^{-1} along the whole studied stretch. The remaining 16% corresponds to the respiration of primary producers. The total respiration per surface area is greater downstream from SAV ($0.99 \text{ g C m}^{-2} \text{ d}^{-1}$ versus $0.51 \text{ g C m}^{-2} \text{ d}^{-1}$ upstream). POC settles in the benthic compartment, where it is biodegraded. Upstream from SAV, the DOC produced by this benthic biodegradation of POC is superior to the DOC consumption by benthic heterotrophic bacteria for growth and respiration: DOC is therefore transferred to the water column by diffusion at the water-sediment interface. On the contrary, downstream from SAV, DOC is transferred from the water column to the benthic layer. Heterotrophic bacteria from the SAV effluent mostly settle downstream from the WWTP (0.23 g C m^{-2} of heterotrophic biomass is accumulated in the benthic layer downstream from SAV versus 0.07 g C m^{-2} upstream), which boosts the sediment demand for DOC. DOC is therefore pumped from the water column for benthic bacterial activity. Benthic respiration is a significant term of the system's total metabolism, since it accounts on average for 29% ($0.15 \text{ g C m}^{-2} \text{ d}^{-1}$) of the total respiration upstream and 32% ($0.32 \text{ g C m}^{-2} \text{ d}^{-1}$) of the total respiration downstream from SAV.

3.4.2. Low-Flow Functioning

At low flow, the system is heterotrophic upstream from SAV, with a net production of CO_2 of $0.08 \text{ g C m}^{-2} \text{ d}^{-1}$, and becomes autotrophic downstream (Figure 6). The heterotrophic respiration rate per surface area is slightly greater in the downstream area, but the difference in upstream and downstream metabolisms is mainly due to processes linked to primary producers. Respiration of primary producers is almost 4 times higher downstream from SAV than upstream (0.59 versus $0.16 \text{ g C m}^{-2} \text{ d}^{-1}$, which represents 39% and 19% of the total river respiration, respectively; see Figure 6), and the primary production rate is almost multiplied by 3 (2.2 versus $0.76 \text{ g C m}^{-2} \text{ d}^{-1}$; see Figure 6).

The Seine River system constitutes a sink of detritic organic matter. Large amounts of POC are accumulated in the sediment layer, where it is biodegraded. Indeed, the hydrolysis of POC is more than 5 times greater in the sediment layer than in the water column. Consecutively, the release of DOC toward the water column is a two-step process. First, DOC is produced in the benthic layer by hydrolysis, which induces higher concentrations in the benthic interstitial water than in the water column. It is then transferred to the water column by diffusion in a second step. Benthic fluxes therefore significantly contribute to the total carbon budget. Moreover, benthic respiration accounts for 33% ($0.28 \text{ g C m}^{-2} \text{ d}^{-1}$) of the total river respiration upstream from SAV and 23% ($0.36 \text{ g C m}^{-2} \text{ d}^{-1}$) downstream from SAV.

3.4.3. High-Flow Functioning

At high flow, the system is heterotrophic (Figure 7). A net CO_2 production of $0.20 \text{ g C m}^{-2} \text{ d}^{-1}$ is estimated upstream from SAV. Downstream from SAV, river respiration is much higher, and CO_2 net production increases fourfold ($0.84 \text{ g C m}^{-2} \text{ d}^{-1}$). Respiration and production rates of primary producers are similar upstream and downstream from the WWTP: respiration rate equals $0.02 \text{ g C m}^{-2} \text{ d}^{-1}$ for both sectors, and production rate is $0.04 \text{ g C m}^{-2} \text{ d}^{-1}$ upstream and $0.03 \text{ g C m}^{-2} \text{ d}^{-1}$ downstream from SAV (Figure 7). Respiration of primary producers accounts for only 2.5% of the total respiration rate. The high respiration rate is mostly linked to high heterotrophic biomasses in the water column and in the sediment layer and to large amounts of substrate (DOC). Contrary to low-flow periods, POC is eroded from the benthic layer and DOC tends to be transferred from the water column to the benthic layer, where it is consumed by heterotrophic bacteria for their growth and respiration. During high-flow periods, benthic respiration constitutes 25% ($0.06 \text{ g C m}^{-2} \text{ d}^{-1}$) of the total river respiration upstream from SAV and as much as 45% ($0.39 \text{ g C m}^{-2} \text{ d}^{-1}$) downstream.

4. Discussion

4.1. Contribution of Benthic and Pelagic Processes to River C Cycling

It is generally assumed that the contribution of benthic processes to the total stream metabolism decreases with higher stream orders [Vannote *et al.*, 1980]. However, our results show that even for large lowland rivers, with low stream bed area per water volume ratio, benthic processes have a significant impact on both OC export to the estuary and in-stream CO_2 net production.

4.1.1. Contribution of Benthic and Pelagic Processes to Carbon Exports to Estuaries

For the 2007–2012 period, the Seine River's TOC yield equals $833 \text{ kg C km}^{-2} \text{ yr}^{-1}$. OC export is highly affected by the seasonal variability of hydrological conditions, since a quarter of this total export occurs during the year's 30 wettest days. This yield estimate is low compared to the global TOC discharge yield of world rivers to the oceans of $3.5\text{--}5 \cdot 10^3 \text{ kg C km}^{-2} \text{ yr}^{-1}$, which was estimated by Ludwig *et al.* [1996] and Stallard [1998]. However, Ludwig *et al.* [1996] showed that European rivers have lower TOC yields than the global estimate ($2.6 \cdot 10^3 \text{ kg C km}^{-2} \text{ yr}^{-1}$ on average). According to Global NEWS model results, the Seine River's DOC yield is lower than those of most of the European rivers ($917 \text{ kg C km}^{-2} \text{ yr}^{-1}$, while average is $1335 \text{ kg C km}^{-2} \text{ yr}^{-1}$ for European rivers) [Harrison *et al.*, 2005]. However, both DOC and POC yields estimated by Global NEWS [Harrison *et al.*, 2005; Beusen *et al.*, 2005] are 2 times higher than the yields we estimate for the 2007–2012 period. Without accounting for river C transformations and storage, global models may overestimate OC export by river systems such as the Seine. OC export by the Seine River occurs mainly in the dissolved form: on average, 111 of the 154 t of OC exported each day to the estuary are DOC (Table 5). This is in agreement with the measurements at the Bougival CarboSeine monitoring station, where DOC constitutes on average 75% of the measured TOC (Figure 4) and with results from previous sampling campaigns (2010–2012) that showed that DOC constituted 68% of the TOC at KP 85 [Vilmin *et al.*, 2015b]. This is also consistent with the conclusions of Meybeck [1982] and Harrison *et al.* [2005], who showed that dissolved organic matter is the major component of organic matter transported by rivers.

OC export by rivers is not only the result of advective transport of dissolved and particulate organic matter from lands to estuaries. Rivers constitute active reaction sites. Both pelagic and benthic processes affect C cycling and impact OC concentrations and fluxes. At a global scale, rivers act as OC sinks [Cole *et al.*, 2007]. Cole *et al.* [2007] estimated that 12% of the OC received by inland waters was sequestered in the sediment. Trinh *et al.* [2012] found high OC retention rates in a large urban tropical river in Vietnam, reaching up to 25% for the dry season. In the Seine River, 10% of the TOC inputs is stored or transformed in bed sediments at a pluriannual time scale (Table 5). During the driest periods, benthic processes contribute to the storage or removal of 25% of the TOC inputs, notably because of high POC accumulation rates.

Battin *et al.* [2008] presented POC transport, which is subject to gravitational settling and hydrodynamic resuspension, as a series of discrete events, while DOC tends to travel with the water. Our results confirm this hypothesis by providing quantitative estimates of these fluxes. Indeed, the calculation of the difference between the sum of POC inflows and the outflow at the estuary ($\Delta\Phi$) shows that two thirds of the entering POC “disappears” in the system during low-flow periods and that 18% of the POC exported at high flow “is created” within the river system (Table 5). This “disappearance” and “creation” of POC is mainly due to accumulation in the benthic layer during low-flow periods and resuspension during the wettest periods.

When accumulated in the benthic layer, the POC nourishes the biological reactor. Indeed, a large proportion of it transforms into DOC, especially during low-flow periods, when part of the produced DOC is then released to the water column. These transformations and sediment-water exchange trends were already pointed out by Flipo *et al.* [2004] for low-flow conditions in a small headwater stream of the Seine River basin. However, even though intense mineralization processes take place in the benthic layer, DOC exchanges at the sediment-water interface affect pluriannual DOC exports to the estuary by less than 1% (Table 5). During low-flow periods, the release of DOC by benthic sediments (2.6 t C d^{-1}) constitutes 5.4% of the total DOC export by the Seine River to the estuary. During high-flow periods 1.6% of the DOC inputs to the system is pumped by the benthic sediments.

4.1.2. Contribution of Benthic and Pelagic Processes to River Metabolism

Most of the world's lakes and rivers are assumed to be net heterotrophic systems [Duarte and Prairie, 2005] and therefore constitute sources of CO_2 to the atmosphere. Aufdenkampe *et al.* [2011] and Raymond *et al.* [2013] provided estimates of global outgassing rates from streams and rivers of 0.56 and 1.8 Pg C yr^{-1} , respectively. Here we estimate the net production of CO_2 within the river system. Even though CO_2 outgassing is not implemented in the model, our river CO_2 production estimates can be compared to estimates of river metabolism.

Battin et al. [2008] found, through a review of river metabolism studies from the literature, that the mean net ecosystem production for rivers (discharge $>0.5 \text{ m}^3 \text{ s}^{-1}$ and Strahler order >5) is $-241 \pm 40 \text{ g C m}^{-2} \text{ yr}^{-1}$. The Seine River from the Paris urban area to the estuary is a heterotrophic system with, for the 2007–2012 period, a total net production of CO_2 of $121 \text{ g C m}^{-2} \text{ yr}^{-1}$. The discrepancy with the global estimate from *Battin et al.* [2008] may be due to the fact that the studied Seine River stretch is larger than the majority of the rivers on which metabolism studies were previously carried out. In fact, in *Battin et al.* [2008], the mean discharge of the 37 studied rivers is 1 order of magnitude smaller than the Seine River's discharge in Paris. The flow conditions and the associated hydrosedimentary processes and biogeochemical transformations may therefore differ from most of these examples from the literature. Slow water velocities, also combined with high nutrient inputs from the upstream river basins and from the large urban effluents, may induce higher primary production rates in the Seine River. Along the study stretch, primary production is pelagic, due to the lack of light at the bottom of the river [*Escoffier et al.*, 2016]. We discuss in the following paragraphs the role of the benthic layer in the total river respiration.

During low-flow periods, total respiration of the Seine River from the Paris urban area to the entrance of the estuary is almost twice that of high-flow periods (48 t C d^{-1} versus 25 t C d^{-1} ; see Figures 6 and 7). The Seine River metabolism is significantly affected by the activity of primary producers at low flow, when respiration of primary producers constitutes 39% of the total respiration downstream from SAV. On the contrary, heterotrophic bacteria control the river metabolism during the wettest periods. In the downstream sector of the study area, the system even shifts from net autotrophy at low flow to net heterotrophy at high flow.

Whatever the hydrological conditions, river bed sediments play a significant role in river metabolism. They constitute important sites for organic matter microbial degradation and mineralization [*Fischer and Pusch*, 2001; *Battin et al.*, 2003]. *Fischer et al.* [2005] compared the role of river channel sediments to a “liver function” in the river's metabolism. In the Seine River system from the Paris urban area to the estuary, respiration of benthic heterotrophic organisms constitute, on average at a pluriannual time scale, one third of the total river respiration. The benthic compartment thus plays a crucial role in C cycling. During the wettest periods, this contribution reaches up to 45% downstream from the major effluent of the Paris urban area. A few previous studies emphasized the role of the benthic compartment in total stream respiration [*Naegeli and Uehlinger*, 1997; *Fellows et al.*, 2001; *Battin et al.*, 2003; *Flipo et al.*, 2007; *Ingendahl et al.*, 2009] (see section 1). *Flipo et al.* [2007] showed that 84% of the total stream respiration occurred in the benthic compartment in a small head-water stream in the Seine River basin subject to the same climatic conditions as the present study area. For low-flow periods, the total respiration rate in this small stream was of the same order of magnitude as in the 7–8 order stretch of Seine River presented here ($0.94 \text{ g C m}^{-2} \text{ d}^{-1}$ versus $1.3 \text{ g C m}^{-2} \text{ d}^{-1}$). The contribution of benthic respiration is larger in the small stream, which is consistent with the river continuum concept from *Vannote et al.* [1980]. Yet benthic respiration is still significant in the large downstream river section. The heterotrophic functioning of large rivers can even be dominated by benthic activity, as shown for the sixth-order Spree River (Germany) by *Fischer and Pusch* [2001].

These results show the importance of the benthic compartment, and thus of hydrosedimentary processes, in the hydrobiogeochemical functioning of large temperate human-impacted rivers. In fact, the benthic layer is an active player in stream metabolism [*Borchardt and Reichert*, 2001]. Moreover, the benthic compartment is not only implicated in river metabolism and C cycling but also in the nitrogen and phosphorus cycles, which are linked to the C cycle via assimilation by living species and mineralization processes [*Vilmin et al.*, 2015b; *Raimonet et al.*, 2015].

4.2. Effect of Large Urban Effluents on River C Cycling

Human activities can cause large perturbations to river C cycling and to the subsequent stream metabolism through large organic inputs and by altering extrinsic factors as water temperature, stream flow, and light availability [*Howarth et al.*, 1991; *Uehlinger et al.*, 2003; *Rees et al.*, 2005; *Tank et al.*, 2010; *Beaulieu et al.*, 2013].

As they constitute important sources of OC, effluents directly impact C fluxes [*Ruggiero et al.*, 2006; *Trinh et al.*, 2012; *Rodríguez-Murillo et al.*, 2015]. OC inputs from effluents represent a significant proportion of the OC in rivers, and decreases in sewage OC have probably played a role in the observed long-term trends of OC in rivers [*Rodríguez-Murillo et al.*, 2015]. In the case of the Seine River for the 2007–2012 period, SAV constitutes 18% of the TOC inputs to the system (Table 5). During low-flow periods, the effluent has a major influence on TOC export. Indeed, SAV TOC inputs constitute 31% of the TOC entering the system (Table 5); most of the entering POC is accumulated in the benthic layer before it can be exported to the estuary. During high-flow

periods, the SAV effluent contributes to only 8.7% of the TOC inputs to the 220 km studied stretch (Table 5) and has therefore little effect on the TOC export to the estuary. During these wettest periods, diffuse inflows (i.e., runoff from agricultural lands) are also higher than at low flow, which explains the large proportion of TOC brought to the system by the Seine, Marne, and Oise upstream basins (87% versus 54% at low flow; see Table 5). *Trinh et al.* [2012] found similar values for a large polluted tropical river in Vietnam (the Day River). They estimated that the conurbation of Hanoi contributed up to 22% of TOC inputs to the system in the dry season (8% in the rainy season).

Besides directly affecting in-stream concentrations, effluents can affect the constitution of river bed sediments, which can induce changes in the biogeochemical functioning of the river system. Urban wastewater effluents induce accumulation of POC and microorganisms [*Trinh et al.*, 2007]. Previous studies showed that increase in OC content of bed sediments occurred in response to the proximity of pollution sources [*Devesa-Rey and Barral*, 2012; *Trinh et al.*, 2012]. In the Seine River, the OC content of bed sediments is about 10% higher downstream from the SAV effluent than in the upstream section (Table 4). High accumulation of heterotrophic biomass occurs downstream from the WWTP: benthic heterotrophic biomass per surface area of bed sediments is 3 times larger downstream than upstream from SAV (Figure 5). This is due to the fact that large amounts of heterotrophic biomass are discharged into the system within the effluent. Moreover, heterotrophic bacteria originating from WWTP effluents are larger than endemic heterotrophic bacteria [*Garnier et al.*, 1992]. They therefore tend to settle in the downstream benthic layer.

Human activities induce changes in river metabolism. The large inputs of particulate and dissolved compounds from effluents (OC, nutrients, etc.) modify the downstream biogeochemical functioning and metabolism. Both production and respiration rates increase in response to disturbance [*Bernot et al.*, 2010; *Feio et al.*, 2010]. *Bernot et al.* [2010], who studied nine streams across the U.S. and Puerto Rico, found production rates in reference streams 30% lower than in urban and agricultural influenced streams. *Ruggiero et al.* [2006] and *Izagirre et al.* [2008] showed that sewage inputs in streams can induce higher heterotrophic activity and ecosystem respiration rates. In the Seine River, total respiration and production rates per surface area are twice larger downstream than upstream from SAV (Figure 5). During low-flow periods, the river system is heterotrophic upstream from SAV and autotrophic in the downstream sector (Figure 6). During these driest periods, primary production rate per surface area downstream from SAV is almost 3 times larger than upstream. This is notably due to the long residence times in the downstream sector (the computed water velocity in Paris is 0.21 m s^{-1} at low flow versus 0.86 m s^{-1} at high flow), combined with favorable climatic conditions (i.e., high temperatures and maximum daily solar radiation; see Table 4). Yet the activity of primary producers might also be promoted by the large nutrient inputs from the upstream river basins and from the large effluents of the Paris urban area.

4.3. Importance of Hydrosedimentary Processes

Even though particle exchanges between the benthic layer and the water column may not always have a significant impact on sediment fluxes to the seas [*Walling et al.*, 2008], these exchange processes between the water column and the benthic layer can have a clear impact on C export and cycling. *Ludwig et al.* [1996] showed that at the global scale, POC export by rivers is highly linked to the total sediment flux.

In order to quantify the effect of hydrosedimentary processes (i.e., sedimentation and resuspension) on OC fluxes, we compare the results of the 6 year simulation with a scenario without particle settling on the river bed.

At a pluriannual time scale (on average for the 2007–2012 period), without accounting for sediment settling, sediment export by the Seine River to its estuary is overestimated by 12% (Table 4). During low-flow periods, without accounting for sedimentation, particle export to the estuary is overestimated by 70% (Table 4). On the contrary, exchange processes between the benthic layer and the water column have very little effect on the particle export during high-flow periods. In fact, the difference between the calculated export fluxes with and without sedimentation is less than 0.5%.

Hydrosedimentary processes have a clear effect on POC export. During low-flow periods, hydrosedimentary processes reduce POC export by 60% (Table 5), due to high particle settling rates on the river bed. They also lead to an increase of the biomass of primary producers by over 30%. Indeed, high particle settling leads to low sediment concentrations in the water column and thus high light availability. Even though hydrosedimentary processes have little effect on total sediment fluxes during high-flow periods, they significantly affect

POC fluxes. In fact, they cause an increase of POC export to the estuary by 16% (Table 5). This can be explained by the fact that during periods of high discharge, POC tends to be resuspended more easily than mineral sediments due to its lower density.

On the contrary, hydrosedimentary processes have very low impact on DOC fluxes (Table 5). They lead to an increase in DOC export by the Seine River to the estuary by 6% during the driest periods, when DOC is produced in the benthic layer by POC biodegradation and tends to be released to the water column, and a decrease by 2% during the wettest periods, when DOC is pumped by the benthic layer for heterotrophic growth and respiration.

Finally, in both simulated scenarios, the calculated respiration rates for both primary producers and heterotrophic bacteria in the water column are similar. Therefore, sediment accumulation on the river bed leads to a significant increase of the total river respiration (by about 50%, since benthic respiration accounts for one third of the total river respiration).

These results confirm the major role of hydrosedimentary processes in river OC cycling and OC export to estuaries. In terms of hydrobiogeochemical modeling, which is being increasingly employed for water resources management purposes, they show that an accurate representation of benthic sediment accumulation and resuspension processes is essential for the estimation of C fluxes in large human-impacted temperate river systems.

5. Conclusion

Our results highlight the major role of benthic dynamics, and thus of hydrosedimentary processes, in C fate in large human-impacted river systems subject to temperate climatic conditions, as the Seine River. On average, the Seine River system acts like a sink of both POC and DOC. During low-flow periods, POC tends to accumulate in large quantities in the benthic layer and DOC, which is produced by POC biodegradation, is transferred to the water column. On the contrary, during high-flow periods, POC is resuspended by the flow from the benthic layer and DOC tends to be transferred from the water column to the sediments, where it is consumed by heterotrophic bacteria for growth and respiration. At a pluriannual time scale the Seine River has a heterotrophic functioning, with a mean net CO_2 production of 12 t C d^{-1} along the 220 km studied stretch. During low-flow periods, the activity of primary producers has a clear effect on stream metabolism, whereas during high-flow periods, the river metabolism is mainly controlled by heterotrophic activity. The benthic layer has a large influence on river metabolism, since benthic respiration accounts on average for one third of the total river respiration. The major effluent of the Paris urban area constitutes a constant source of OC to the system and represents a significant amount of TOC (31%) inputs to the system during the driest periods. Finally, the fine representation of biogeochemical and hydrosedimentary processes allows for the quantification of OC fluxes and transformations in the Seine River from the Paris urban area to the entrance of the estuary. We estimate that on average, out of the daily 170 t of TOC entering the system, 154 t is exported to the estuary, 2 t is transformed in the water column as a result of production and respiration processes, and 14 t is transferred to the benthic layer, where 10 t is respired.

It is well recognized that large rivers are important components of the global C cycle. This work shows the necessity of accounting for both biogeochemical processes and hydrosedimentary processes (i.e., benthic accumulation) to quantify C cycling in river systems properly. Models are increasingly used to assess the effect of anthropogenic activities on the environment at large spatiotemporal scales and to support water resources management decisions. In addition to changing C loads to river systems, process-based OC transformation rates and benthic dynamics, which are also affected by human pressures, should be implemented into global models.

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