https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Open Access
Discussions

Title page

Modeling inorganic carbon dynamics in the Seine River continuum in France

Audrey Marescaux[1], Vincent Thieu[1], Nathalie Gypens[2], Marie Silvestre[3], Josette Garnier[1]

[1]Sorbonne Université, CNRS, EPHE, Institut Pierre Simon Laplace FR 636, UMR 7619 METIS, Paris, France
[2]Université Libre de Bruxelles, Ecologie des Systèmes Aquatiques, Brussels, Belgium
[3]Sorbonne Université, CNRS, Federation Ile-de-France of Research for the Environment FR3020, Paris, France

Correspondence email : Audreymarescaux@gmail.com

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences Discussions

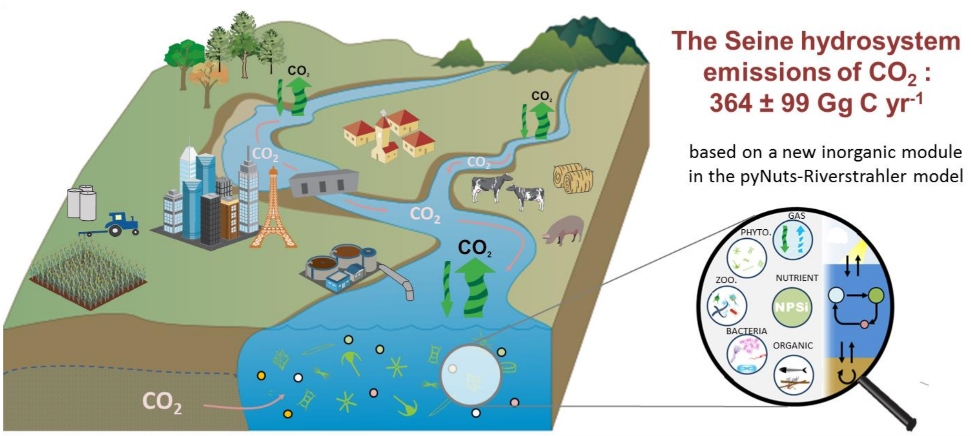
Abstract

Inland waters have been recognized as an active component of the carbon cycle where transformations and transports are associated with carbon dioxide (CO_2) outgassing. We propose a modeling approach by formalizing an inorganic carbon module integrated into the biogeochemical model, pyNuts-Riverstrahler, to estimate the carbon fate in the aquatic continuum. Our approach was implemented on the human-impacted Seine River (France) taking into account point sources (including the largest wastewater treatment plant in Europe, reaching a treatment capacity of 6 10^6 inhab eq), and diffuse constraints to the model. Both sources were characterized by field measurements in groundwater and in wastewater treatment plants, and by existing databases. In average, we calculated DIC concentrations from 25 to 92 mgC L^{-1} depending of the aquifers while in WWTP effluents our measurements of DIC averaged 70 mgC L^{-1}.

On the period studied (2010–2013), yearly averaged simulated CO_2 emissions from the hydrosystem were estimated at 364 ± 99 Gg C yr^{-1}. Simulations of dissolved inorganic carbon, total alkalinity, pH and CO_2 concentrations showed good agreement with observations, and seasonal variability could be reproduced. Metabolism in the Seine hydrographic network highlighted the importance of benthic activities in small head streams while planktonic activities were mainly observed downstream in larger rivers. In contrast to the 1990s, the net ecosystem productivity remained negative throughout all the years and at every place within the river network, highlighting the heterotrophy of the basin. In parallel, CO_2 supersaturation with respect to atmospheric concentrations of the basin was shown. Outgassing was the most important in lower order streams while peaks were simulated downstream of the major wastewater treatment effluent.

Keywords: CO2 outgassing; inorganic carbon modeling; instream metabolisms; waste- and ground water inputs; carbon budget ; temperate Seine River

Graphical abstract:



Highlights:

- The module of inorganic carbon was successfully implemented in the PyNuts-Riverstrahler model.
- CO_2 riverine concentrations are modulated by groundwater discharge and instream metabolism.
- CO_2 emissions account for 31% of inorganic carbon exports, the rest being exported as DIC.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

1. Introduction

Rivers have been demonstrated to be active pipes for transport, transformation, storage and outgassing of inorganic and organic carbon (Cole et al., 2007). Although there are large uncertainties on flux quantification from inland waters, carbon dioxide (CO_2) outgassing has been estimated to be a significant efflux to the atmosphere, subjected to regional variabilities (Cole et al., 2007; Battin et al., 2009a; Aufdenkampe et al., 2011; Lauerwald et al., 2015; Regnier et al., 2013; Raymond et al., 2013a; Sawakuchi et al., 2017; Drake et al., 2017). These variabilities are controlled by regional climate and watershed characteristics and are related to terrestrial carbon exports under different forms, from organic to inorganic, and dissolved to particulate. Organic carbon entering rivers can originate from terrestrial ecosystems as plant detritus, soil leaching or soil erosion and groundwater supply, but it can also be synthesized instream by photosynthesis or brought by dust particles (Prairie and Cole, 2009; Drake et al., 2017). Inorganic carbon sources originate from groundwater, soil leaching and exchange by diffusion at the air–water interface, depending on partial pressure of CO_2 (pCO_2) at the water surface with respect to atmospheric pCO_2 (Cole et al., 2007; Drake et al., 2017; Marx et al., 2018). Additional carbon exchanges, e.g., incorporation into biomineralized structures or resuspension, occur at the water–sediment interface and can be buried (Regnier et al., 2013b). As a whole, oligo- and mesotrophic hydrosystems generally act as a source of carbon while surface of eutrophic systems can be undersaturated with respect to atmospheric pCO_2 (Prairie and Cole, 2009; Xu et al., 2019; Yang at al., 2019).

Direct measurements of pCO_2 along the drainage network are still too scarce to accurately support temporal and spatial analyses of CO_2 variability. While calculations from pH, temperature and alkalinity may help reconstruct spatiotemporal patterns of CO_2 dynamics (Marescaux et al., 2018b), only modeling tools can predict the fate of carbon in whole aquatic systems. Indeed, modeling approaches have made it possible to simulate and quantify carbon fluxes between different reservoirs: atmosphere, biosphere, hydrosphere and lithosphere (e.g., Bern-SAR, Joos et al., 1996; ACC2, Tanaka et al., 2007; TOTEM, Mackenzie et al., 2011; MAGICC6, Meehl et al., 2007). In addition to these box approaches, a number of more comprehensive mechanistic models, describing biogeochemical processes involved in carbon cycling and CO_2 evasion, have been set up for oceans (e.g., Doney et al., 2004; Aumont et al., 2015), coastal waters (e.g., Borges et al., 2006; Gypens et al., 2004, 2009, 2011) and estuaries (e.g., Cai and Wang, 1998; Volta et al., 2014, Laruelle et al., 2019). In inland waters, the NICE-BGC model (Nakayama, 2016) accurately represents CO_2 evasion at the global scale. However, to our knowledge, whereas several river models, including Riverstrahler (Billen et al., 1994; Garnier et al., 2002) describe the carbon cycle through organic matter input and degradation by aquatic microorganisms (e.g., PEGASE, Smitz et al., 1997; ProSe, Vilmin et al., 2018; QUAL2Kw, Pelletier et al., 2006; QUAL-NET, Minaudo et al., 2018, QUASAR, Whitehead et al., 1997), none of them describes the inorganic carbon cycle including carbon dioxide outgassing.

The biogeochemical riverine model, Riverstrahler (Billen et al., 1994; Garnier et al., 1995) is a generic model of water quality and biogeochemical functioning of large river systems.

The Seine River (northwestern France) has long been studied using the Riverstrahler model. For example, the model has made it possible to quantify deliveries to the coastal zone and understand eutrophication phenomena (Billen and Garnier, 2000; Billen et al., 2001; Passy et al., 2016), nitrogen transformation and N_2O emissions (Garnier et al., 2007; Garnier et al., 2009; Vilain et al., 2012) as well as nitrate retention (Billen and Garnier, 2000; Billen et al., 2018), and organic carbon metabolism (Garnier and Billen, 2007; Vilmin et al., 2016).

It is only recently that we investigated pCO_2 and emphasized the factors controlling pCO_2 dynamics in the Seine River (Marescaux et al., 2018b).

The purpose of the present study is the implementation of a generic module of inorganic carbon into the newly developed pyNuts modeling environment for the Riverstrahler model in order to quantify the sources, transformations, sinks and gaseous emissions of inorganic carbon. A further aim in newly implementing this CO_2 module was to quantify and discuss autotrophy versus heterotrophy patterns in regard to CO_2 concentrations and supersaturation in the drainage network. In future works, a systematic coupling with an estuary model could enable to accurately calculate carbon delivery fluxes to the ocean as already proposed for the year 2010 by Laruelle et al. (2019).

2. Material and methods

2.1. Description of the Seine basin

Situated in northwestern France within 46.950 – 50.0167 north and 0.117 – 4.000 east, the Seine basin (~76,285 km²) has a temperate climate and a pluvio-oceanic hydrologic regime (Figure 1). The mean altitude of the basin is 150 m above sea level (ASL) with 1% of the basin reaching more than 550 m ASL in the Morvan (Guerrini et al., 1998). The annual water flow at Poses (stream order 7, basin area 64,867 km²), the most downstream monitoring station free from tidal influence, averaged 490 $m^3 s^{-1}$ in the 2010–2013 period (the HYDRO database, http://www.hydro.eaufrance.fr, last accessed 2019/03/26). The major tributaries include the Marne and upper Seine rivers upstream from Paris, and the Oise River downstream from Paris (Figure 1a). Three main reservoirs, storing water during winter and sustaining low flow during summer, are located upstream on the Marne River and the upstream Seine and its Aube tributary (Figure 1a). The total storage capacity of these reservoirs is 800 10^6 m^3 (Garnier et al., 1999).

The maximum water discharge of these tributaries occurs during winter with the lowest temperature and rate of evapotranspiration; the opposite behavior is observed during summer (Guerrini et al., 1998).

Except for the crystalline rocks in the north and from the highland of the Morvan (south), the Seine basin is for the most part located in the lowland Parisian basin with sedimentary rocks (Mégnien, 1980; Pomerol and Feugueur, 1986; Guerrini et al., 1998). The largest aquifers are in carbonate rock (mainly limestone and chalk) or detrital (sand and sandstone) material separated by impermeable or less permeable layers.

The concept of Strahler stream order (SO) (Strahler, 1957) was adopted for describing the geomorphology of a drainage network in Riverstrahler model (Billen et al., 1994). The smaller perennial streams are order 1. Only confluences between two river stretches with the same SO produce an increase in Strahler ordination (SO+1) (Figure 1). The mean hydrophysical characteristics of the Seine River are aggregated by stream orders in Table 1.

The Seine basin is characterized by intensive agriculture (more than 50% of the basin, CLC - EEA, 2012). The Seine basin is densely populated (~ 230 inhabitants km^{-2}). The population is mostly concentrated in the Paris conurbation (12.4 million inhabitants in 2015) (Figure 1) (INSEE, 2015). Located 70 km downstream of Paris, the largest wastewater treatment plant in Europe (Seine Aval, SAV WWTP) can treat up to 6 10^{6} inhab eq per day, releasing 15.4 m^{3} s^{-1} into the lower Seine River (Syndicat interdépartemental pour l’assainissement de l’agglomération parisienne; French acronym SIAAP, http://www.siaap.fr/, last accessed 2019/03/04).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Discussions

Table 1 Mean characteristics of the Seine River watershed by Strahler stream order[1]

SO	number streams	draining area	Cumulated length	Width	Depth	Slope	discharge	stream velocity
		km^2	*km*	*m*	*M*	*$m\ m^{-1}$*	*$m^3\ s^{-1}$*	*$m\ s^{-1}$*
1	2643	30,097	10,688	2.42	0.14	0.00952	0.15	0.34
2	603	10,635	4488	5.12	0.29	0.00345	0.67	0.36
3	148	7798	2936	8.30	0.44	0.00224	2.04	0.46
4	47	6690	1792	22.15	0.79	0.00177	6.13	0.32
5	13	8627	1044	45.01	1.10	0.00103	24.89	0.45
6	4	7864	636	77.69	2.51	0.00100	82.22	0.42
7	1	4573	467	186.18	2.61	0.00101	416.20	0.81

[1] The hydrographic network and the slopes (S, $m\ m^{-1}$) were provided by the Agence de l'Eau Seine Normandie (French acronym AESN, http://www.eau-seine-normandie.fr/, last accessed 2019/03/04); water discharges by the national Banque Hydro database (http://www.hydro.eaufrance.fr/, last accessed 2019/03/04); mean width (W, m) is assumed to follow the empirical relationship with the upstream watershed area (WSA, km^2) (see Eq. 1; Billen et al., 1994):

$$W = 0.8\, WSA^{\frac{1}{2}} \qquad \text{Eq. 1}$$

The mean depth (D, m) is related to the slope (S, $m\ m^{-1}$) and water flow (Q, $m^3\ s^{-1}$) by the relationship derived from Manning's formula (see Eq. (2), Billen et al., 1994):

$$D = [0.045Q(W(S^{1/2}))^{-1}]^{3/5} \qquad \text{Eq. 2}$$

The stream velocity ($m\ s^{-1}$) is calculated from the water discharge and the wetted area.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

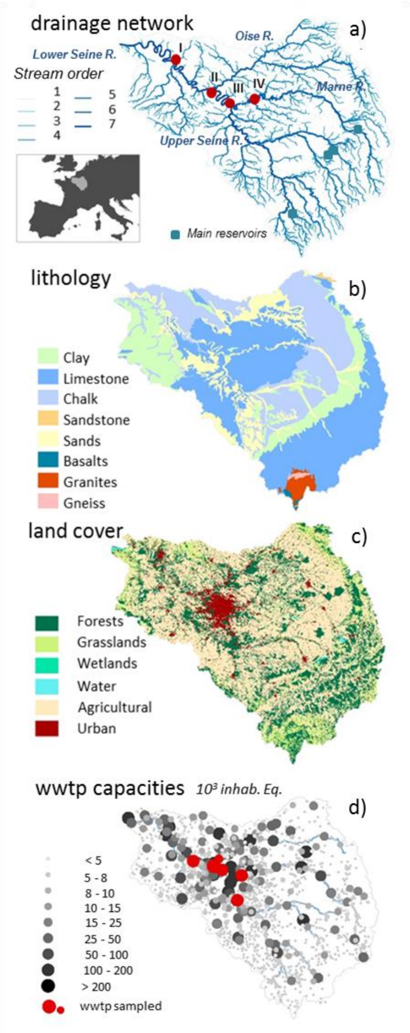


Figure 1 Characteristics of the Seine basin: a) drainage network according to Strahler stream orders (Strahler, 1952, 1957), monitoring stations (I: Poses, II: Poissy (Downstream Paris), III: Paris, IV: Ferté-sous-Jouarre (Upstream Paris); b) the lithology according to Albinet, (1967); c) land use according to the Corine Land Cover database, with six simplified classes (EEA, 2012); d) wastewater treatment plants of the basin. Red dots are the WWTPs sampled in 2018.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

2.2. The pyNuts-Riverstrahler model and its biogeochemical model, RIVE

The core of the biogeochemical calculation of the pyNuts-Riverstrahler model (described hereafter) is the RIVE model (e.g., Billen et al., 1994; Garnier et al., 1995; Garnier et al., 2002; Servais et al., 2007) (https://www.fire.upmc.fr/rive/), which simulates concentrations of oxygen, nutrients (nitrogen (N), phosphorus (P) and silica (Si)), particulate suspended matter, and dissolved and particulate organic carbon (three classes of biodegradability) in a homogeneous water column. Biological compartments are represented by three taxonomic classes of phytoplankton (diatoms, Chlorophyceae and Cyanobacteria), two types of zooplankton (rotifers with a short generation time and microcrustaceans with a long generation time), two types of heterotrophic bacteria (small autochthonous and large allochthonous with a higher growth rate than the small ones), as well as two types of nitrifying bacteria (ammonium-oxidizing bacteria and nitrite-oxidizing bacteria).

The model also describes benthic processes (erosion, organic matter degradation, denitrification, etc.) and exchanges with the water column with the explicit description of benthic organic matter, inorganic particulate P and benthic biogenic Si state variables. The benthic component does not explicitly represent all the anaerobic reduction chains, denitrification being the major anaerobic microbial process.

A detailed list of the state variables of the RIVE model is provided in S1. Most of the kinetic parameters involved in this description have been previously determined through field or laboratory experiments under controlled conditions and are fixed a priori (see detailed description of all kinetics and parameters values in Garnier et al., 2002). To date, there has been no explicit representation of inorganic carbon in the RIVE model (see this new input in S1).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

PyNuts is a modeling environment that can calculate the constraints (diffuse and point sources) to the Riverstrahler model (Raimonet et al., 2018; Desmit et al., 2018). As Riverstrahler manages the calculation of the RIVE model according to a Lagrangian routing of water masses along the hydrographic network (Billen et al., 1994), PyNuts-Rivertrahler is a generic model of water quality and biogeochemical functioning of large drainage networks that simulates water quality within entire drainage networks.

In PyNuts-Riverstrahler, modeling units can be described as a set of river axes with a spatial resolution of 1 km (axis-object), or they can be aggregated to form upstream basins that are idealized as a regular scheme of tributary confluences where each stream order is described by mean characteristics (stream order-object). Here, the Seine basin was divided into 80 modeling units, including eight axes (axis-object) and 72 upstream basins (stream order-object) (S2).

Runoffs were calculated over the whole Seine basin using water discharge measurements at 48 gauged stations (source: Banque Hydro database, http://www.hydro.eaufrance.fr/, last accessed 2019/08/29). Surface and base flow contributions were estimated applying the BFLOW automatic hydrograph separation method (Arnold and Allen, 1999) over the recent time series of water discharges (2010–2017). For the study period (2010–2013), the mean base flow index (BFI = 0.71) of the Seine basin indicates the extent of the groundwater contribution to river discharge, with spatial heterogeneity following the main lithological structures (Figure 1b), but not significant differences when summarizing the BFI criteria by Strahler order (not shown).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences Discussions

2.2.1. Development of an inorganic carbon module

Introducing the carbonate system

This module represented in Figure 2 was developed based on the model described in Gypens et al. (2004) and adapted for freshwater environments (N. Gypens and A.V. Borges, personal communication). It aims at computing the speciation of the carbonate system based on two new state variables: dissolved inorganic carbon (DIC) and total alkalinity (TA), making it possible to calculate carbon dioxide (CO_2). The module uses three equations (see S3: Eqs. 1, 2, 3) that also calculate bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydronium (H_3O^+). Indeed, two variables of the carbonate system are sufficient to calculate all the other components (Zeebe and Wolf-Gladrow, 2001). Here, DIC and TA were selected because the biological processes involved in their spatiotemporal variability along the aquatic continuum were already included in the RIVE model (Figure 2). We calculated pH as a function of total alkalinity and dissolved inorganic carbon using the Culberson equation (Culberson, 1980) (S3.4).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

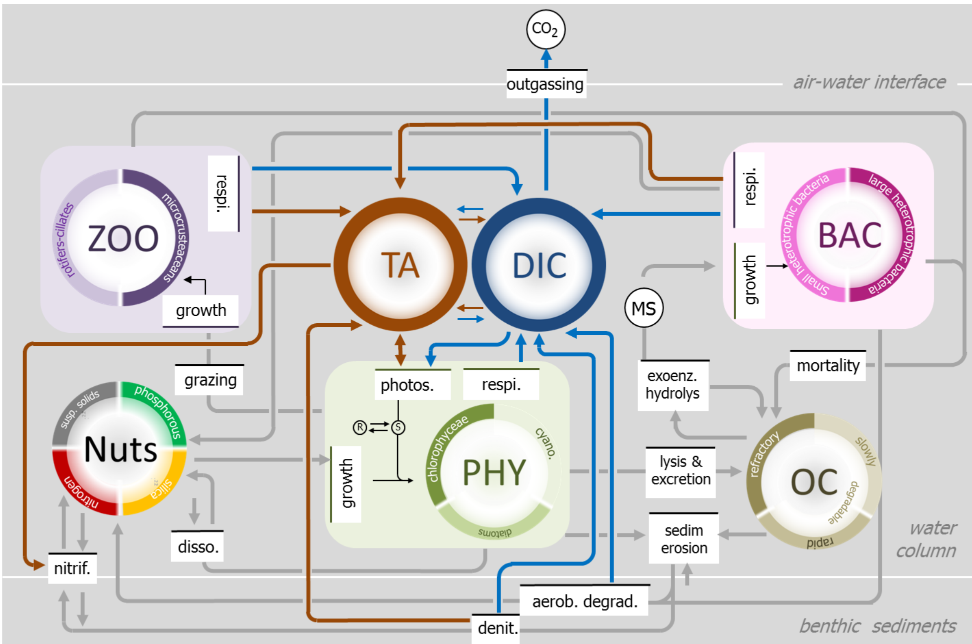


Figure 2 Schematic representation of the ecological RIVE (inspired from Billen et al. 1994, Garnier & Billen, 1994), with grey lines indicating the main processes simulated in the water column and at the interface with sediment (oxygen not shown), and implementation of the new inorganic module, based on TA (maroon) and DIC (blue) lines

Aquatic processes affecting TA and DIC

The exchange of CO_2 between the water surface and the atmosphere increases or decreases DIC, depending on the gas transfer velocity (*k*-value) and the CO_2 gradient concentrations at the water surface–atmosphere interface (Table 2, Eq. 3 and S3.5). Dissolved or particulate organic matter is mostly degraded by microbial activities (more or less quickly depending on their biodegradability), resulting in CO_2 and HCO_3^- production (Servais et al., 1995), thus inducing a change in DIC and TA concentrations in the water column (Table 2, Eq. 4, Figure 2). Photosynthesis and denitrification processes also affect DIC and TA (Table 2, Eqs. 5–7), while instream nitrification only influences TA (Table 2, Eq. 8, Figure 2).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Discussions

236 *Table 2 Stoichiometry of the biogeochemical processes, influencing dissolved inorganic carbon and total*
237 *alkalinity in freshwaters taken into account in the new inorganic carbon module. TA and DIC expressed in*
238 *mol:mol of the main substrate (either C or N)*

Process	Equation	DIC	TA	Eq.
FCO_2	$CO_2(aq) \leftrightarrow CO_2(g)$	±1	0	3
Aerobic degradation	$C_{106}H_{263}O_{11}N_{16}P + 106O_2 \rightarrow 92CO_2 + 14HCO_3^- + 16NH_4^+ + HPO_4^{2-} + 92H_2O$	+1	+14/106	4
Photosynthesis (NO_3^- uptake)	$106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+ \rightarrow C_{106}H_{263}O_{11}N_{16}P + 138O_2$	-1	+17/106	5
Photosynthesis (NH_4^+ uptake)	$106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \rightarrow C_{106}H_{263}O_{11}N_{16}P + 106O_2 + 15H^+$	-1	-15/106	6
Denitrification	$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$	+1	+4/5	7
Nitrification	$NH_4^+ + 2O_2 \rightarrow 2H^+ + H_2O + NO_3^-$	0	-2	8

239 **State equations and parameters of the inorganic carbon module**

240 These processes affecting TA and DIC result in equations governing inorganic carbon
241 dynamics as:

$$TA = TA_{t-1} + dt.\frac{dTA}{dt} + \mathrm{TA_{inputs}} \quad \text{Eq. 9}$$

242 with:

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

$$\frac{dTA}{dt} = (\frac{14}{106}\frac{(respbact + respZoo + respBent)}{M(C)} + \left(\frac{4}{5}Denit - 2.nitr[\text{'}AOB\text{'}]\right).\, M(N)^{-1} + (\frac{17}{106}\,\frac{uptPhyNO_3^-}{uptPhyN} - \frac{15}{106}\,\frac{uptPhyNH_4^+}{uptPhyN}).phot\,.M(O_2)^{-1})1000 \qquad \text{Eq. 10}$$

where TA_{t-1} is the value of total alkalinity (µmol L^{-1}) at the previous time step (t−1). $Respbact$, $RespZoo$, $respBent$ are respectively the heterotrophic planktonic respiration of bacteria, zooplankton and benthic bacteria already included in RIVE (mgC L^{-1} h^{-1}). $M(C)$ is the molar mass of the carbon (12 g mol^{-1}). $Denit$ and $nitr[\text{'}AOB\text{'}]$ are respectively the processes of denitrification and nitrification by ammonia-oxidizing bacteria (AOB) as implemented in the RIVE model (mgN L^{-1} h^{-1}); $M(N)$ is the molar mass of the nitrogen (14 g mol^{-1}). $phot$ is the net photosynthesis (mgO_2 L^{-1} h^{-1}). $uptPhyN$ is the nitrogen uptake by phytoplankton (mgN L^{-1} h^{-1}) which is differentiated for nitrate ($uptPhyNO3^-$, mgC L^{-1} h^{-1}) and ammonium ($uptPhyNH4^+$, mgC L^{-1} h^{-1}), and $M(O_2)$ is the molar mass of the dioxygen (32 g mol^{-1}). TA_{inputs} is TA (µmol L^{-1}) entering the water column by diffuse sources (groundwater and subsurface discharges) and point sources (WWTPs).

$$DIC = DIC_{t-1} + dt.\,\frac{dDIC}{dt} + DIC_{inputs} \qquad \text{Eq. 11}$$

with:

$$\frac{dDIC}{dt} = (respbact + respZoo + respBent) + denit\,.M(C).M(N)^{-1} + phot.M(C).M(O_2)^{-1} + \frac{F_{CO_2}}{depth} \qquad \text{Eq. 12}$$

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences Discussions
Open Access
EGU

where DIC_{t-1} is the value of dissolved inorganic carbon (mgC L^{-1}) at the previous time step (t−1). F_{CO_2} is the CO_2 flux at the water–atmosphere interface in mgC m^{-2} h^{-1} described in S3.5; depth is the water column depth (m).

The different values of constants and parameters used in the inorganic carbon module are introduced in Table 2. The full inorganic carbon module is described in S3 (3.1 to 3.5).

2.2.2. Input constraints of the pyNuts-Riverstrahler model

Diffuse sources from soil and groundwater

Diffuse sources are taken into account by assigning a yearly mean concentration of carbon and nutrients to subsurface and groundwater flow components, respectively. These concentrations are then combined with a 10-day time step description of surface and base flows to simulate the seasonal contribution of diffuse emissions to the river system. For nutrients, several applications of the Riverstrahler on the Seine River basin refined the quantification of diffuse sources: e.g., Billen and Garnier (2000) and Billen et al. (2018) for nitrogen; Aissa-Grouz et al. (2016) for phosphorus; Billen et al. (2007), Sferratore et al. (2008) and Thieu et al. (2009) for N, P and Si. In this study we revised our estimates for diffuse organic carbon sources and propose TA and DIC values for the Seine basin. The summary of all the model's carbon-related inputs are shown in Table 3.

Dissolved organic carbon (DOC) input concentrations were extracted from the AESN database (http://www.eau-seine-normandie.fr/, last accessed 2019/03/04) and averaged by land use for subsurface sources (mean, 3.13 mgC L^{-1}; sd, 4.56 mgC L^{-1}; 3225 data for 2010–2013). For groundwater sources, concentrations were extracted from the ADES database (www.ades.eaufrance.fr, last accessed 2019/03/04) and averaged by MESO waterbodies (French acronym: Masse d'Eau SOuterraine, see S4; mean, 0.91 mgC L^{-1}; sd, 0.8 mgC L^{-1};

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

16,000 data for 2010–2013). These concentrations were similarly separated into three pools of different biodegradability levels, with 7.5% rapidly, 17.5% slowly biodegradable and 75% refractory DOC for subsurface sources and 100% refractory DOC for groundwater flow (Garnier, unpublished).

Total POC inputs were calculated based on estimated total suspended solid (TSS) fluxes, associated with a soil organic carbon (SOC) content provided by the LUCAS Project (samples from agricultural soil, Tóth et al., 2013), the BioSoil Project (samples from European forest soil, Lacarce et al., 2009) and the Soil Transformations in European Catchments (SoilTrEC) Project (samples from local soil data from five different critical zone observatories (CZOs) in Europe, Menon et al., 2014) (Aksoy et al., 2016). TSS concentrations were calculated using fluxes of TSS provided by WaTEM-SEDEM (Borrelli et al., 2018) and runoffs averaged over the 1970–2000 period (SAFRAN-ISBA-MODCOU, SIM; Habets et al., 2008). The POC mean was 8.2 mgC L^{-1}; sd, 10.4 mgC L^{-1} in subsurface runoff, and 0.8 mgC L^{-1}; sd, 1.0 mgC L^{-1} in groundwater discharge. The same ratio of DOC reactivity was applied for three classes of POC degradability.

DIC and TA are brought by subsurface and groundwater discharges (Venkiteswaran et al., 2014). DIC is defined by the sum of bicarbonates (HCO_3^-), carbonates (CO_3^-) and CO_2. Unlike HCO_3^- and CO_3^- measured in groundwater on a regular basis by French authorities (ADES, www.ades.eaufrance.fr, last accessed 2019/03/04), CO_2 concentrations were not measured in their survey. TA values are also provided in the ADES database.

To calculate DIC concentrations in groundwaters, we therefore used our own CO_2 measurements, equaling on average 15.92 mgC-CO_2 L^{-1}; sd, 7.12 mgC-CO_2 L^{-1} (55 measurements in six piezometers in the Brie aquifer in 2016–2017) (see methodology in Marescaux et al., 2018a). DIC and TA were averaged for the 48 unconfined hydrogeological

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

MESO units of the basin (see concentrations in S4) on the recent period (2010–2015), including the simulation period. In Figure 3, a summary of TA and DIC inputs by MESO units is shown by grouping MESO units according to lithology and geological ages.

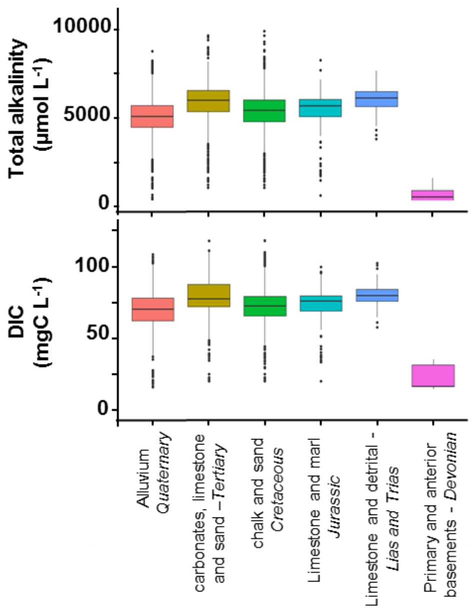


Figure 3 Boxplots of total alkalinity (µmol L^{-1}) and dissolved inorganic carbon (DIC, mgC L^{-1}) groundwater concentrations by grouping the MESO units. The lower, intermediate and upper parts of the boxes represent, respectively, the 25th, 50th and 75th percentiles and the circles represent the outlier values (source: ADES). The color code is the same as the one in S4 spatially representing the MESO units of the basin

Documenting TA and DIC diffuse sources based on MESO units ensures good representation of their spatial heterogeneity in the Seine River basin. Carbonate waters showed higher TA and DIC mean concentrations while crystalline waters had the lowest mean concentrations in TA and DIC (primary and anterior basements from Devonian, Figure 3). Aquifers from

Tertiary and alluvium of Quaternary showed more heterogeneous distribution of their concentrations (Figure 3). TA and DIC by MESO units were then spatially averaged at the scale of each modeling unit of the pyNuts-Riverstrahler model (80 modeling units, subdivided according to Strahler ordination, S3), thus forming a semi-distributed estimate of groundwater concentrations.

TA and DIC measurements in lower order streams cannot be considered as representative of subsurface concentrations because lower order streams are expected to strongly degas in a few hundred meters, as shown for N_2O in Garnier et al. (2009) and CO_2 in Öquist et al. (2009). We have considered similar concentrations and spatial distribution for subsurface components that those obtained for groundwater (from 25 to 92 mgC L^{-1} DIC, and from 663 to 5580 µmol L^{-1} TA, Figure 3).

Point sources from WWTP effluents

The pyNuts-Riverstrahler model integrates carbon and nutrient raw emissions from the local population starting from the collection of household emissions into sewage networks until their release after specific treatments in WWTPs. In the Seine River basin, most of these releases are adequately treated before being discharged to the drainage network. DOC discharge from WWTPs was described according to treatment type, ranging from 2.9 to 9.4 gC $inhab^{-1}$ day^{-1} while POC discharge ranged from 0.9 to 24 gC $inhab^{-1}$ day^{-1} based on the sample of water purification treatment observed in the Seine basin (Garnier et al., 2006; Servais et al., 1999).

TA and DIC were measured at eight WWTPs selected to reflect various treatment capacities (from 6 10^3 inhab eq to 6 10^6 inhab eq) and different treatment types (activated, sludge, Biostyr® Biological Aerated Filter) in the Seine River basin. Sampling and analysis protocols are provided in S5. This sampling did not allow us to highlight differences in per capita TA

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

and DIC emissions. Consequently, we used a fixed value of 3993 µmol L^{-1} for TA and 70 mgC L^{-1} for DIC, which correspond to the weighted mean by WWTP capacity of our measurements and are in agreement with values from Alshboul et al. (2016) found in the literature.

Point sources from reservoirs

Nutrients and organic carbon cycling within the three reservoirs of the Seine River network were simulated using the same biogeochemical RIVE model adapted for stagnant aquatic systems (Garnier et al., 1999). Despite the absence of an inorganic carbon module in the modeling of reservoirs, we used mean measurements of TA and DIC in reservoirs as occasional inputs to the river network. The Der lake reservoir was sampled three times (2016/05/24, 2016/09/12, 2017/03/16) and among others, TA and DIC were measured (see Table 3). Recent sampling campaigns showed that TA and DIC are similar for the three reservoirs (X. Yan, pers. comm.).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Table 3 Summary of the carbon related inputs of the pyNuts-Riverstrahler model

Input variables	Flow	Database	averaged	values	source
DOC	subsurface	AESN	land use	mean: 3.13 mgC L^{-1}; sd: 4.56 mgC L^{-1};	http://www.eau-seine-normandie.fr/
	groundwater	ADES	MESO units	mean: 0.91 mgC L^{-1}; sd: 0.8 mgC L^{-1}	www.ades.eaufrance.fr
POC	subsurface	LUCAS, BioSoil and SoilTrEC Projects	based on estimated total suspended solids (TSS) fluxes, associated with a soil organic carbon (SOC) content	mean: 8.2 mgC L^{-1}, sd: 10.4 mgC L^{-1}	(Aksoy et al., 2016)
	groundwater			mean: 0.8 mgC L^{-1}, sd: 1.0 mgC L^{-1}	
DIC	subsurface	ADES	MESO units	from 25 to 92 mgC L^{-1}	www.ades.eaufrance.fr
	groundwater			from 25 to 92 mgC L^{-1}	
TA	subsurface	ADES	MESO units	from 663 to 5580 µmol L^{-1}	www.ades.eaufrance.fr
	groundwater			from 663 to 5580 µmol L^{-1}	
DOC	Point sources	Measurements	According to WWTP treatment and capacity	2.9 to 9.4 gC $inhab^{-1}$ day^{-1}	(Garnier et al. 2006; Servais et al. 1999)
POC	Point sources	Measurements		0.9 to 24 gC $inhab^{-1}$ day^{-1}	
DIC	Point sources	Measurements	weighted mean by WWTP capacity	70 mgC L^{-1}	This study
TA	Point sources	Measurements	weighted mean by WWTP capacity	3993 µmol L^{-1}	This study
DIC	Reservoirs	Measurements in the Der Lake	by year	mean: 23 mgC L^{-1}, sd: 4 mgC L^{-1}	This study
TA	Reservoirs	Measurements in the Der Lake	by year	mean: 1890 µmol L^{-1}, sd: 350 µmol L^{-1}	This study

2.2.3. Observational data

We selected the 2010–2013 timeframe for setting up and validating the new inorganic module. This period includes the year 2011, which was particularly dry (mean annual water discharge at Poses, 366 m^3 s^{-1}) and 2013 wet (mean annual average water discharge at Poses, 717 m^3 s^{-1}) while 2010 and 2012 showed intermediate hydrological conditions (mean annual average water discharges at Poses, 418 m^3 s^{-1} and 458, m^3 s^{-1}, respectively) (data source: Banque Hydro).

pCO_2 values (ppmv) were calculated using CO2SYS software algorithms (version 25b06, Pierrot et al., 2006) based on existing data collected by the AESN. pH, total alkalinity and water temperature data sets were used for the 2010–2013 selected period (8693 records of

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Discussions

these three variables, i.e., around 1209 stations distributed throughout the Seine basin, measurements that were taken at fixed day time –9:00-15:00 UTC–) and could not represent diurnal fluctuations). The carbonate dissociation constants (K1 and K2) applied were calculated from Millero (1979) with zero salinity and depending on the water temperature. Because pCO_2 calculations from pH and TA can lead to overestimation of pCO_2 (Abril et al., 2015), the pCO_2 calculated data were corrected by a relationship established for the Seine River and based on pCO_2 field measurements (Marescaux et al., 2018b). To compute the interannual average over the 2010–2013 time period, data were averaged monthly, then annually at each measurement station and then spatially averaged (i.e., by Strahler orders). Four stations offering sufficient data for the 2010–2013 time period were selected for appraising seasonal patterns. They are located along the main stem of the Marne-Lower Seine River: Poses (the outlet), Poissy (downstream of the SAV WWTP), Paris and Ferté-sous-Jouarre (upstream of Paris) (Figure 1a).

All data were processed using R (R Core team, 2015) and QGIS (QGIS Development Team, 2016). Kruskal-Wallis tests were used to compare simulated and measured pCO_2 averages.

2.2.4. Evaluation of the model

Root Mean Square Errors normalized to the range of the observed data (NRMSE) were performed to evaluate the pyNuts-Riverstrahler model including the inorganic module, indicating the variability of the model results with respect to the observations, normalized to the variability of the observations. NRMSE were performed on inter-annual variations per decade for the 2010-2013 time period, combining observations and simulations at four main monitoring stations along the longitudinal profile of the Seine River: Poses, Poissy (Downstream Paris), Paris, Ferté-sous-Jouarre (Upstream Paris).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences Discussions
Open Access

3. Results

3.1. Simulations of spatial and seasonal variations of pCO_2.

3.1.1. CO_2 from lower order streams to larger sections of the Seine River

Simulations of CO_2 concentrations averaged for 2010–2013 by Strahler orders showed that pyNuts-Riverstrahler succeeds in reproducing the general trends of CO_2 observations (7565 data) (Figure 4). Although not significant, CO_2 concentration means tend to decrease from lower order streams (SO1) (width < 100 m) to SO5, and to finally increase in the higher order streams (width > 100 m) from SO6 to SO7, downstream of the Paris conurbation. Some discrepancy appears for order 1, with simulations higher than observations while for orders 2–7 simulations were conversely lower than observations. The corresponding *k*-values calculated for the Seine ranged from 0.04 to 0.23 m h^{-1} with higher values in the first streams and lower values in larger rivers (not shown), with CO_2 outgassing positively related to *k*-value (S4.5 eq. 25).

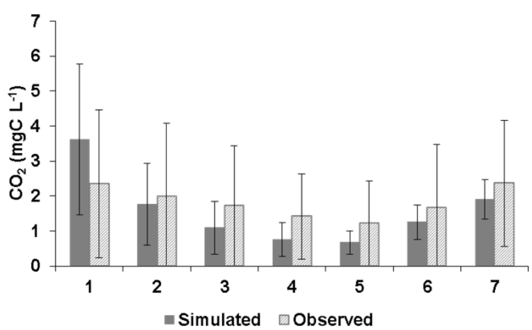


Figure 4 Carbon dioxide concentrations in the Seine waters (CO_2, mgC-CO_2 L^{-1}) simulated by the pyNuts-Riverstrahler model (dark grey) and observed (light grey) as a function of the stream order averaged on the 2010–2013 period (whiskers indicating standard deviations)

3.1.2. Profiles of the main stem Marne – Lower Seine (at Poses)

On the same period (2010-2013), a focus on the main stem from the Marne River (SO6) until the outlet of the Seine River (Poses, SO7) showed that longitudinal variations are clearly represented by the model. Higher concentrations of CO_2 downstream of Paris, and a peak of CO_2 concentrations immediately downstream of the SAV WWTP werefollowed by a progressive decrease until the estuary (Figure 5). Note that the estuarine CO_2 concentrations were specifically modeled in Laruelle et al. (2019), using these outputs of the Riverstrahler simulations.

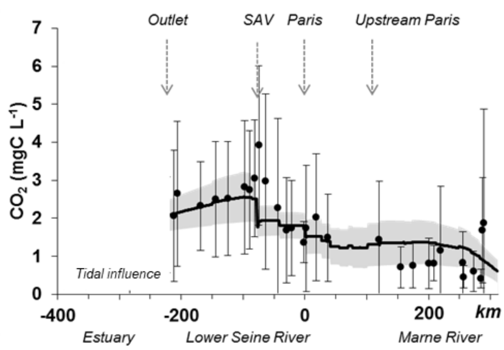


Figure 5 Observed (dots) and simulated (line) mean carbon dioxide concentrations (CO_2, mgC L^{-1}) along the main stem of the Marne River (km −350 to 0) and the lower Seine River (km 0–350) averaged over the 2010–2013 period. The simulation envelope (grey area) represents standard deviations of CO_2 simulated. Whiskers are standard deviations between observed CO_2 concentrations.

3.1.3. Seasonal variations

Upstream, within Paris, and downstream of Paris, simulations provided rather good levels of CO_2, DIC, TA and pH (Figure 6). In addition to a satisfactory range of values, DIC and TA simulations showed the observed seasonal patterns with a depletion of concentrations

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Discussions

occurring in summer/autumn related to low-flow support by the reservoirs. Indeed, reservoirs showed lower TA and DIC concentrations than rivers (Table 3). In addition to the intra-/inter-stream order variabilities of CO_2 (Figure 4), CO_2 highly varied seasonally (Figure 6). Although simulated CO_2 concentrations fitted rather well with the level of the observations (NRMSE = 15%), the model tended to overestimate the winter values upstream and within Paris (Figure 6, left).

For DIC, simulations upstream from Paris (Figure 6, right) seem lower than observations (but summer data are missing); however, downstream at the other three stations selected, simulations accurately represented the observations (Figure 6, NRMSE = 15%). Seasonal variations of TA were satisfactorily reproduced by the simulations, although they were slightly underestimated by the model at the stations upstream and downstream of Paris (Figure 6, NRMSE = 25%). Regarding pH, simulations were in a similar range as the observations (range, 7.5–8.5), and lower summer pH values in the lower Seine were correctly simulated by the model (Figure 6, NRMSE = 17%).

Hydrology and Earth System Sciences
Open Access
Discussions

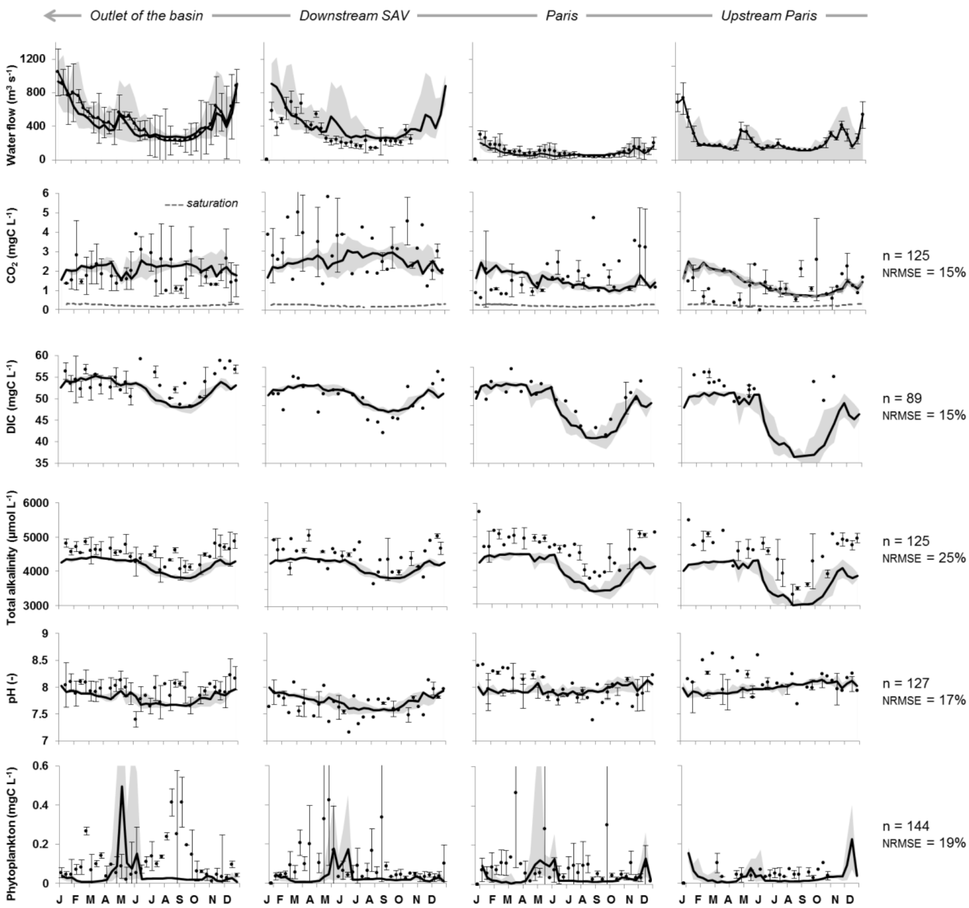


Figure 6 Ten-day simulated (lines) and observed (dots) water discharges over the 2010–2013 period (Q, $m^3 s^{-1}$), concentrations of carbon dioxide (CO2, mgC L^{-1}, and CO2 sat, mgC L^{-1}), dissolved inorganic carbon (DIC, mgC L^{-1}), total alkalinity (TA, µmol L^{-1}), pH (-), and phytoplankton (mgC L^{-1}). Simulation envelope corresponds to standard deviations. For observed data, whiskers are standard deviations. Four monitoring stations of interest along the main stem Marne-Poses are shown: Ferté-sous-Jouarre (upstream of Paris on the Marne River), Paris (upstream at Charenton), downstream of the SAV WWTP, and at the outlet of the basin (Poses). NRMSE were performed on inter-annual variations per decade for the 2010-2013 time period, combining observations and simulations at four main monitoring stations.

Although the level of phytoplankton biomass was adequately simulated, the summer bloom observed at the outlet was not reproduced, whereas the early spring bloom observed in the

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

lower Seine was simulated with a time lag compared to the observations (Figure 6, bottom, NRMSE = 19%).

3.1.4. Selection of a gas transfer velocity

4.

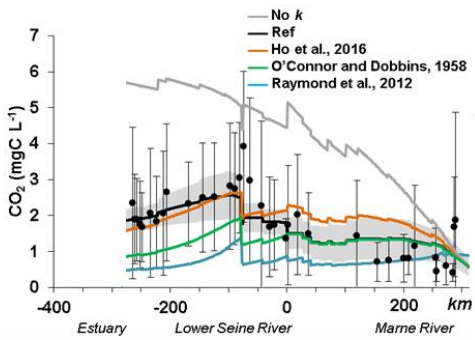


Figure 7 Influence of the gas transfer velocity formalisms along the main stem of the Seine River basin (Marne – Lower Seine River) impacted riverine CO_2 concentrations

The way of taking into account the gas transfer velocity in the modeling approach could explain these discrepancies in SO6 and SO7 (Figure4). Different values of *k* were explored (Figure 7). Indeed, the gas transfer velocity value reported by Alin et al. (2011) was used for streams and rivers up to 100 m wide, as they recommended. Whereas these *k*-values provided adequate simulations in the river up to 100 m wide, for river widths greater than 100 m, we tested different *k*. In larger stream orders, we showed that calculations of *k* according to the equation 2 of Table 5 of Raymond et al. 2012, induced a too high outgassing while without using any *k* value or using Ho et al. (2016), the opposite behavior with a much to low outgassing of CO_2 was observed.

Therefore, for river widths greater than 100 m, a k_{600} equation based on O'Connor and Dobbins, (1958) and Ho et al. (2016), neglecting the term related to the wind, and providing the most accurate CO_2 concentrations, was selected (see S3 and 6 for more information's on the selection of *k* and the tests performed):

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences Discussions

Although these results can be improved, organic and inorganic carbon and total alkalinity budgets can be calculated at the scale of a whole drainage basin for the first time.

4.1. Alkalinity, inorganic and organic carbon budgets

We established an average inorganic and organic budget for the period studied (2010–2013) (Table 4). The budget of inorganic and organic carbon (IC and OC) of the entire Seine River basin (from headwater streams to the beginning of the estuary) shows the high contribution of external inputs (sum of point and diffuse sources accounted for 92% and 68% of IC and OC inputs, respectively) and riverine exports (68% and 66% of IC and OC outputs, respectively). These exports were at least one order of magnitude higher for the IC budget (Table 4). The substantial contribution of the Seine aquifer water flow led the IC flux brought by groundwater to dominate over those from the subsurface (respectively, 57.5% vs. 34% of total IC inputs), while for OC, the subsurface contributions were higher than groundwater contributions (54% vs. 14% of the total OC fluxes).

Interestingly, the relative contributions of point sources to OC inputs were higher than for IC (23% and 7% of the OC and IC inputs, respectively) (Table 4).

Heterotrophic respiration by microorganisms accounted for only 1.5% of the IC inputs. Similarly, IC losses by net primary production also accounted for a small proportion, i.e., 0.6% of the IC inputs. For the OC budget, despite a contribution of autochthonous inputs from instream biological metabolisms (NPP and nitrification, 9% of inputs, and heterotrophic respiration, 7%), which was relatively high compared to their proportion in IC fluxes (2.3%), allochthonous terrestrial inputs still dominated the OC budget (Table 4).

The Seine River, at the outlet, exported 68% of the IC entering or produced in the drainage network, and 66% of OC brought to the river (including both particulate and dissolved forms)

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Open Access
Discussions

(Table 5). Instream OC losses were related to heterotrophic respiration (7%) and to a net transfer to the benthic sediment compartment, including sedimentation and erosion processes (estimated at 28% of losses). In the IC budget, ventilation of CO_2 was a substantial physical process (31% of the overall losses) (Table 4).

Similar calculation was performed for total alkalinity (TA) budget. As for inorganic carbon, the contribution of internal processes remained relatively low compared to the high levels of TA in lateral inputs (diffuse sources: 93 %; point sources: 6 %) and flows exported to the basin outlet (97 %). Indeed, instream production mostly relied on heterotrophic respiration (< 1%) while denitrification appeared negligible. Photosynthesis might also produce or consume alkalinity whether NO_3^- or NH_4^+ is the preferential N source of phytoplankton's uptake, but it resulted in our budget in a net reduction TA (2%), while nitrification also contributed to less than 1% of TA output.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

503 *Table 4 Budget of the Seine hydrosystem for inorganic and organic carbon (kgC km^{-2} yr^{-1}) and Total alkalinity*
504 *(mol km^{-2} yr^{-1}) as calculated by the pyNuts-Riverstrahler model averaged on the period 2010-2013. * TA input*
505 *related to NPP refer to the net difference between TA produced by photosynthesis on NO_3 uptake and*
506 *photosynthesis on NH_4 uptake (reducing alkalinity)**Net sediment loss is the difference between the erosion and*
507 *the sedimentation calculated by the model*

2010-2013	**Processes involved in inorg C budget**	kgC km^{-2} yr^{-1}	%
Input to river	Diffuse sources from subroot	5963	34.4
	Diffuse sources from groundwater	9968	57.5
	Urban point sources	1135	6.6
	Heterotrophic respiration	266	1.5
	Denitrification	0	0.0
Output from river	Delivery to the outlet	12483	68.4
	Ventilation	5619	30.8
	Nitrification	37	0.2
	NPP	105	0.6
2010-2013	**Processes involved in TA budget**	mol km^{-2} yr^{-1}	%
Input to river	Diffuse sources from subroot	360983	*34.9*
	Diffuse sources from groundwater	604145	*58.4*
	Urban point sources	66770	*6.4*
	Heterotrophic respiration	2972	*0.3*
	Denitrification	0	*0.0*
Output from river	Delivery to outlet	1004299	*97.1*
	Nitrification	6219	*0.6*
	NPP *	24352	*2.4*
2010-2013	**Processes involved in org C budget**	kgC km^{-2} yr^{-1}	%
Input to river	Diffuse sources from subroot	870	53.9
	Diffuse sources from groundwater	227	14.1
	Urban point sources	375	23.2
	Nitrification	37	2.3
	NPP	105	6.5
Output from river	Delivery to the outlet	1086	65.7
	Heterotrophic respiration	110	6.7
	Net sedimentation **	456	27.6

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Open Access
Discussions

4.2. Carbon aquatic processes

Whereas IC and OC budgets of the Seine hydrosystem were clearly dominated by external terrestrial inputs and outputs through deliveries at the coast, an attempt was made here to analyze instream processes involved in the IC and OC cycles (Figure 8, Figure 9).

Average spatial distribution of IC processes, as calculated by the model, was mapped for the 2010–2013 period (Figure 8). Benthic activities were the greatest in smaller streams. In contrast, net primary production and heterotrophic planktonic respiration, which both followed a similar spatial pattern, increased as Strahler order increased, reaching their highest values in the lower Seine River. All these biological processes involved in the IC cycle were therefore highly active in the main stem of the river, while on the other hand CO_2 outgassing mainly occurred in the basin's small headwater streams (Figure 9).

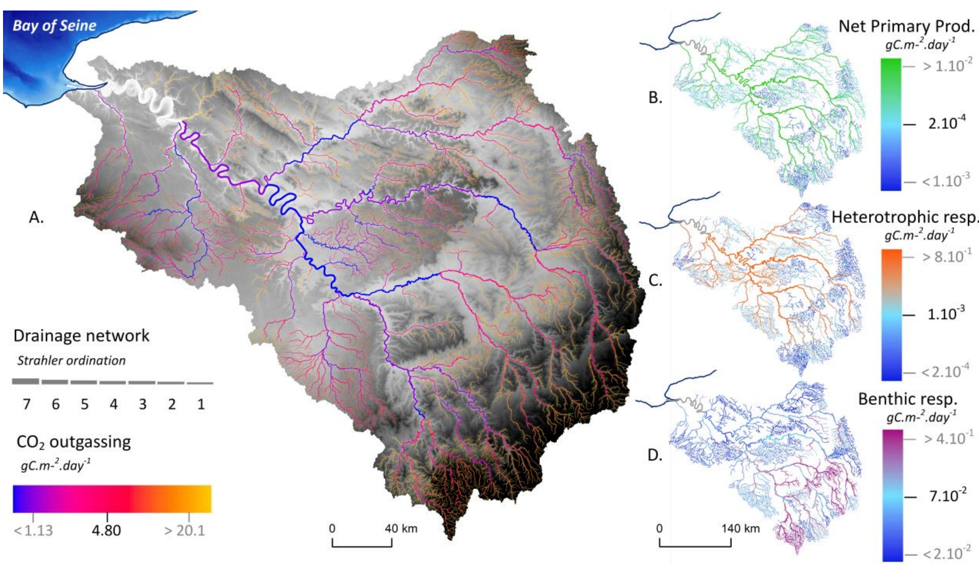


Figure 8. Instream processes involved in the inorganic carbon cycle simulated by pyNuts-Riverstrahler and averaged on the 2010–2013 period for the whole Seine River network. a) CO2 outgassing (blue–yellow, gC m^{-2} day^{-1}); b) net primary production (blue–green, gC m^{-2}

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

day^{-1}*); c) heterotrophic planktonic (blue–violet); d) benthic respiration (blue–orange, gC m*$^{-2}$ *day*$^{-1}$*) are represented in the hydrographic network.*

Regarding the OC processes, mostly linked to biological activity, they were analyzed in terms of ecosystem metabolism (Figure 9). The net ecosystem production (NEP, gC m^{-2} day^{-1}) is defined as:

$$\text{NEP} = \text{NPP} - \text{Het. Respiration}$$

where NPP is the net primary production (gC m^{-2} day^{-1}) depending on the growth of phytoplankton. NPP contributes to phytoplankton biomass building that constitutes a stock of organic carbon, emitted in turn as CO_2 by respiration (Het. respiration, gC m^{-2} day^{-1}).

Simulations showed that NEP would remain negative in the entire drainage network (Figure 9). However, NEP has to be analyzed with caution since the phytoplankton pattern was not adequately represented (see Figure 6). In SO1, this negative NEP was associated with almost no NPP, and heterotrophic respiration was dominated by benthic activities (see Figure 8). In SO5, NEP was less negative than in SO1 (Figure 9), heterotrophic respiration was lower than in SO1 while NPP was higher. In the lower Seine River (SO7), NPP increased as well as heterotrophic respiration, which reached its highest value in this downstream stretch receiving treated effluents from WWTPs. Therefore, the increase in NPP did not result in positive NEP. The entire drainage network was thus supersaturated in CO_2 with respect to atmospheric concentrations, and constituted a source of CO_2. This supersaturation was the highest in smaller orders, lower in intermediate orders and increased again in the lower Seine River (Figure 4, see also Figure 8).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

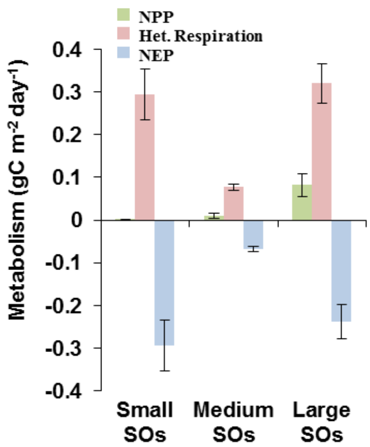


Figure 9 Metabolism for small, intermediate and large stream orders (SO) (here respectively represented by SO1, SO5, and SO7) of the Seine basin simulated by pyNuts-Riverstrahler and averaged over the 2010–2013 period. Net primary production (NPP, gC m^2 day^{-1}), heterotrophic respiration (Het. respiration, gC m^2 day^{-1}), net ecosystem production (NEP, gC m^2 day^{-1})

4. Discussion

4.1. Evaluation of the model

Simulated CO_2 concentrations tend to be higher than observed for SO1. These differences may be related to the high variability of CO_2 in SO1, and the scarcity of measurements in spring. However, Öquist et al. (2009) estimated that up to 90% of daily soil DIC import into streams was emitted to the atmosphere within 200 m. Since soil emissions were very difficult to capture, we considered that concentrations in groundwater (DIC and TA) closely reflect the composition of diffuse sources, much like soil composition. This assumption probably underestimates the DIC/TA ratio brought to the river in lower order streams. Differently from SO1, simulated concentrations in SO2–7 are lower than the observed values (Figure 4).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Overall, the NRMSE indicating a percentage of variation was less than 20%, except for TA (25%).

Regarding gas transfer velocity values, an equation for large rivers with no tidal influence using wind speed could be more appropriate (Alin et al., 2011) and could decrease NRMSE. However, the Riverstrahler model does not consider wind as an input variable, which would have required the model to have a much higher spatiotemporal resolution to reflect its spatiotemporal heterogeneity in the Seine basin, with for example, the diurnal cycle affected by phenomena such as breezes (Quintana-Seguí et al., 2008). Future work with direct *k* measurements and/or a new representation of *k*-values in the model could help improve outgassing simulations with pyNuts-Riverstrahler.

Regarding seasonal patterns, DIC and alkalinity amplitudes are suitably captured and the level of the values was correct. DIC and TA observations showed a strong decrease from June/July to November (maximum amplitude decrease, 10 mgC L^{-1} and 1000 µmol L^{-1}), as illustrated by the model. For the Seine River, the water flow decrease in summer was mainly related to the decrease in runoff water, meaning that the groundwater contribution was comparatively higher at this time. According to our measurements, these groundwaters were more concentrated in TA, DIC and CO_2 than runoff water. However, water released by upstream reservoirs (supporting low flow in the downstream section of the Seine network) accounted for a significant proportion of the river discharge during summer and was characterized by lower TA, DIC and CO_2 concentrations. Then the decrease observed was related to the contribution of reservoirs. These results strongly encourage the implementation of an inorganic carbon module in the modeling of reservoirs, already coupled with Riverstrahler for nutrients and organic carbon (Garnier et al., 1999).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

For phytoplankton, although the biomass level is consistent with the observations, the seasonal pattern was not satisfactory reproduced by the model. However, algal blooms has been considerably reduced compared to those observed in the 1990s when chlorophyll a reached 150 µgChla L^{-1} (Garnier et al., 1995). The RIVE model phytoplankton parameters were determined through laboratory experiments at that time when amplitude algal blooms were much higher than presently, after improvement of treatments in WWTPs strongly reducing river eutrophication (Romero et al. 2016). New laboratory experiments for possibly taking into account additional phytoplankton groups or species in these new trophic conditions and/or mixing stochastic and mechanistic modeling could be required to better represent phytoplankton temporal dynamics in the model. In addition, in future work, testing different pH calculation formulations (e.g. using Follows et al., 2006) could improve our pH simulations

4.2. Export fluxes

The new implementation of an inorganic carbon module in pyNuts-Riverstrahler allows estimating CO_2 outgassing of the Seine River at 364 ± 100 GgC yr^{-1}. This is significantly lower than in our previous estimate of 590 GgC yr^{-1} using CO_2 measurements only (Marescaux et al., 2018a). This difference is not fully compensated by the discrepancy of the simulations performed (NRMSE 15%) but is also due to the fact that, in this previous study, we used the same *k*-value for all stream orders based on Eq. 5 in Table 2 in Raymond et al. (2012). The more accurate description of the *k*-value adopted here with different k-values for small and high stream orders would be responsible for less outgassing than in our previous study. The outgassing by surface area of river of 1302 ± 352 gC m^{-2} yr^{-1} is in the middle of the range of the average estimates from other studies (ranging from 70 to 4008 gC m^{-2} yr^{-1}; Li et al., 2013 and references therein, e.g., Butman and Raymond, 2011). More precisely, a focus on temperate river outgassing estimates for the St. Lawrence River (Yang et al., 1996),

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Ottawa River (Telmer and Veizer, 1999), Hudson River (Raymond et al., 1997) and Mississippi River (Dubois et al., 2010) shows lower rates (from 70 to 1284 gC m^{-2} yr^{-1}) than in the Seine River. This high variability for these temperate rivers is highly dependent on whether or not the first-order streams were considered in the outgassing. Similar to our study, Butman and Raymond (2011) took into account lower order streams and rivers while lower estimates correspond to studies investigating large rivers, excluding lower order streams. CO_2 concentrations (see Figure 2). Indeed, outgassing are often greater in headwater streams than in large rivers due to higher CO_2 concentrations and headwater streams have higher gas transfer velocities (Marx et al., 2017; Raymond et al., 2012a). The mapping of CO_2 outgassing in the Seine basin clearly shows these spatial trends, with smaller streams releasing more CO_2 than median and larger rivers (see Figure 8).

Regarding organic carbon, Meybeck (1993) estimated the DOC export to the ocean for temperate climate at 1.5 gC m^{-2} yr^{-1}, a value that is higher than our OC estimate of 1.1 gC m^{-2} yr^{-1} for the Seine River basin, before entering the estuarine section. This might be explained by the low altitude of the Seine River, limiting erosion (Guerrini et al., 1998;) and by the change in the trophic state of rivers after the implementation of water directives in the late 1990s Rocher and Azimi, 2017; Romero et al., 2016). In addition, the CO_2/OC ratio of the export to the estuary of the Seine hydrosystem is 5.2, which is higher than this ratio for the Mississippi River (4.1; Dubois et al., 2010b; Li et al., 2013), for example, and may be related to considerable outgassing from headwater streams taken into account in our study. Note, however, that the small Seine River basin exports only 70 ± 99 GgC yr^{-1} compared to the large Mississippi River with exports amounting to 2435 GgC yr^{-1} OC (Dubois et al., 2010), with its surface area more than 40 times greater than the Seine. Interestingly, the Seine River export is estimated at three times less than the export calculated in 1979 (250 Gg C yr^{-1} , Kempe, 1984). This difference must be related to improvements in water treatments in the basin, with DOC concentrations in the Seine River 2.8 times lower since the 1990s (Rocher and Azimi, 2017) and to a remarkable reduction in phytoplankton blooms (Aissa Grouz et al., 2016).

We estimate DIC export of the Seine River at 820 ± 220 GgC yr^{-1}, a value higher than basins of the same size or even larger (e.g., Ottawa River, drainage are, 149,000 km^2, 520 GgC yr^{-1} , Telmer and Veizer, (1999); Li et al. (2013)). The high concentrations of HCO_3^- in the Seine basin already documented and related to the lithology of the Seine basin (limestone and gypsum beds from Cretaceous and Tertiary) (Kempe, 1982; 1984) may explain this high export to the river outlet. With both high CO_2 and DIC exports, the ratio of CO_2/DIC exports from the Seine River is the same as the overall ratio (0.5, Li et al., 2013).

4.3. Metabolism

Model simulations with the new inorganic carbon module can be used to analyze spatial variations of CO_2 in regard to instream metabolism activities. The model highlights the importance of benthic activities in headwater streams (Figure 8) that decreased downstream as heterotrophic planktonic activities increased in larger rivers, a typical pattern described by the river continuum concept (RCC, Vannote et al., 1980) and quantified for the Seine River (Billen et al., 1994; Garnier et al., 1995; Garnier and Billen, 2007). These results are also in agreement with those by Hotchkiss et al. (2015), which suggested that the percentage of CO_2 emissions from metabolism increases with stream size while CO_2 emissions of lower order streams were related to allochthonous terrestrial CO_2. Regarding headwater streams, Battin et al. (2009b) described benthic activities as the highest (as also observed in our study, Figure 8) where microbial biomass is associated with streambeds characterized by exchanges with subsurface flow bringing nutrients and oxygen and increasing mineralization.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Mean NEP would remain negative in the entire basin resulting from heterotrophic conditions producing CO_2 (Figure 8 and Figure 9). However, even though the level of phytoplankton biomass was correctly simulated, the summer downstream bloom, which was not reproduced by the model, could lead to some NPP underestimation. As expected, NPP in lower order streams was lower than in higher SOs due to shorter water residence times. Benthic respiration of lower order streams was significant (Figure 9) and made NEP highly negative. Also, small SOs were the most concentrated in CO_2 due to the groundwater contribution. Intermediate stream orders showed the smallest CO_2 or heterotrophic respirations with NEP less than −0.1 gC m^{-2} day^{-1}. This can be explained by an increase of NPP due to lower dilution rate than the phytoplankton growth rate (Garnier et al., 1995), and to a reduced ratio of the bottom sediment to water column volume, decreasing heterotrophic respiration. In higher stream orders both NPP and heterotrophic respiration were the highest, however leading to negative NEP lower than SO1 (Figure8 and Figure 9). Despite photosynthesis reduced CO_2 concentrations (Figure 6), the highest SOs were affected by wastewater effluents, resulting in overall negative NEP.

On the recent 2010–2013 period studied herein, and in all SOs, the NPP never exceeded heterotrophic respiration (ratio NPP:Het.-Resp or P:R < 1) (Figure 9). Whereas in the past, eutrophication of the Seine River led to a P:R ratio above 1 in large rivers, at least during spring blooms, with P and R values increasing up to 2.5 gC m^{-2} day^{-1} (Garnier and Billen, 2007), the P:R ratio is now systematically below 1. These changes, linked to an overall decrease in biological metabolism, are explained by the improvements of treatment in WWTPs decreasing the organic carbon load discharged into rivers and associated pollution, and hence decreasing the CO_2 concentration along the main stem of the Seine River (Marescaux et al., 2018b). Improvement of treatments in wastewater reduced nutrient inputs to the river, especially phosphates, today a limiting nutrient to algal development in SO5 and

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Open Access
Discussions
EGU

6, reducing algal peaks from 150 µgChla L^{-1} in the 1990s to often less than 50 µgChla l^{-1} presently (Romero et al., 2016; Aissa-Grouz et al., 2016).

5. Conclusion

The first simulations with the river biogeochemical pyNuts-Riverstrahler model including the processes involved in the inorganic carbon cycle, represent the CO_2 concentrations and outgassing along the Seine hydrosystem quite accurately.

The sensitivity of simulations to different gas transfer velocity values highlighted the need for additional measurements in the Seine River to choose the best model equation or to propose a new one. In addition, revisiting the phytoplankton description in the model could enable a better simulation of the temporal dynamics of phytoplankton. In the future, an explicit representation of the anaerobic reduction chain of the benthos could enable to specify the benthos impact on TA and DIC in a greater variety of ecosystems.

CO_2 concentrations appear to be controlled differently along the Seine hydrosystem. In small orders, concentrations are mainly driven by groundwater discharges. In larger rivers, in addition to the influence of groundwater and low-flow support by upstream reservoirs, concentrations show patterns linked to hydrosystem metabolisms. Indeed, blooms tend to decrease CO_2 concentrations, although the hydrosystem remains heterotrophic and supersaturated with respect to the atmospheric CO_2 concentrations. Heterotrophic respiration increases CO_2 concentrations with peaks downstream of WWTP effluents enriched in organic carbon.

Around 31% of the DIC inputs, widely dominated by soils, groundwater and/or WWTP effluents, are outgassed, while 68% are exported to the estuary. IC inputs and outputs are estimated at ten times the OC inputs and outputs.

Hydrology and Earth System Sciences Discussions
Open Access EGU

Data availability

The datasets generated during the current study are available from the corresponding author on reasonable request.

Author contribution

All the authors contributed to the design of the study. J.G. and V.T. are co-supervisors of the PhD. A.M. participated as a PhD student in the field campaigns, lab chemical analyzes and implement the new inorganic carbon module. N.G. and M.S. provided technical and scientific support for the modelling. A.M. wrote the first draft of the manuscript, and all the co-authors helped to interpret the data and write the article.

Competing interests statement

The authors declare no competing financial or non-financial interest.

Acknowledgements

The project leading to this application received funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No. 643052. A PhD grant was attributed to Audrey Marescaux. Many thanks are due to Sébastien Bosc, Anunciacion Martinez Serrano and Benjamin Mercier for their kind participation in the fieldwork and for their assistance with chemical analyses in the lab. We thank Muriel Chagniot (Veolia Water, France), and the operators of the Veolia WWTPs for their precious help in organizing the field campaigns. The SIAAP (Vincent Rocher) is also sincerely acknowledged for their contribution to sampling the largest WWTP of the Paris

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences Discussions

conurbation and the long-term view on treatments in the SIAAP WWTPs provided by their recent book (Rocher and Azimi, 2017). Vincent Thieu (assistant professor at the University Pierre and Marie Curie, Paris) and Josette Garnier (Research Director at the Centre National de la Recherche Scientifique, France) are co-supervisors of the PhD. Nathalie Gypens is professor at the Université Libre de Bruxelles (Belgium). Marie Silvestre is GIS engineer at the Centre National de la Recherche Scientifique (France).

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Discussions

References

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F., Ochieng Omengo, F., Geeraert, N., Deirmendjian, L., Polsenaere, P. and Borges, A. V.: Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, Biogeosciences, 12(1), 67–78, doi:10.5194/bg-12-67-2015, 2015.

Aissa-Grouz, N., Garnier, J. and Billen, G.: Long trend reduction of phosphorus wastewater loading in the Seine: determination of phosphorus speciation and sorption for modeling algal growth, Environ. Sci. Pollut. Res., 1–14, doi:10.1007/s11356-016-7555-7, 2016.

Aksoy, E., Yigini, Y. and Montanarella, L.: Combining soil databases for topsoil organic carbon mapping in Europe, PLoS One, 11(3), 1–17, doi:10.1371/journal.pone.0152098, 2016.

Alin, S. R., Rasera, M. D. F. F. L. M. M. D. F. F. L. F. L., Salimon, C. I., Richey, J. E., Holtgrieve, G. W., Krusche, A. V. and Snidvongs, A.: Physical controls on carbon dioxide transfer velocity and flux in low-gradient river systems and implications for regional carbon budgets, J. Geophys. Res., 116(G1), 17, doi:10.1029/2010JG001398, 2011a.

Alin, S. R., Rasera, M. M. D. F. F. L., Salimon, C. I., Richey, J. E., Holtgrieve, G. W., Krusche, A. V. and Snidvongs, A.: Physical controls on carbon dioxide transfer velocity and flux in low-gradient river systems and implications for regional carbon budgets, J. Geophys. Res., 116(G1), 17, doi:G01009 10.1029/2010jg001398, 2011b.

Alshboul, Z., Encinas-Fernández, J., Hofmann, H., Lorke, A., Encinas-ferna, J., Hofmann, H., Lorke, A., Encinas-Fernández, J., Hofmann, H. and Lorke, A.: Export of dissolved methane and carbon dioxide with effluents from municipal wastewater treatment plants, Environ. Sci. Technol., 0(ja), doi:10.1021/acs.est.5b04923, 2016.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Arnold, J. G. and Allen, P. M.: Automated methods for estimating baseflow and ground water recharge from streamflow records, J. Am. Water Resour. Assoc., 35(2), 411–424, doi:10.1111/j.1752-1688.1999.tb03599.x, 1999.

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., Aalto, R. E. and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9(1), 53–60, doi:10.1890/100014, 2011.

Aumont, O., Ethé, C., Tagliabue, A., Bopp, L. and Gehlen, M.: PISCES-v2: An ocean biogeochemical model for carbon and ecosystem studies, Geosci. Model Dev., 8(8), 2465–2513, doi:10.5194/gmd-8-2465-2015, 2015.

Battin, T. J., Kaplan, L. a., Findlay, S., Hopkinson, C. S., Marti, E., Packman, A. I., Newbold, J. D. and Sabater, F.: Biophysical controls on organic carbon fluxes in fluvial networks, Nat. Geosci., 2(8), 595–595, doi:10.1038/ngeo602, 2009a.

Battin, T. J., Luyssaert, S., Kaplan, L. a., Aufdenkampe, A. K., Richter, A. and Tranvik, L. J.: The boundless carbon cycle, Nat. Geosci., 2(9), 598–600, doi:10.1038/ngeo618, 2009b.

Billen, G. and Garnier, J.: Nitrogen transfers through the Seine drainage network : a budget based on the application of the ‘ Riverstrahler ’ model, Hydrobiologia, 139–150, 2000.

Billen, G., Garnier, J. and Hanset, P.: Modelling phytoplankton development in whole drainage networks: the RIVERSTRAHLER Model applied to the Seine river system, Hydrobiologia, 289(1–3), 119–137, doi:10.1007/BF00007414, 1994.

Billen, G., Garnier, J., Ficht, A., Cun, C., Curie, M., Anti-pollution, C., Billen, G., Garnier, J., Ficht, A. and Cun, C.: Modeling the Response of Water Quality in the Seine River Estuary to Human Activity in its Watershed Over the Last 50 Years, Estuaries, 24(6), 977–993, 2001.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Billen, G., Garnier, J., Némery, J., Sebilo, M., Sferratore, a, Barles, S., Benoit, P. and Benoît, M.: A long-term view of nutrient transfers through the Seine river continuum., Sci. Total Environ., 375(1–3), 80–97, doi:10.1016/j.scitotenv.2006.12.005, 2007.

Billen, G., Ramarson, A., Thieu, V., Théry, S., Silvestre, M., Pasquier, C., Hénault, C. and Garnier, J.: Nitrate retention at the river–watershed interface: a new conceptual modeling approach, Biogeochemistry, 139(1), 31–51, doi:10.1007/s10533-018-0455-9, 2018.

Borges, A. V., Schiettecatte, L. S., Abril, G., Delille, B. and Gazeau, F.: Carbon dioxide in European coastal waters, Estuar. Coast. Shelf Sci., 70(3), 375–387, doi:10.1016/j.ecss.2006.05.046, 2006.

Borrelli, P., Van Oost, K., Meusburger, K., Alewell, C., Lugato, E. and Panagos, P.: A step towards a holistic assessment of soil degradation in Europe: Coupling on-site erosion with sediment transfer and carbon fluxes, Environ. Res., 161(November 2017), 291–298, doi:10.1016/j.envres.2017.11.009, 2018.

Cai, W.-J. and Wang, Y.: The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia, Limnol. Oceanogr., 43(4), 657–668, doi:10.4319/lo.1998.43.4.0657, 1998.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J. and Melack, J.: Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget, Ecosystems, 10(1), 172–185, doi:10.1007/s10021-006-9013-8, 2007.

Culberson, C. H.: Calculation of the in situ pH of seawater, Limnol. Oceanogr., 25(1), 150–152, doi:10.4319/lo.1980.25.1.0150, 1980.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Desmit, X., Thieu, V., Billen, G., Campuzano, F., Dulière, V., Garnier, J., Lassaletta, L., Ménesguen, A., Neves, R., Pinto, L., Silvestre, M., Sobrinho, J. L. and Lacroix, G.: Reducing marine eutrophication may require a paradigmatic change, Sci. Total Environ., 635(September), 1444–1466, doi:10.1016/j.scitotenv.2018.04.181, 2018.

Doney, S. C., Lindsay, K., Caldeira, K., Campin, J. M., Drange, H., Dutay, J. C., Follows, M., Gao, Y., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Madec, G., Maier-Reimer, E., Marshall, J. C., Matear, R. J., Monfray, P., Mouchet, A., Najjar, R., Orr, J. C., Plattner, G. K., Sarmiento, J., Schlitzer, R., Slater, R., Totterdell, I. J., Weirig, M. F., Yamanaka, Y. and Yool, A.: Evaluating global ocean carbon models: The importance of realistic physics, Global Biogeochem. Cycles, 18(3), doi:10.1029/2003GB002150, 2004.

Drake, T. W., Raymond, P. A. and Spencer, R. G. M.: Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty, Limnol. Oceanogr. Lett., (November), doi:10.1002/lol2.10055, 2017.

Dubois, K. D., Lee, D. and Veizer, J.: Isotopic constraints on alkalinity, dissolved organic carbon, and atmospheric carbon dioxide fluxes in the Mississippi River, J. Geophys. Res. Biogeosciences, 115(G2), n/a-n/a, doi:10.1029/2009JG001102, 2010.

EEA: Copernicus Land Monitoring Service - Corine Land Cover (CLC)., 2012.

Garnier, J. and Billen, G.: Production vs. respiration in river systems: an indicator of an “ecological status”., Sci. Total Environ., 375(1–3), 110–24, doi:10.1016/j.scitotenv.2006.12.006, 2007.

Garnier, J., Billen, G. and Coste, M.: Seasonal succession of diatoms and Chlorophyceae in the drainage network of the Seine River: Observation and modeling, Limnol. Oceanogr., 40(4), 750–765, doi:10.4319/lo.1995.40.4.0750, 1995.

Garnier, J., Leporcq, B., Sanchez, N., Phillippon, Garnier, J., Leporcq, B., Sanchez, N. and Philippon: Biogeochemical mass-balances (C, N, P, Si) in three large reservoirs of the Seine Basin (France), Biogeochemistry, 47(2), 119–146, doi:10.1023/A:1006101318417, 1999.

Garnier, J., Billen, G., Hannon, E., Fonbonne, S., Videnina, Y. and Soulie, M.: Modelling the Transfer and Retention of Nutrients in the Drainage Network of the Danube River, Estuar. Coast. Shelf Sci., 54, 285–308, doi:10.1006/ecss.2000.0648, 2002.

Garnier, J., Billen, G. and Cébron, A.: Modelling nitrogen transformations in the lower Seine river and estuary (France): Impact of wastewater release on oxygenation and N2O emission, Hydrobiologia, 588(1), 291–302, doi:10.1007/s10750-007-0670-1, 2007.

Garnier, J., Billen, G., Vilain, G., Martinez, A., Silvestre, M., Mounier, E. and Toche, F.: Nitrous oxide (N2O) in the Seine river and basin: Observations and budgets, Agric. Ecosyst. Environ., 133(3–4), 223–233, doi:10.1016/j.agee.2009.04.024, 2009.

Garnier, J., Ramarson, A., Billen, G., Théry, S., Thiéry, D., Thieu, V., Minaudo, C. and Moatar, F.: Nutrient inputs and hydrology together determine biogeochemical status of the Loire River (France): Current situation and possible future scenarios, Sci. Total Environ., 637–638, 609–624, doi:10.1016/j.scitotenv.2018.05.045, 2018.

Guerrini, M.-C., Mouchel, J.-M., Meybeck, M., Penven, M. J., Hubert, G. and Muxart, T.: Le bassin de la Seine : la confrontation du rural et de l’urbain, in La Seine en son bassin. Fonctionnement écologique d’un système fluvial anthropisé, edited by M. Meybeck, G. de Marsily, and E. Fustec, pp. 29–73., 1998.

Gypens, N., Borges, a. V. and Lancelot, C.: Effect of eutrophication on air-sea CO2 fluxes in the coastal Southern North Sea: A model study of the past 50 years, Glob. Chang. Biol., 15, 1040–1056, doi:10.1111/j.1365-2486.2008.01773.x, 2009.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Gypens, N., Lacroix, G., Lancelot, C. and Borges, a. V.: Seasonal and inter-annual variability of air-sea CO2 fluxes and seawater carbonate chemistry in the Southern North Sea, Prog. Oceanogr., 88(1–4), 59–77, doi:10.1016/j.pocean.2010.11.004, 2011.

Habets, F., Boone, A., Champeaux, J. L., Etchevers, P., Franchistéguy, L., Leblois, E., Ledoux, E., Le Moigne, P., Martin, E., Morel, S., Noilhan, J., Seguí, P. Q., Rousset-Regimbeau, F. and Viennot, P.: The SAFRAN-ISBA-MODCOU hydrometeorological model applied over France, J. Geophys. Res. Atmos., 113(6), 1–18, doi:10.1029/2007JD008548, 2008.

Ho, D. T., Coffineau, N., Hickman, B., Chow, N., Koffman, T. and Schlosser, P.: Influence of current velocity and wind speed on air-water gas exchange in a mangrove estuary, Geophys. Res. Lett., 43(8), 3813–3821, doi:10.1002/2016GL068727.Received, 2016.

Hotchkiss, E. R., Hall, R. O., Sponseller, R., Butman, D., Klaminder, J., Laudon, H., Rosvall, M. and Karlsson, J.: Sources and control of CO2 emissions change with the size of sreams and rivers, Nat. Geosci., 8(August), doi:10.1038/ngeo2507, 2015.

INSEE: French National Institute of Statistics and Economic Studies, Recensement de la population 2015., 2015.

Joos, F., Bruno, M., Fink, R., Siegenthaler, U., Stocker, T. F., Le Quéré, C. and Sarmiento, J. L.: An efficient and accurate representation of complex oceanic and biospheric models of anthropogenic carbon uptake, Tellus, Ser. B Chem. Phys. Meteorol., 48(3), 397–417, doi:10.1034/j.1600-0889.1996.t01-2-00006.x, 1996.

Kempe, S.: Long-term records of CO2 pressure fluctuations in fresh waters, Transp. carbon Miner. major world rivers, part 1, (May 1982), 91–332 [online] Available from: citeulike-article-id:12388435, 1982.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Kempe, S.: Sinks of the anthropogenically enhanced carbon cycle in surface fresh waters, J. Geophys. Res., 89(D3), 4657, doi:10.1029/JD089iD03p04657, 1984.

Lacarce, E., Le Bas, C., Cousin, J. L., Pesty, B., Toutain, B., Houston Durrant, T. and Montanarella, L.: Data management for monitoring forest soils in Europe for the Biosoil project, Soil Use Manag., doi:10.1111/j.1475-2743.2009.00194.x, 2009.

Laruelle, G. G., Marescaux, A., Gendre, R. Le, Garnier, J., Rabouille, C. and Thieu, V.: Carbon dynamics along the Seine River network: Insight from a coupled estuarine/river modeling approach, Front. Mar. Sci., doi:10.3389/fmars.2019.00216, 2019.

Lauerwald, R., Laruelle, G. G., Hartmann, J., Ciais, P. and Regnier, P. A. G.: Spatial patterns in CO_2 evasion from the global river network, Global Biogeochem. Cycles, 29(5), 534–554, doi:10.1002/2014GB004941, 2015.

Li, S., Lu, X. X. and Bush, R. T.: CO2 partial pressure and CO2 emission in the Lower Mekong River, J. Hydrol., 504, 40–56, doi:10.1016/j.jhydrol.2013.09.024, 2013.

Mackenzie, F. T., De Carlo, E. H. and Lerman, A.: Coupled C, N, P, and O Biogeochemical Cycling at the Land-Ocean Interface, Elsevier Inc., 2011.

Marescaux, A., Thieu, V. and Garnier, J.: Carbon dioxide, methane and nitrous oxide emissions from the human-impacted Seine watershed in France, Sci. Total Environ., 643, 247–259, doi:10.1016/j.scitotenv.2018.06.151, 2018a.

Marescaux, A., Thieu, V., Borges, A. V. and Garnier, J.: Seasonal and spatial variability of the partial pressure of carbon dioxide in the human-impacted Seine River in France, Sci. Rep., 8, 13961, doi:10.1038/s41598-018-32332-2, 2018b.

Marx, A., Dusek, J., Jankovec, J., Sanda, M., Vogel, T., van Geldern, R., Hartmann, J. and

Barth, J. A. C.: A review of CO2 and associated carbon dynamics in headwater streams: A global perspective, Rev. Geophys., 55(2), 560–585, doi:10.1002/2016RG000547, 2017.

Marx, A., Conrad, M., Aizinger, V., Prechtel, A., Van Geldern, R. and Barth, J. A. C.: Groundwater data improve modelling of headwater stream CO2outgassing with a stable DIC isotope approach, Biogeosciences, 15(10), 3093–3106, doi:10.5194/bg-15-3093-2018, 2018.

Meehl, G. A., Stocker, T. F., Collins, W. D., Friedlingstein, P., G., A. T., Gregory, J. M., Kitoh, A., Knutti, R., Murphy, J. M., N. and A., Raper, S. C. B., Watterson, I. G., J., W. A., Zhao, Z.-C.: Global Climate Projections, in Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller, p. 996, Cambridge, United Kingdom and New York, NY, USA., 2007.

Mégnien, C.: Synthèse géologique du bassin de Paris, edited by C. Mégnien, Édition du B.R.G.M. [online] Available from: https://books.google.fr/books?id=x0w9bwAACAAJ, 1980.

Menon, M., Rousseva, S., Nikolaidis, N. P., van Gaans, P., Panagos, P., de Souza, D. M., Ragnarsdottir, K. V., Lair, G. J., Weng, L., Bloem, J., Kram, P., Novak, M., Davidsdottir, B., Gisladottir, G., Robinson, D. A., Reynolds, B., White, T., Lundin, L., Zhang, B., Duffy, C., Bernasconi, S. M., De Ruiter, P., Blum, W. E. H. and Banwart, S. A.: SoilTrEC: A global initiative on critical zone research and integration, Environ. Sci. Pollut. Res., doi:10.1007/s11356-013-2346-x, 2014.

Meybeck, M.: Riverine transport of atmospheric carbon: Sources, global typology and budget, Water, Air, Soil Pollut., 70(1–4), 443–463, doi:10.1007/BF01105015, 1993.

Millero, F. J.: The thermodynamics of the carbonate system in seawater, Geochim. Cosmochim. Acta, 43(10), 1651–1661, doi:10.1016/0016-7037(79)90184-4, 1979.

Minaudo, C., Curie, F., Jullian, Y., Gassama, N. and Moatar, F.: QUAL-NET, a high temporal-resolution eutrophication model for large hydrographic networks, Biogeosciences, 15(7), 2251–2269, doi:10.5194/bg-15-2251-2018, 2018.

Nakayama, T.: New perspective for eco-hydrology model to constrain missing role of inland waters on boundless biogeochemical cycle in terrestrial???aquatic continuum, Ecohydrol. Hydrobiol., 16(3), 138–148, doi:10.1016/j.ecohyd.2016.07.002, 2016.

O’Connor, D. J. and Dobbins, W. E.: Mechanism of reaeration in natural streams, Trans. Am. Soc. Civ. Eng., 123, 641–684, 1958.

Öquist, M. G., Wallin, M., Seibert, J., Bishop, K. and Laudon, H.: Dissolved Inorganic Carbon Export Across the Soil / Stream Interface and Its Fate in a Boreal Headwater Stream, Environ. Sci. Technol., 43(19), 7364–7369, 2009.

Passy, P., Le Gendre, R., Garnier, J., Cugier, P., Callens, J., Paris, F., Billen, G., Riou, P. and Romero, E.: Eutrophication modelling chain for improved management strategies to prevent algal blooms in the Bay of Seine, Mar. Ecol. Prog. Ser., 543, 107–125, doi:10.3354/meps11533, 2016.

Pelletier, G. J., Chapra, S. C. and Tao, H.: QUAL2Kw - A framework for modeling water quality in streams and rivers using a genetic algorithm for calibration, Environ. Model. Softw., 21(3), 419–425, doi:10.1016/j.envsoft.2005.07.002, 2006.

Pierrot, D., Lewis, D. E. and Wallace, D. W. R.: MS Excel Program Developed for CO2 System Calculations. ORNL/CDIAC-105a, Carbon Dioxide Inf. Anal. Center, Oak Ridge

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Natl. Lab. U.S. Dep. Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a, 2006.

Pomerol, C. and Feugueur, L. L.: Bassin de Paris: Ile de France, Pays de Bray, Masson, Paris. [online] Available from: https://books.google.fr/books?id=SAoeAQAAMAAJ, 1986.

Prairie, Y. T. and Cole, J. J.: Carbon , Unifying Currency, Encycl. Inl. Waters, 2(December), 743–746, doi:http://dx.doi.org/10.1016/B978-012370626-3.00107-1, 2009.

QGIS Development Team: QGIS Geographic Information System 2.18, Open Source Geospatial Found. [online] Available from: http://qgis.osgeo.org/, 2016.

Quintana-Seguí, P., Le Moigne, P., Durand, Y., Martin, E., Habets, F., Baillon, M., Canellas, C., Franchisteguy, L. and Morel, S.: Analysis of near-surface atmospheric variables: Validation of the SAFRAN analysis over France, J. Appl. Meteorol. Climatol., 47(1), 92–107, doi:10.1175/2007JAMC1636.1, 2008.

R Core team: R Core Team, R A Lang. Environ. Stat. Comput. R Found. Stat. Comput. Vienna, Austria. ISBN 3-900051-07-0, URL http//www.R-project.org/., 55, 275–286 [online] Available from: http://www.mendeley.com/research/r-language-environment-statistical-computing-96/%5Cnpapers2://publication/uuid/A1207DAB-22D3-4A04-82FB-D4DD5AD57C28, 2015.

Raymond, P. A., Caraco, N. F. and Cole, J. J.: Carbon dioxide concentration and atmospheric flux in the Hudson River, Estuaries, 20(2), 381–390, doi:10.1007/BF02690380, 1997.

Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., Laursen, A. E., McDowell, W. H. and Newbold, D.: Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers, Limnol. Oceanogr. Fluids Environ., 2(0), 41–53,

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

doi:10.1215/21573689-1597669, 2012.

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P. and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, 503(7476), 355–359, doi:10.1038/nature12760, 2013.

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. a., Laruelle, G. G., Lauerwald, R., Luyssaert, S., Andersson, A. J., Arndt, S., Arnosti, C., Borges, A. V., Dale, A. W., Gallego-Sala, A., Goddéris, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRowe, D. E., Leifeld, J., Meysman, F. J. R., Munhoven, G., Raymond, P. a., Spahni, R., Suntharalingam, P. and Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean, Nat. Geosci., 6(8), 597–607, doi:10.1038/ngeo1830, 2013a.

Regnier, P., Arndt, S., Goossens, N., Volta, C., Laruelle, G. G., Lauerwald, R. and Hartmann, J.: Modelling Estuarine Biogeochemical Dynamics: From the Local to the Global Scale, Aquat. Geochemistry, 19(5–6), 591–626, doi:10.1007/s10498-013-9218-3, 2013b.

Rocher, V. and Azimi, S.: Evolution de la qualité de la Seine en lien avec les progrès de l'assainissement, Johanet., Paris., 2017.

Romero, E., Le Gendre, R., Garnier, J., Billen, G., Fisson, C., Silvestre, M. and Riou, P.: Long-term water quality in the lower Seine: Lessons learned over 4 decades of monitoring, Environ. Sci. Policy, 58, 141–154, doi:10.1016/j.envsci.2016.01.016, 2016.

Sawakuchi, H. O., Neu, V., Ward, N. D., Barros, M. de L. C., Valerio, A. M., Gagne-Maynard, W., Cunha, A. C., Less, D. F. S., Diniz, J. E. M., Brito, D. C., Krusche, A. V. and Richey, J. E.: Carbon Dioxide Emissions along the Lower Amazon River, Front. Mar. Sci., 4(March), 1–12, doi:10.3389/fmars.2017.00076, 2017.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Servais, P., Billen, G. and Hascoët, M. C.: Determination of the biodegradable fraction of dissolved organic matter in waters, Water Res., 21(4), 445–450, doi:10.1016/0043-1354(87)90192-8, 1995.

Servais, P., Billen, G., Goncalves, A. and Garcia-Armisen, T.: Modelling microbiological water quality in the Seine river drainage network: past, present and future situations, Hydrol. Earth Syst. Sci. Discuss., 11(5), 1581–1592, doi:10.5194/hessd-4-1153-2007, 2007.

Sferratore, A., Billen, G., Garnier, J., Smedberg, E., Humborg, C. and Rahm, L.: Modelling nutrient fluxes from sub-arctic basins: Comparison of pristine vs. dammed rivers, J. Mar. Syst., 73(3–4), 236–249, doi:10.1016/j.jmarsys.2007.10.012, 2008.

Smitz, J. S., Everbecq, E., Deliège, J.-F., Descy, J.-P., Wollast, R. and Vanderborght, J. P.: PEGASE, une méthodologie et un outil de simulation prévisionnelle pour la gestion de la qualité des eaux de surface, Trib. l'eau, 588(4), 73–82, 1997.

Strahler, A. N.: Quantitative Analysis of Watershed Geomorphology, Geophys. Union Trans., 38(6), 913–920, doi:10.1029/TR038i006p00913, 1957.

Tanaka, K., Kriegler, E., Bruckner, T., Georg, H., Knorr, W. and Raddatz, T.: Aggregated Carbon Cycle, Atmospheric Chemistry, and Climate Model (ACC2) – description of the forward and inverse modes, Reports Earth Syst. Sci. Max Planck Institue Meteorol. Hambg., 188(January), 2007.

Telmer, K. and Veizer, J.: Carbon fluxes, pCO2 and substrate weathering in a large northern river basin, Canada: Carbon isotope perspectives, Chem. Geol., 159, 61–86, doi:10.1016/S0009-2541(99)00034-0, 1999.

Thieu, V., Billen, G. and Garnier, J.: Nutrient transfer in three contrasting NW European watersheds: the Seine, Somme, and Scheldt Rivers. A comparative application of the Seneque/Riverstrahler model., Water Res., 43(6), 1740–54, doi:10.1016/j.watres.2009.01.014, 2009.

Thieu, V., Silvestre, M., G., B., J., G., Passy, P. and Lassaletta, L.: Nutrient transfer in aquatic continuum and delivery to coastal zone: rising up the challenge of a generic application of the Riverstrahler ecological model to the watershed domain of the European North Atlantic Ocean, in 2nd International Conference: Integrative Sciences and Sustainable Development of Rivers. Lyon - France, p. 2., 2015.

Tóth, G., Jones, A. and Montanarella, L.: LUCAS Topsoil Survey: Methodology, Data, and Results, Publ. Off. Eur. Union, …, doi:10.2788/97922, 2013.

Vannote, R. L., Minshall, G. W., Cummins, K. W., Sedell, J. R. and Cushing, C. E.: The River Continuum Concept, Can. J. Fish. Aquat. Sci., 37(1), 130–137, doi:10.1139/f80-017, 1980.

Venkiteswaran, J. J., Schiff, S. L. and Wallin, M. B.: Large carbon dioxide fluxes from headwater boreal and sub-boreal streams, PLoS One, 9(7), 22–25, doi:10.1371/journal.pone.0101756, 2014.

Vilain, G., Garnier, J., Passy, P., Silvestre, M. and Billen, G.: Budget of N2O emissions at the watershed scale: Role of land cover and topography (the Orgeval basin, France), Biogeosciences, 9(3), 1085–1097, doi:10.5194/bg-9-1085-2012, 2012.

Vilmin, L., Flipo, N., Escoffier, N., Rocher, V. and Groleau, A.: Carbon fate in a large temperate human-impacted river system: Focus on benthic dynamics, Global Biogeochem. Cycles, 30(7), 1086–1104, doi:10.1002/2015GB005271, 2016.

https://doi.org/10.5194/hess-2019-601
Preprint. Discussion started: 17 December 2019

Hydrology and Earth System Sciences
Open Access
Discussions

Vilmin, L., Flipo, N., Escoffier, N. and Groleau, A.: Estimation of the water quality of a large urbanized river as defined by the European WFD: what is the optimal sampling frequency?, Environ. Sci. Pollut. Res., 25(24), 23485–23501, doi:10.1007/s11356-016-7109-z, 2018.

Volta, C., Arndt, S., Savenije, H. H. G., Laruelle, G. G. and Regnier, P.: C-GEM (v 1.0): A new, cost-efficient biogeochemical model for estuaries and its application to a funnel-shaped system, Geosci. Model Dev., 7(4), 1271–1295, doi:10.5194/gmd-7-1271-2014, 2014.

Whitehead, P. G., Williams, R. J. and Lewis, D. R.: Quality simulation along river systems (QUASAR): Model theory and development, Sci. Total Environ., 194–195, 447–456, doi:10.1016/S0048-9697(96)05382-X, 1997.

Yang, C., Telmer, K. and Veizer, J.: Chemical dynamics of the "St. Lawrence" riverine system: δDH2O, δ18OH2O, δ13CDIC, δ34Ssulfate, and dissolved87Sr/86Sr, Geochim. Cosmochim. Acta, 60(5), 851–865, doi:10.1016/0016-7037(95)00445-9, 1996.

Zeebe, R. and Wolf-Gladrow, D.: CO2 in Seawater-Equilibrium, Kinetics, Isotopes, Elsevier, 100, doi:10.1016/S0422-9894(01)80002-7, 2001.