Modeling the biogeochemical functioning of the Seine estuary and its coastal zone: Export, retention, and transformations

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Abstract

The model ECO-MARS3D, successfully applied thus far to coastal ecosystems, has been extended to encompass the Seine estuary up to Poses, at the limit between the river and the estuary. We used updated bathymetric data and thoroughly calibrated the hydrodynamics and the sedimentary dynamics in the turbidity maximum zone (TMZ). Biogeochemical processes related to oxygen were newly implemented, and freshwater phytoplankton and zooplankton groups were added to the existing marine groups. The simulations allowed us to evaluate the filter effect of the estuary with regard to the main nutrients (N, P, and Si). Today, this filter role appears quite limited and variable depending on the hydrology. On average, considering three different hydrological years, the estuary was able to retain (at least temporarily) 19 kt N yr^{-1}, 10 kt Si yr^{-1}, and 0.7 kt P yr^{-1}, amounting to −13%, −11%, and −27% of the total N, Si, and P inputs, respectively. Seasonal differences in the filtering capacity (lower in winter than in summer) were similar between wet and dry years. Nutrient retention was higher in the upstream fluvial estuary than in the TMZ, the former being mostly characterized by uptake, the latter by remineralization. At the coastal zone, the dry year showed greater risk of eutrophication. Despite lower discharge and lower nutrient fluxes, inputs were confined into a shallower layer, close to the coastline, where nutrients were concentrated and allowed phytoplankton to thrive. Differences in the N : P : Si ratios (lower P-deficit during dry years) could also underpin the larger proliferations, and notably the larger dinoflagellate blooms during dry years.

Estuaries are complex systems influenced by both terrestrial and marine drivers. This variety of forcing factors induces a wide range of environmental conditions within small spatial scales, with multiple interactions, making a complete understanding of their functioning difficult (Cloern et al. 2016).

The Seine estuary occupies an area of intense human activity and plays a fundamental role in the industrial and logistics sectors in France. The estuary shelters the largest inland port for container traffic in France and the second largest in Europe (http://www.haropaports.com/fr/le-havre). About 48% of the overall freight transport from and to Greater Paris (> 10 million inhabitants) passes through the logistics zone of the Le Havre harbor, and an expansion of this activity is foreseen in the coming decades (Merk et al. 2011). Numerous morphological changes have taken place during the past century to accommodate this burgeoning activity, notably the channeling of a large part of the riverbed and the construction of regulation weirs and levees (Foussard et al. 2010; Lemoine and Verney 2015). These deep physical transformations have impacted the ecological function of the estuary, yet the extent of such impacts and the specific underlying drivers are only partly characterized.

Besides being productive natural ecosystems and providing habitat to a large number of aquatic species, estuaries are transitional systems that act as buffer zones for river inputs and play a key role as global sinks of carbon (Howard et al. 2017; Macreadie et al., 2017). The so-called estuarine filter can retain, permanently or temporarily, a large part of the solutes and particles transported by the river, and the passage through the estuary can biogeochemically transform many compounds (e.g., Kennish 2002; McGlathery et al. 2007; Dürr et al. 2011;

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Statham 2012). As a result of this complex storage and transformation dynamics, estuaries have been shown to alleviate the nutrient load entering coastal waters in many places around the world. Increasing pollution issues and extensive land reclamation, however, have caused a serious degradation in many of these estuarine systems (Orive et al. 2002; Lotze et al. 2006; Bricker et al. 2008; Waycott et al. 2009; Howarth et al. 2011).

Turner et al. (1994) and Turner and Millward (1994) found that an appreciable amount of the trace metals and micropollutants entering the Dee estuary (north-east Wales) remained in the estuary and did not reach coastal waters, and similar results were obtained for phthalate esters, a widespread type of polymeric contaminant (Turner and Rawling 2000). These authors emphasized the significance of sorptive removal for elements having a strong particle affinity, particularly in those estuaries with a well-developed turbidity maximum zone (TMZ). Likewise, Canton et al. (2012) reported very quick transformation and consumption processes in the short transit time between the Leyre River mouth and the waters of Arcachon Bay during productive periods. In the Seine, Garnier et al. (2010) estimated that the lower estuary is able to retain about 7% of the annual N inputs, 4% of dissolved silica inputs, and over 30% of inorganic P inputs. The study provided a valuable first quantification of the estuarine retention, although it only considered the downstream part of the estuary (i.e., the TMZ) and the authors used a simplified model that accounted for the main biogeochemical transformations but left many hydro-sedimentary processes aside.

The growing public concern for environmental issues has led the French authorities to launch initiatives combining the assessment of the ecological status of the estuary and restoration measures, as evidenced by the number of plans and governmental programs put forward in the past few years (e.g., the Global Management Plan for the Seine estuary; the Seine-Aval Programme, and the establishment of the Estuary Council; *see* Ducrotoy and Dauvin [2008] and Fisson et al. [2014] for further details). A careful delimitation of the role of the estuary in terms of nutrient biogeochemistry and the potential impact of morphological changes on this role is therefore vital before costly restoration measures are undertaken.

Within this context, the present work aims at assessing the role of the Seine estuary in the transformation, storage, and elimination of nutrients, analyzing what are the main biogeochemical processes and what are the estuarine sections where these occur. We provide a detailed budget of the main nutrient elements along estuarine waters and discuss how human activities have altered the functioning of the system. Additionally, using data from years with contrasted hydrological conditions, we test whether the estuarine filter shows strong seasonal and/or interannual variations, and examine to what extent these temporal changes in the processing of nutrients affect the marine domain.

An important achievement of the study is the development of a detailed mechanistic model that encompasses the entire river–estuary–marine continuum, from the upper dam in Poses to the outer bay, so that we can address the functioning of estuarine and coastal waters together, with a single model, and have a much better understanding of the interconnections between the two systems than that achieved in previous studies.

Materials and methods

Study area

The study area comprises the Seine estuary from Poses (the upper limit of tidal propagation) to Honfleur (at the sea boundary) and the nearby coastal waters of the Seine Bight (Fig. 1). The estuary is ~ 160 km long and occupies 50 km^2. It is a macrotidal-type estuary, shallow, and vertically mixed at flood tide, with two major sections: a freshwater section, from Poses to Caudebec, and a lower section influenced by salinity, from Caudebec to the coastal zone.

The estuary is the outlet of the Seine drainage basin, characterized by a high population density (on average, 200 inhabitants km^{-2}), heavy industrial activity, and intensive agriculture. The estuary itself is home to about 1 million inhabitants, mostly located in the city of Rouen and its outskirts, and comprises two large commercial ports, one in Rouen and one in Le Havre.

The average water flow of the Seine River at the entrance of the estuary is ~ 470 m^3 s^{-1}, with marked intra-annual differences between winter and summer flows (~ 250 m^3 s^{-1} in the summer and over 700 m^3 s^{-1} in the winter) and between wet and dry years (two- to three-fold differences; Romero et al. 2016, and references therein). River discharge influences the mean residence time in the estuary, which spans from 17–18 d for a discharge of 200 m^3 s^{-1} at Poses to 5–7 d for a discharge of 1000 m^3 s^{-1} (Le Hir et al.1999; Even et al. 2007). The estuary is also characterized by the formation of a TMZ. The TMZ is generally located between Honfleur and Tancarville, but it can move upstream depending on the tidal cycle and the river flow or it can be flushed out into the Seine Bight during winter flood events (Etcheber et al. 2007; Garnier et al. 2008, 2010).

The morphology of the estuary has been severely altered over the past century to ease navigation and foster commercial activities. By the end of the 1970s, the construction of dykes and seawalls improved the shipping conditions so that large vessels could reach the inland port of Rouen, and downstream of Tancarville, the waterway became a quasi-linear cemented channel that is regularly dredged. As a result, the surface of the intertidal zone has been dramatically reduced from more than 130 km^2 in 1850 to less than 30 km^2 at the beginning of the 21st century (Dauvin et al. 2006). In 1998, an extension project for Le Havre harbor (Port 2000) was approved, and several compensatory actions were planned to keep the balance between the economic development objectives and the protection of aquatic habitats. In a first restoration effort in 2005
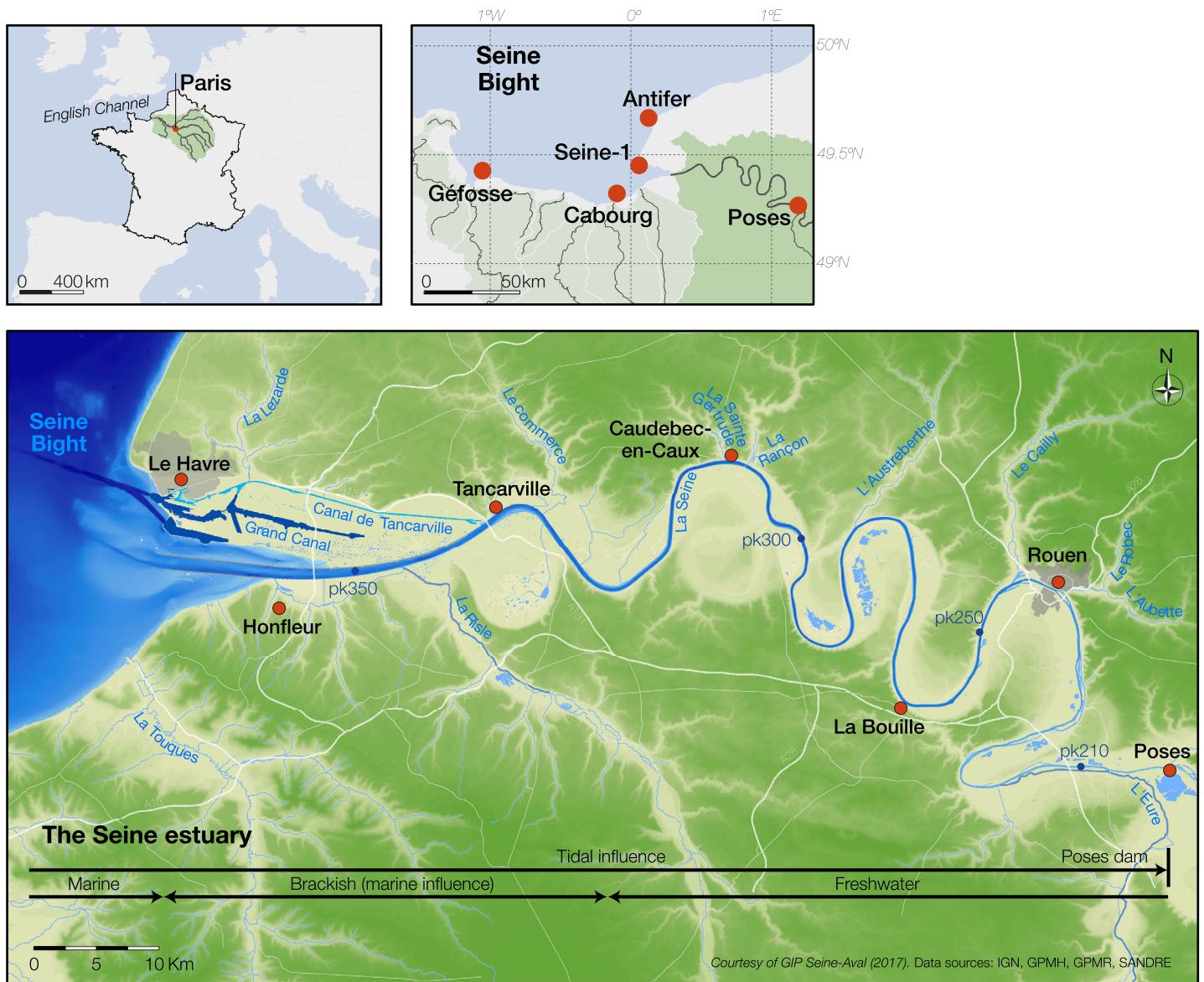
Fig. 1. A detailed map of the Seine estuary, including some of the stations where validation data were obtained. The regular track of the artificial channels downstream of Tancarville, and the two large commercial ports of Le Havre and Rouen can be clearly observed. Numbers along the river refer to the stream kilometer (where km 0 [pk0] corresponds to the river in Paris). On top, the location of the Seine River basin within France (left); and the domain of the ECO-MARS3D model with the four marine validation stations used (right).

some breaches were opened in the dykes to favor the connectivity between the estuary and the nearby salt marshes (Ducrotoy and Dauvin 2008; Ducrotoy 2010, and references therein).

The ECO-MARS3D model

This study applies the three-dimensional hydrodynamic model "Model for Applications at Regional Scale" (MARS3D) developed by the French Research Institute for the Exploitation of the Sea (IFREMER). Lazure and Dumas (2008) give a thorough description of the fundamentals involved in the MARS numerical modeling system. The model was originally built to provide realistic descriptions of coastal phenomena and it can be coupled to a number of complementary modules that deal with specific issues, such as algal blooms, contaminants, fishing practices, and sediment dynamics.

In the present study, two modules have been used: one describing the sedimentary dynamics of sand mud mixtures (the Sediment module; Le Hir et al. 2011) and the other describing the biogeochemical processes (the Ecological module, called ECO-MARS3D; Cugier et al. 2005a). The Sediment module comprises two types of particles: a light sediment class injected via the river and streams that simulates suspended matter inputs and a heavy sediment class initialized in the

estuary that makes up the TMZ. The Ecological module includes multiple chemical transformations, oxygen dynamics, and the processes related to the activity of phytoplanktonic and zooplanktonic organisms in both the water column and the benthos.

The ECO-MARS3D has been successfully applied in several studies thus far, mostly concerning the English Channel and the Seine Bight (e.g., Cugier et al., 2005*a*,*b*, 2010; Passy et al. 2016), so one of the key novelties of the present study is indeed the integration of the estuarine domain. In our configuration, the spatial domain of the model comprises the whole Seine estuary, from Poses to Honfleur, and a nearby coastal strip covering about 11,000 km^2 (Fig. 1). A series of adjustments and modifications have been made to account for the estuary's distinctive features, which are therefore fully novel and specific to this study: (1) phytoplankton and zooplankton groups are split into two compartments—freshwater and marine—with a threshold salinity of 5, above or below which the mortality coefficient of the respective organisms is increased fivefold; (2) the water column is divided into 10 layers using a topographically conformal vertical coordinate system (the so-called sigma [σ] coordinate system), as well as a sediment layer; (3) oxygen, which plays an essential role in many estuarine processes, was incorporated as a new state variable in the model; and (4) a realistic framework was used in terms of the physics and the morphology of the estuary, with up-to-date bathymetric data.

Hydrodynamics-governing equations are thoroughly described in Lazure and Dumas (2008) and Cugier and Le Hir (2002), and the principles and calculations of the Ecological module can be found in Cugier et al. (2005*a*) and Passy et al. (2016). Additionally, as many of the ecological processes involved have been improved or adapted to the characteristics of the estuary, the parameters and the calculation formulae are listed in Supporting Information Appendices S1 and S2.

Broadly, the Ecological module is an Nutrient–Phytoplankton–Zooplankton–Detrital (NPZD) model that includes three major nutrient elements (N, P, and Si), in both dissolved and detrital forms, at the water column and the sediment compartments. P is also considered in its particulate form, and dissolved N includes NH_4^+ and NO_3^-. Phytoplankton organisms are expressed in the model in terms of their nitrogen content and they are divided into three groups in the marine compartment (diatoms, dinoflagellates, and nano-phytoplankton) and two groups in the freshwater compartment (green algae [*Chlorophyceae*] and diatoms). Zooplankton consist of two different groups, discretized according to their size: microzooplankton graze on diatoms, nano-phytoplankton, green algae, and detrital organic matter, while meso-zooplankton are only present in marine waters and feed on diatoms, dinoflagellates, and microzooplankton. Benthic diatoms come from the falling and resuspension of both marine and freshwater cells; finally, zoobenthos feed exclusively on diatoms. The model also includes salinity, temperature, oxygen, and suspended matter

as state variables. A diagram with all these processes is presented in Fig. 2.

With regard to the spatial configuration, the model is run using a 500-m resolution Cartesian grid that covers the estuary and a small part of the Seine Bight (Fig. 1). The grid includes realistic flow sections and estuary length, which allows for a better description of the Seine estuary and the TMZ.

We were particularly concerned about producing accurate simulations of the estuarine transit times and the timing of nutrient arrival at the coastal zone, so the tidal propagation within the estuary was intensively calibrated. The following physical characteristics measured (Brenon and Le Hir 1999; Dupont 2001) were respected during the modeling process: (1) at low tide, the TMZ was centered 2–3 km downstream from Honfleur, with a downstream limit at km 352 and an upstream limit at km 340, close to Tancarville (Fig. 1); (2) at high tide, the TMZ was centered around km 340, with a downstream limit at km 354 and an upstream limit at km 335.

Boundary conditions

The model is forced with tidal harmonic components at the marine boundaries, with measured or calculated flows and concentrations at river boundaries, with wind-induced stresses at the surface, and with measured meteorological time series for water temperature calculation (Cugier et al. 2005*a*).

On the seaward boundary, bathymetric data and the tidal components were provided by the French Navy Oceanographic Department (Service Hydrographique et Océanographique de la Marine), and the biogeochemical variables came from the MANGA configuration of the ECO-MARS3D model, a setup that encompasses the English Channel and the Bay of Biscay and uses a 16-km-resolution grid and a 4-d time step (Ménesguen et al. 2018).

Landward boundary conditions came from the RiverStrahler model (Billen et al. 2001, 2007; Passy et al. 2013, 2016) and from the French national database on industrial and wastewater emissions (http://www.irep.ecologie.gouv.fr/IREP/index.php). We considered the discharge of the Seine, the Eure, the Risle, and three other estuarine tributaries (Aubette, Cailly, and Austreberthe; Fig. 1), plus the direct inputs from industry and wastewater treatment plants (WWTPs) located within the estuary, such as those collecting the sewage from the cities of Le Havre and Rouen. Moreover, the RiverStrahler model provides the outputs from nine coastal rivers (from east to west, the Touques, Dives, Orne, Seulles, Aure, Vire, Taute, Douve, and Saire; Fig. 1) discharging along the Lower Normandy coast. Bathymetry and flow sections of the Seine River and the estuary were derived from the Rouen Port Authority database.

The meteorological data were furnished by the French Meteorological Agency via the ARPEGE model (Météo-France). Data for wind, air temperature, air moisture, atmospheric pressure, cloud cover, and sunshine duration were available every 6 h at a spatial resolution of 0.5°. Wind speed and wind
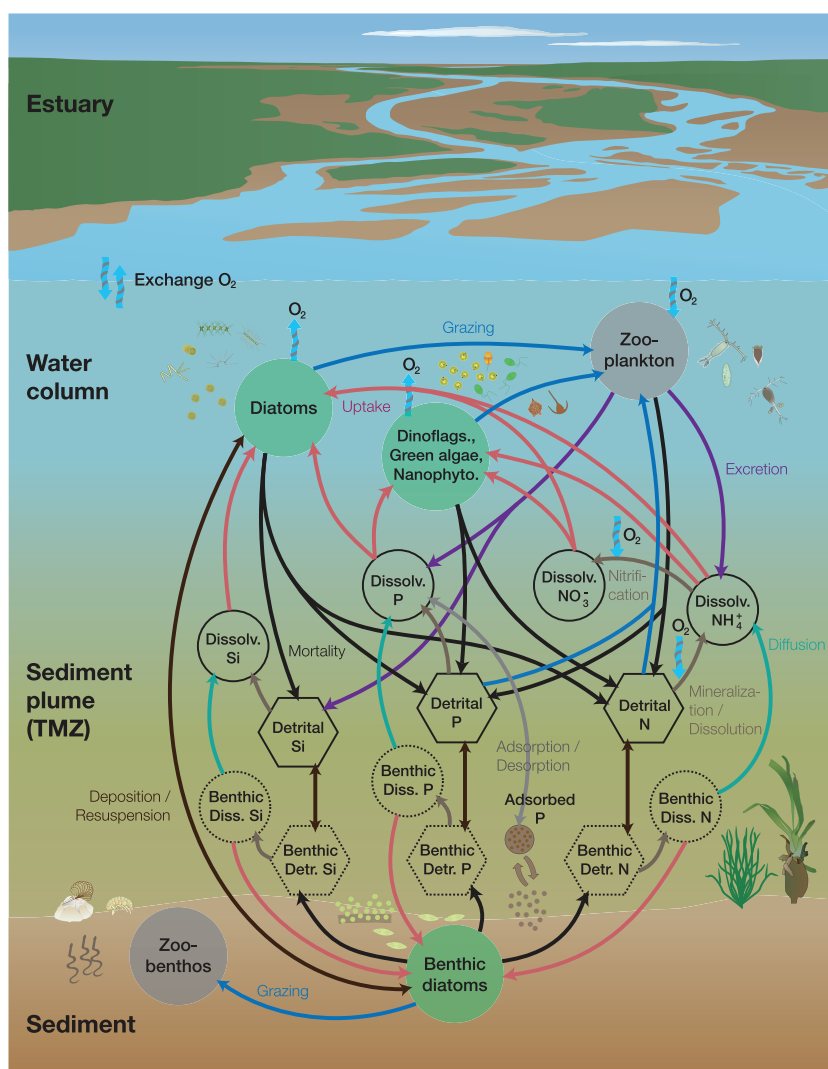
Fig. 2. Flow diagram of the MARS3D Ecological module, with the water column and sediment compartments and the exchanges between them.

direction measurements were used to derive sea temperature and surface wind-induced stress.

Validation measurements

The performance of the model was tested with a large set of measured data. River flow information was provided by the Ministry for Ecology and Sustainable Development through the French national hydrologic databank (Banque HYDRO, www.hydro.eaufrance.fr), and water quality measurements were kindly supplied by the Service de Navigation de la Seine and the Seine water authority (Agence de l'Eau Seine-Normandie). We selected the uppermost location of the study area (Poses), and several stations along the Seine estuary.

Physicochemical data for the marine stations of the Seine Bight came from the Réseau Hydrologique du Littoral Normand network (http://archimer.ifremer.fr/doc/00426/53754/), and marine phytoplankton data corresponded to the Réseau

d'Observation et de Surveillance du Phytoplankton et des Phycotoxines (REPHY) network, both managed by the IFREMER.

Validation data for dissolved and particulate nutrient concentrations (N, P, and Si), dissolved oxygen, chlorophyll, and suspended matter were collected monthly or bimonthly depending on the station, while freshwater plankton concentrations were less frequent, sometimes only available during the summer period of selected years.

Results

In order to investigate the biogeochemical role of the estuary in different hydrological conditions, simulations were performed during a 3-yr period (2011–2013). An additional year was used as a spin-up initial year to stabilize the ecosystemic and sediment variables prior to the target period. Broadly, 2012 was an average year in terms of rainfall and river discharge,
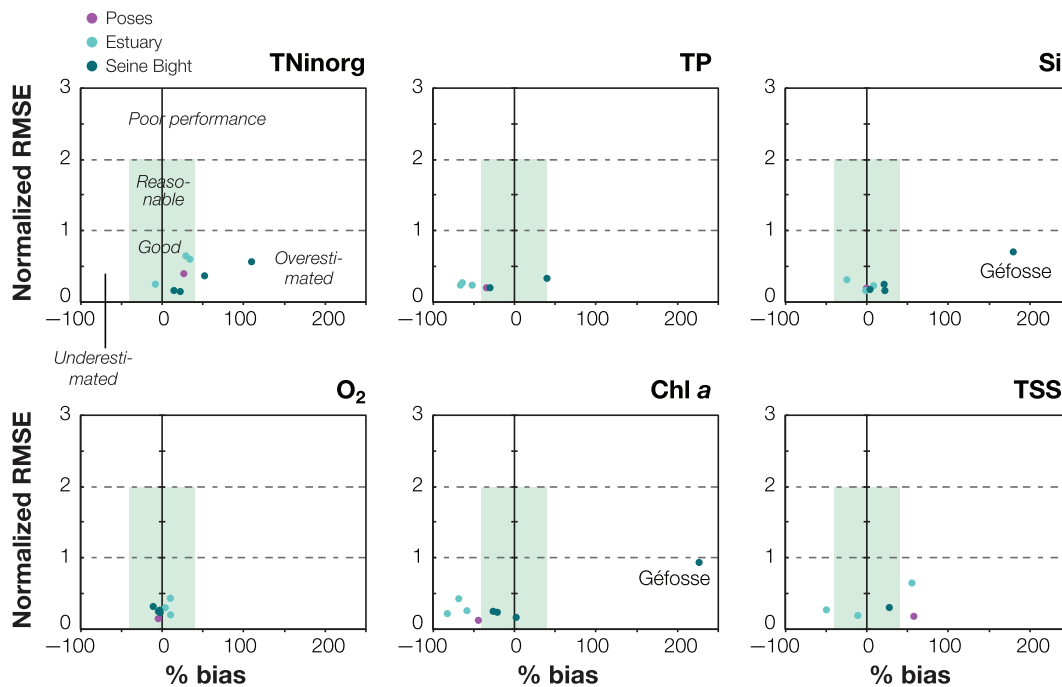
Fig. 3. General validation plots to assess the correspondence between the modeled (daily averages) and the observed (instantaneous measurements) data. The normalized root-mean-square error (N-RMSE) vs. the percentage of bias is shown for several estuarine and marine stations; the results at Poses, the most upstream station of the study area, are colored in violet. The greenish area indicates the model's good performance zone.

which allowed for the determination of representative mean retention and export values in the estuary. The year 2011 was dry, notably during the summer period, and 2013 was wetter than the average, with river flow values significantly higher than the climatological mean (Romero et al. 2016).

Moreover, most of the current wastewater treatment (WWTP) technologies (dephosphatation and nitrification) were already implemented in 2009 (with the exception of an improved denitrification process put in place in Achères WWTP, upstream of the study area, in 2012), so the model results provide a reliable picture of the present impacts and functioning of estuarine waters.

We shall note, prior to describing the results, that the term retention is broadly used in the manuscript to refer to all storage or elimination processes that decrease the flux of nutrients, either between the most upstream and downstream parts of the estuary (i.e., Poses to Honfleur) or between specific stations. This does not mean that the retained nutrients may be permanently removed from the system—such as occurs, for instance, with denitrification; in some cases, the abatement is temporary: the estuarine filter just acts as a transitory trap and after some time (days to years) and several physicochemical transformations, nutrients are released back to the water column. We consider, however, that even when retention processes are not

permanent removal processes, the delay in the export of nutrients toward marine waters favored by estuarine systems also constitutes an effective (albeit temporary) filtering mechanism.

General validation of the model

The RiverStrahler model and its coupling with the ECO-MARS3D were successfully tested and the results were published in Passy et al. (2016). The hydrosedimentary characteristics are essentially the same, so no further validation is presented in this study. Nevertheless, the fitness of the freshwater model can be seen in the validation figures at Poses, as the results of this station correspond to the RiverStrahler outputs (Fig. 3).

The overall performance of the ECO-MARS3D model for the different variables is presented in Figs. 3–4. The model shows good fit in both the estuarine domain and the Seine Bight, and the results on the TMZ are very satisfactory, despite the complexity of the processes occurring in this sector. Dissolved oxygen, newly introduced in this model version, shows very low bias in all stations, and the modeled curve follows the measurements closely (Fig. 4), both in time and in magnitude. The Géfosse marine station exhibits the highest deviations of all validation points, with the model tending to overestimate silicate and chlorophyll concentrations. Géfosse is located far west from the Seine River mouth, in an inlet
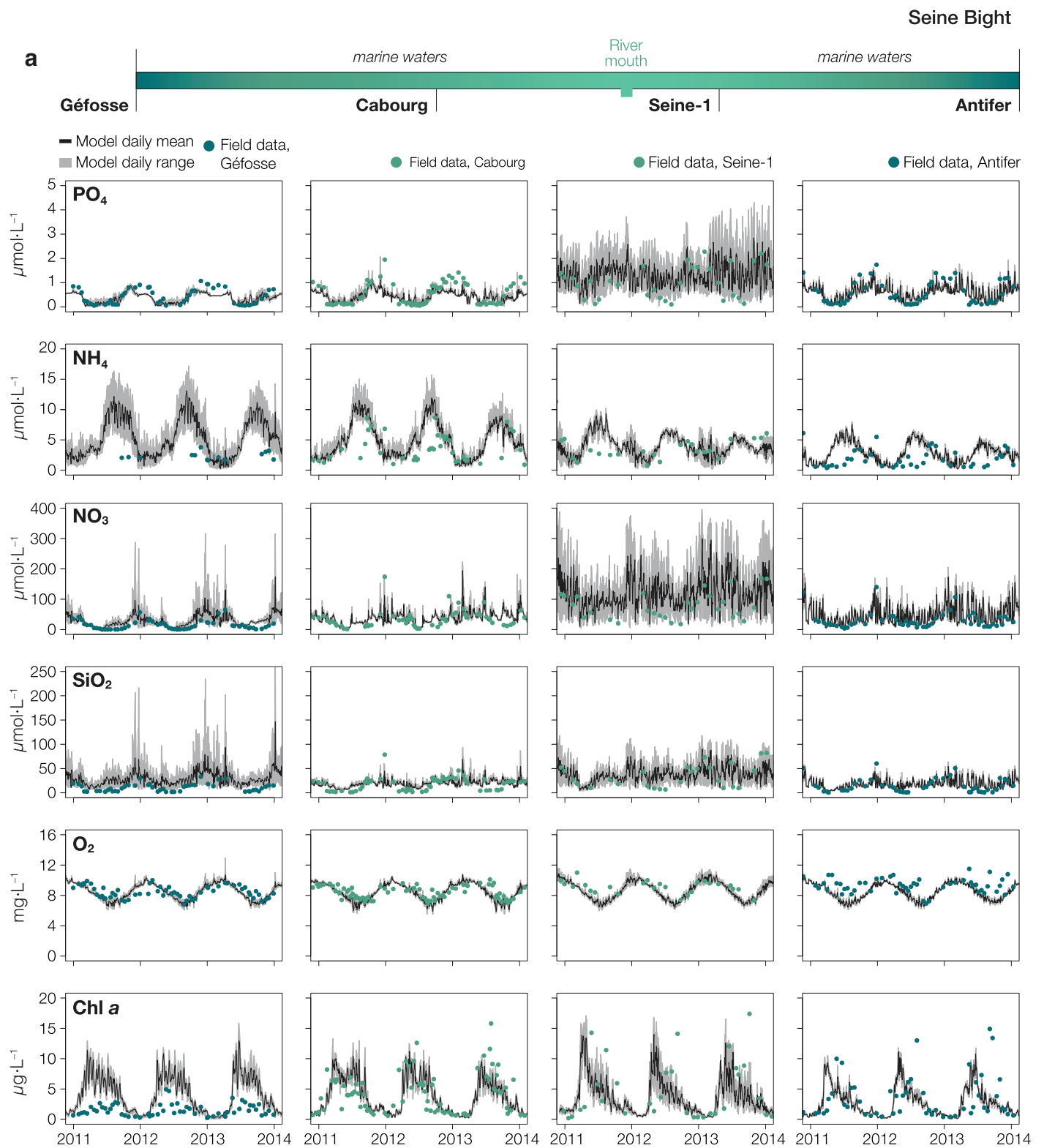
Fig. 4. Spatiotemporal validation of the model for several water column parameters during the 2011–2013 period. Modeled daily values (mean and range) and the corresponding observations at **(a)** four marine stations (Géfosse, Cabourg, Seine-1, and Antifer) within the Seine Bight and **(b)** four estuarine stations (from Poses to Honfleur). The salinity gradient is shown on top.
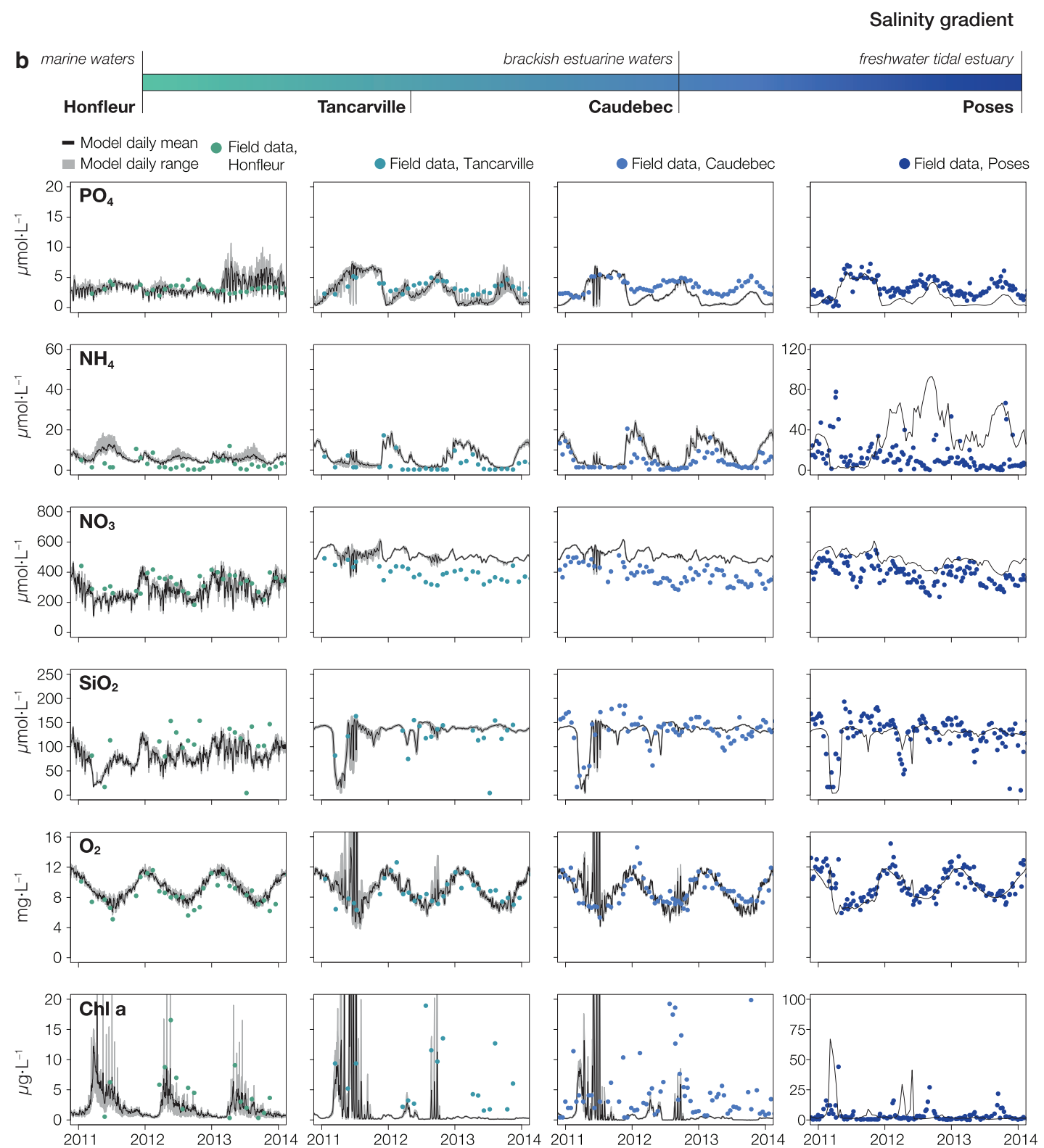
Fig. 4. (Continued)

Table 1. Fluxes of N, P, and Si (kt yr^{-1}) in five stations of the estuary for three different years. The average annual values are in bold characters. N-ICEP and P-ICEP (t C yr^{-1} km^{-2}) are the indices of eutrophication potential (see text for calculation details) and are calculated for the waters leaving the estuary (Le Havre station).

Estuarine stations		Annual nutrient fluxes (kt yr^{-1})			
		2011	**2012**	**2013**	**Average**
Poses	N_{tot}	93.5	110.7	190.2	**131.5**
	P_{tot}	1.7	1.6	2.7	**2.0**
	Si_{tot}	44.0	59.4	109.8	**71.1**
Caudebec	N_{tot}	94.2	111.6	173.3	**126.4**
	P_{tot}	1.5	1.4	2.1	**1.6**
	Si_{tot}	46.8	60.6	100.2	**69.2**
Tancarville	N_{tot}	94.5	111.9	174.0	**126.8**
	P_{tot}	1.7	1.6	2.2	**1.8**
	Si_{tot}	46.8	60.5	100.3	**69.2**
Honfleur	N_{tot}	96.4	114.4	177.4	**129.4**
	P_{tot}	1.6	1.6	2.0	**1.7**
	Si_{tot}	49.3	63.5	104.3	**72.4**
Le Havre	N_{tot}	91.3	109.6	168.8	**123.2**
	P_{tot}	1.5	1.5	2.0	**1.7**
	Si_{tot}	47.2	61.2	99.5	**69.3**
	N-ICEP	5.4	6.4	9.6	**7.1**
	P-ICEP	−0.6	−1.0	−1.9	**−1.2**

affected by the export of four coastal rivers and close to the edge of the 16-km grid used to setup the marine boundary conditions, and these are likely the cause for some of the differences observed.

Spatiotemporal dynamics of the estuarine and coastal water masses

The daily variability of nutrients, oxygen, and chlorophyll during the 2011–2013 period is shown in Fig. 4. In marine waters (Fig. 4a), nitrate, phosphate, and silica are high in the winter and low in the summer, while ammonium shows overall higher values during the warm period. The temporal

dynamics is accurately reproduced by the model, particularly in those stations that are closer to the outlet of the estuary (i.e., Seine-1 and Cabourg). Seine-1, the station that is most affected by the river outflow and the TMZ, is also the marine station with the least regular annual cycles, and these variations are adequately captured in our simulations. The model also gives a good fit for the timing and the magnitude of the annual chlorophyll peak; chlorophyll values are only overestimated in Géfosse, the furthest marine station.

In the estuary, nutrient concentrations are remarkably higher than in marine coastal waters and the seasonal patterns are less clear, partly due to the interference of the tide (Fig. 4b). The curves modeled for oxygen, silica, and phosphate match well the observed data, while nitrate concentrations are slightly overestimated in the upstream stations and accurately reproduced downstream, at Honfleur. Ammonium concentrations are also accurately represented in all estuarine stations except at Poses, where the actual measurements after the year 2012 are often much lower than the modeled values. This is mainly due to the gradual implementation from 2012 on of an improved nitrification/denitrification treatment in the Achères WWTP, which was difficult to take completely into account in the RiverStrahler simulations. Despite the overestimation at Poses, the model is able to closely reproduce the variations of both ammonium and nitrate downstream and in the coastal zone.

The dynamics of chlorophyll at the intermediate estuarine stations is very complex, and there are numerous peaks throughout the year that the model is not able to fully resolve. However, the annual variations are appropriately represented at the uppermost (Poses-La Bouille) and the lowermost (Honfleur) sections, and the modeled values are within a reasonable range throughout the estuary.

N, P, and Si budgets: Export and processing by the estuarine filter
Annual budget in the estuary

The retention and processing of nutrients before they reach the sea, commonly known as the filter effect, is one of the most important functions of estuaries. This filtering role,

Estuarine filter (Poses - Le Havre)
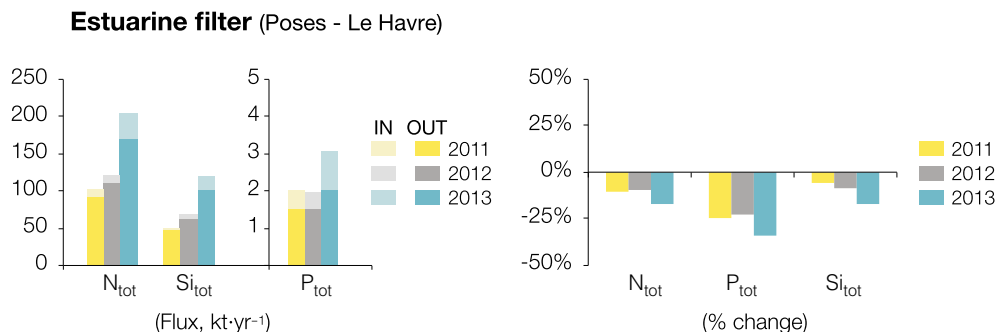
Fig. 5. The estuarine filter, from Poses to Le Havre, for three different years: 2011 (dry), 2012 (average), and 2013 (wet). The absolute nutrient fluxes entering and leaving the estuary are shown on the left, and the percentage of change is shown on the right. N_{tot} refers to nitrogen, P_{tot} to phosphorus, and Si_{tot} to silica.
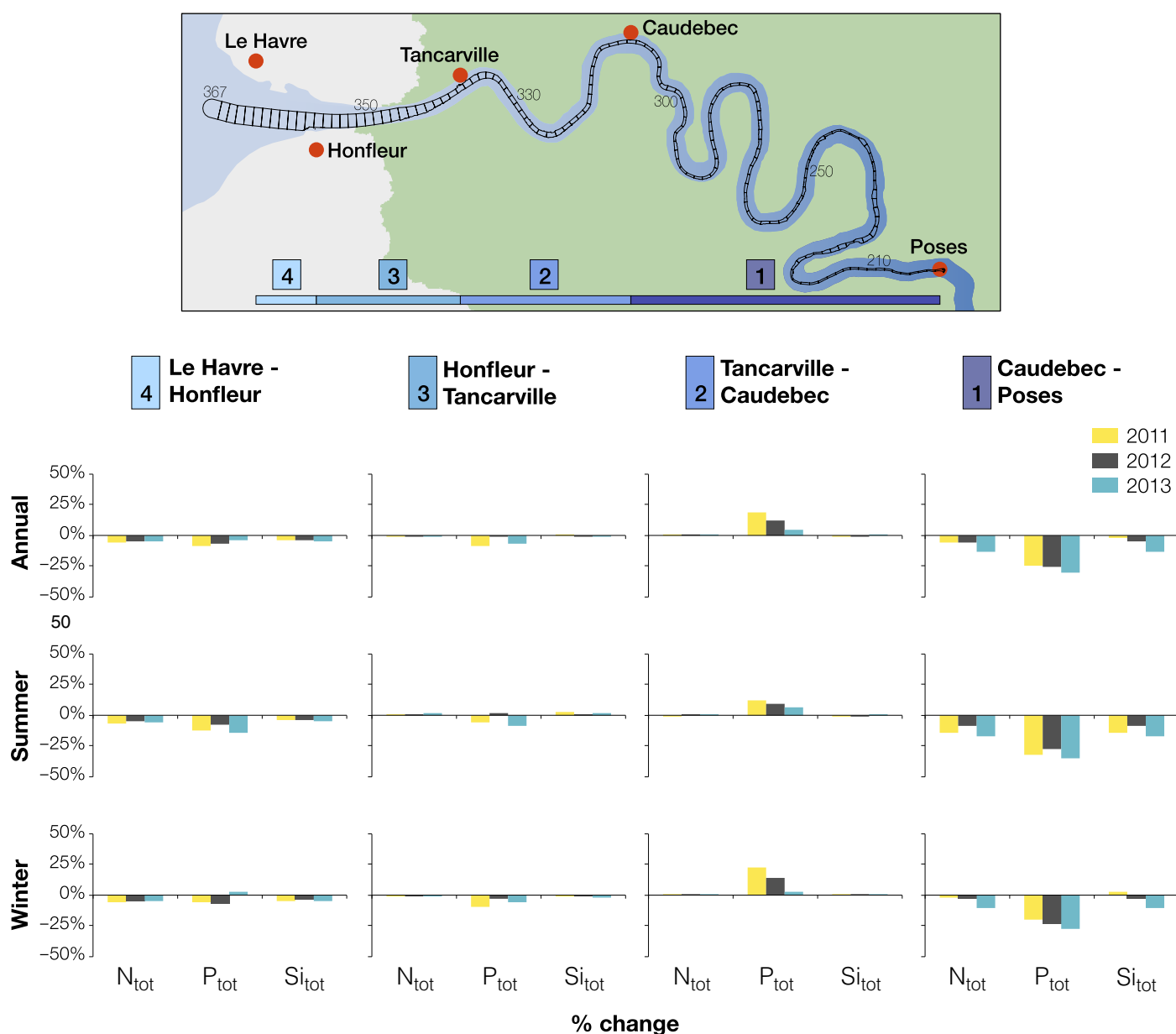
Fig. 6. Nutrient budgets (% of change between two stations) for nitrogen (N_{tot}), phosphorus (P_{tot}), and silica (Si_{tot}) in four different sections of the Seine estuary and for different periods of the year. From top to bottom: The whole year, the summer period (April–September), and the winter period (October–March). A schematic map of the estuary with the four sections studied is shown on top. Numbers on the map indicate the kilometric points.

however, can vary considerably from year to year depending on the hydrological conditions. Table 1 gathers the calculated annual fluxes for 2011, 2012, and 2013, at several estuarine stations. Figs. 5–6 show the annual changes in nitrogen, phosphorus, and silica fluxes for the entire estuarine profile (Poses-Le Havre) and for different sections along the estuary. These budgets compare the sum of upstream and lateral inputs of all forms of N, Si, and P with the calculated downstream output from the section concerned, thus assessing the integrated retention of each element over the period. Keep in mind, as

explained above, that retained nutrients may either be permanently removed (as is the case for denitrification) or can be stored, more or less temporarily, in the benthic compartment. Because of this benthic storage, "negative retention," i.e., release of nutrients, can occur within a particular segment of the estuary during a certain period of time, if inputs by sedimentation of particulate forms are lower than release to the water column by either resuspension, desorption, or mineralization.

During an average year in terms of rainfall and flow (2012), for the whole estuary, reductions of N and Si fluxes reach
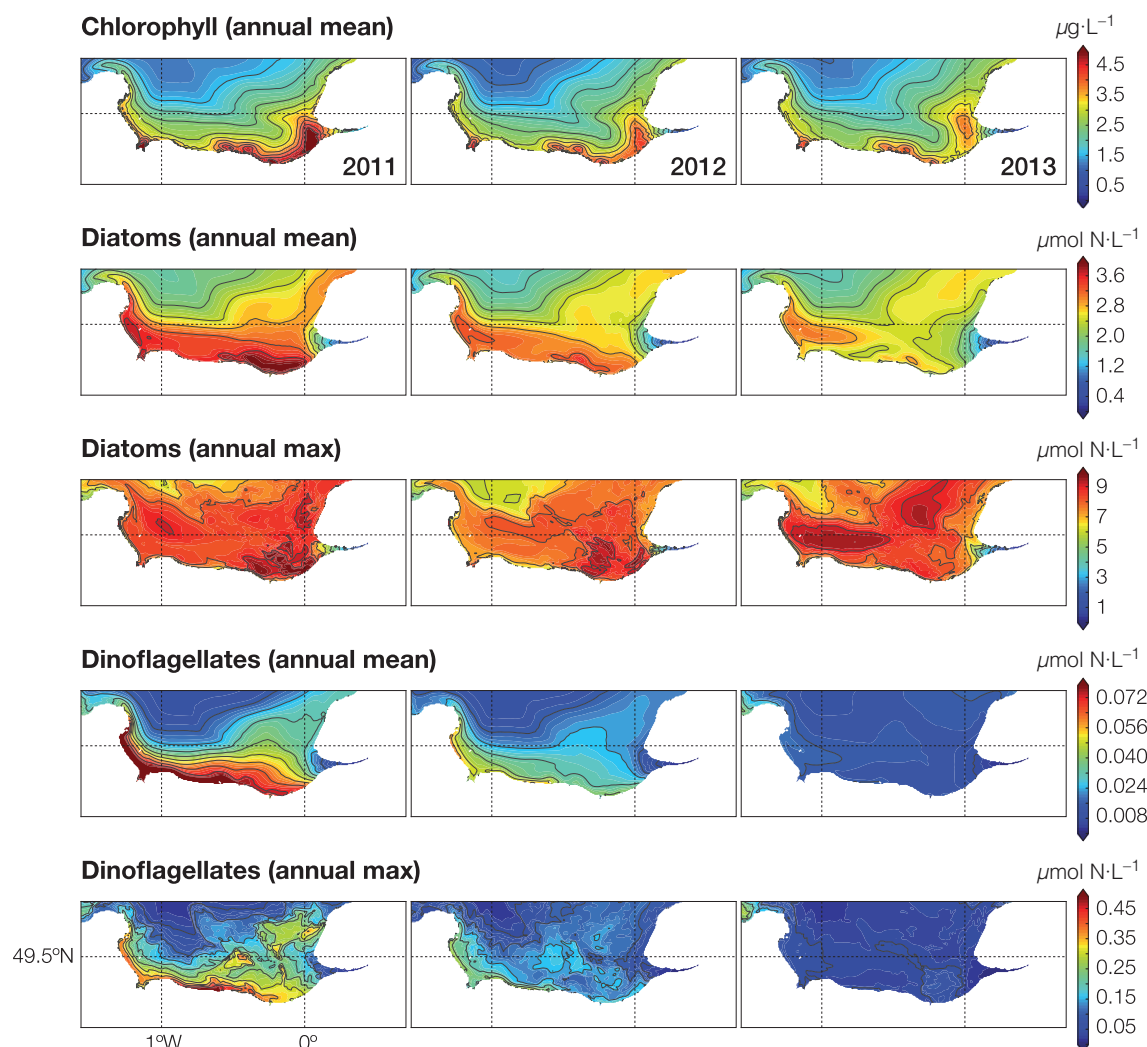
Fig. 7. (top) Mean concentration of chlorophyll in the Seine Bight for 3 yr: 2011 (dry), 2012 (average), and 2013 (wet). **(bottom)** Mean and maximum concentration of diatoms and dinoflagellates for the same 3 yr.

approximately −10% (−10% and −9%, respectively), but the decrease in total phosphorus is greater, approximately −23% (Fig. 5). Total P fluxes decrease significantly in the upstream sections of the estuary (between Poses and Caudebec the abatement is −0.5 kt P yr⁻¹), and there is a small release, probably by desorption of P at the entrance of the TMZ, between Caudebec and Tancarville (Fig. 6). The dynamics along the estuary—that is, major reductions within the upstream part and slight decreases downstream, mostly occurring between Honfleur and Le Havre—and the overall percentages of reduction are similar during dry years (cf. 2011), with −11% for N, −6% for Si, and −25% for P. Surprisingly, the filter effect increases during wet years such as 2013: −17% for N, −17% for Si, and −34% for P, with increasing incoming nutrient and particulate matter fluxes.

Note that although the differences in the percentage of nutrient reduction between wet and dry years remain within a narrow range, changes in the nutrient load processed by the estuary

and the total export to the sea can indeed be large. Thus, under dry conditions, the estuary receives 103 kt N yr⁻¹, 50 kt Si yr⁻¹, and 2.0 kt P yr⁻¹, and it exports 91 kt N yr⁻¹, 47 kt Si yr⁻¹, and 1.5 kt P yr⁻¹; conversely, during wet years, total inputs amount to 204 kt N yr⁻¹, 120 kt Si yr⁻¹, and 3.1 kt P yr⁻¹, while exports are 169 kt N yr⁻¹, 100 kt Si yr⁻¹, and 2.0 kt P yr⁻¹.

On average, considering the three hydrological years, the estuary is able to retain 19 kt N yr⁻¹, 9.8 kt Si yr⁻¹, and 0.7 kt P yr⁻¹, amounting to −13%, −11%, and −27% of the incoming N, Si, and P fluxes, respectively.

Seasonal and spatial variability

We further examined whether the estuarine filter was more effective at a specific time of the year. Seasonality and the timing of nutrient inputs—and therefore also the ability to retain them—are very important when assessing the potential consequences at sea, because phytoplankton blooms may vary in composition depending on the nutrient load and the relative

nutrient ratio, but also on the time of the year, as the warm period and stratified waters are in general more favorable to small algae and/or motile organisms such as dinoflagellates.

We broadly divided the year into two large periods: the summer season (from April to September) and the winter season (from October to March) and checked for differences between the two. As shown in Fig. 6, the functioning of the estuary does not seem to vary substantially between the two periods, although the filter effect is somewhat enhanced in the summer, when the residence time of the water in the estuary is longer.

Regardless of the season, the largest reductions occur consistently in the upper part, and there is a slight release of P in the TMZ throughout the year. During the summer months, there is also a small increase of N and Si (+1% for N and +1.8% for Si) between Tancarville and Honfleur, in the area of brackish waters. On average, for the 3 yr, overall winter retention is −10% for N, −8% for Si, and −22% for P, and summer figures are −17% for N, −15% for Si, and −35% for P.

Phytoplankton biomass at sea

The amount of nutrients exported from the estuary to the marine environment directly affects the biomass of phytoplankton within the Seine Bight. We used the model to assess the total algal biomass in marine waters and the potential blooms of diatoms and dinoflagellates during our study period, 2011–2013 (Fig. 7).

Chlorophyll concentrations (a typical indicator of phytoplankton biomass) were mapped for the 3 yr and highlighted the importance of the hydrological conditions for the proliferation of algae: chlorophyll values at sea were higher during the dry year (2011) than during the average and wet years (2012 and 2013, respectively).

We also analyzed the response of diatoms and dinoflagellates, the two major phytoplankton groups in the bay. As shown in Fig. 7, both groups present the largest concentrations in the western part of the bay, along the Normandy coast, and not only the total biomass but also the spreading of the blooms increases under dry conditions.

Regarding dinoflagellates, the growth of these nonsiliceous algae is often favored under conditions of imbalanced N and P fluxes in excess with respect to silica (on the basis of the general N : P : Si ratios described for planktonic organisms; Brzezinski 1985; Redfield 1934; Redfield et al. 1963). We calculated the N- and P-Index of Coastal Eutrophication Potential (ICEP; Billen and Garnier 2007) of the annual flux delivered at the outlet of the estuary (Le Havre station; Table 1). ICEP values are expressed in t C yr^{-1} km^{-2} and represent the carbon biomass potentially produced in the receiving coastal waters sustained by the flux of nitrogen or phosphorus delivered in excess over silica. Positive ICEP values thus indicate a condition for nonsiliceous algal development. These results show positive N-ICEPs (on average, 7 t C yr^{-1} km^{-2}) and slightly negative

P-ICEPs (on average, −1.2 t C yr^{-1} km^{-2}) and may suggest that P controls the growth of nonsiliceous algae. The difference among N, P, and Si is particularly severe during wet years (2012), with N-ICEP of 9.6 t C yr^{-1} km^{-2} but P-ICEP of −1.9 t C yr^{-1} km^{-2}. The highest (less negative, −0.6 t C yr^{-1} km^{-2}) P-ICEP value is found for the dry year 2011, when N-ICEP is still high (5.4 kg C yr^{-1} km^{-2}), which leads to the largest phytoplankton development in the bay, unfortunately including dinoflagellates (Fig. 7).

Discussion

The filter effect of the estuary

Estuaries are very dynamic systems in terms of physical and chemical processes; they can constitute powerful biogeochemical reactors at the interface between the terrestrial and the marine compartments, able to significantly lower the flux of nutrients from land to sea. The Seine estuary, like many others around the world, is an area of great economic importance for the region, and as such, it sustains numerous human activities and is subject to multiple environmental pressures. One of the most common consequences of this environmental stress is the loss of the estuarine buffer role.

The buffering capacity of estuaries can indeed vary widely. Statham (2012) reviewed how estuaries might act as sources or sinks for certain nutrient species depending on the hydrological or the physicochemical conditions. The water quality of the Seine River has largely improved during the past decades, and the consequent decrease in the continental fluxes of nutrients has led to a significant amelioration of the estuarine water conditions (Romero et al. 2016). Eutrophic and low-oxygen episodes, which occurred regularly during the warm period in the past, are seldom observed now, and a decline in the total phytoplankton biomass of the nearby bay has also been reported (Passy et al. 2013; Romero et al. 2013). On the basis of a 40-yr data set, Romero et al. (2016) examined whether increasing/decreasing trends and turning points in water quality were consistent over time in both the river and the estuarine stretches. The authors found that although several transformations may occur within estuarine waters, these processes were not intense enough to decouple the dynamics of the estuary from that of the river, and argued that the estuary played a limited buffer role.

To what extent past changes in the channel morphology and the progressive improvement in the nutrient status have affected the filtering capacity of the Seine estuary remains, however, unexplored. Land reclamation and hydraulic management for increasing harbor activities have caused the loss of intertidal and benthic habitats, which are known to be hotspots for denitrification and water-sediment exchange processes. In accordance, some of the past N and P removal capacity may have been reduced. There are few, if any, recent estimations on the actual percentage of nutrient removal in estuarine waters, so one of the key assets of the present work

is precisely the calculation of nutrient budgets throughout the estuary. Our model integrates the main biogeochemical transformations in both the water column and the sediment layer, so it offers a reliable picture of the major processes involved.

According to our results, the fluvial estuary, between Poses and Caudebec, is the most effective in terms of buffering capacity. The largest drops in nutrient fluxes occur consistently in this upstream section, and several factors may play a part. First, it is the longest estuarine section considered, with about 108 km, which allows for longer reaction times; the enhanced filtering effect in the summer, when water residence times are longer, is supportive of this explanation. Second, the upper reaches of the estuary are the least turbid; higher light availability promotes the growth of algae, and therefore an efficient uptake of nutrients. Indeed, the upper part of the Seine estuary, immediately after Poses, behaves as an autotrophic system (Garnier et al. 2001). Chlorophyll concentrations reach here the highest values, with peaks two to three times higher than the concentrations found downstream. This is a well-lit section, rich in nutrients, where the growth of phytoplankton is favored by the low turbidity (~ 22 mg suspended solids L^{-1}), and there is a net consumption of N, P, and Si. Sebilo et al. (2006) identified this upper part of the estuary to be important also for nitrification processes. Some nitrification may add to the decrease of ammonium in this sector, although ammonium inputs have largely dropped thanks to improved wastewater treatments and nitrification processes are no longer a major factor. Accordingly, the seasonal anoxia episodes that were observed in estuarine waters in the past do not occur anymore.

In the lower estuary, not only the turbid waters of the TMZ but also the artificial morphology, with partly cemented channels and frequent dredging activities, restrict the growth of benthic and planktonic algae. Entering the salinity gradient, in the section Caudebec–Tancarville, there are positive in-out percent changes for P_{tot} (Fig. 6), which should be explained by sediment release, whereas this section is neutral for N and Si. In the Tancarville–Honfleur and Honfleur–Le Havre sections, nutrient abatement is low, although in the range of 3–9% for P_{tot}.

Turbidity increases when approaching Caudebec, but much more around Tancarville (~ 400 mg suspended solids L^{-1}, with peaks higher than 3000 mg L^{-1}). Poor light availability limits the growth of phytoplankton, and high concentrations of suspended matter and organic carbon—partly derived from land and partly due to the death of freshwater algae from upstream waters—foster the microbial loop and heterotrophic metabolism (Garnier et al. 2008). Nutrient uptake and remineralization processes here are close to equilibrium, which may explain why nutrient variations are low (aside from the sediment/particle–water P exchanges).

In the most downstream marine section, between Honfleur and Le Havre, nutrient decreases are approximately −5% for all nutrients, regardless of the season and the hydrological conditions. This suggests a dynamic balance between dilution and biological consumption, the former process dominating removal pathways in the winter and the latter prevailing in the summer.

Phosphorus water-sediment exchange

The other most significant feature of the estuarine nutrient dynamics is the release of phosphorus within the Caudebec–Tancarville section, where both salinity and TSS increase. P flux increases are related to P desorption from the sediment and the suspended particles, a process that is favored by the salinity gradient in the area. In saline waters, anions such as SO_4^{2-}, OH^-, and F^- compete with phosphate for adsorption sites, causing P desorption (Froelich 1988; Millero et al. 2001; Zhang and Huang 2011). Increases in dissolved P in the TMZ sector had been described by Némery and Garnier (2007). P desorption is further enhanced if dissolved P concentrations in the water column are low, which is the case for the Seine in recent years (Romero et al. 2016). The largest variations in the adsorption–desorption process occur in the winter (+3% and +22% for wet and dry years, respectively), while summer values range between +7% and +12%. This is in accordance with the results of Vilmin et al. (2015), who found that in the upstream Seine River, the release of reactive phosphorus by the riverbed sediments occurred mainly during high-flow periods, i.e., in the winter time. The contrasting release of P between summer/winter periods and dry/wet years may thus be the result of a compromise between sufficient flow to dilute P concentrations in the water column and to induce mixing and sediment resuspension, and enough residence time to allow for the exchange.

Using a simplified model that only considered nutrient transformations within the final part of the estuary (the TMZ from Caudebec to Honfleur), Garnier et al. (2010) calculated reductions of about 15–40% of incoming N and P, and no significant changes for silica. These figures are similar to our overall estuarine retention, but higher than the estimates of the model for the TMZ. If we analyze the fluxes between Caudebec and Honfleur, marginal changes of N and Si (+0.2% and −0.3% for an average year, respectively) and slight P increases (about +5%) are obtained. The differences may be due to the fact that Garnier et al. (2010) used a 0-D model where the TMZ functioned as a fluidized bed reactor at the outlet of the freshwater estuary: integrated over the tidal cycles, the total pool of particulate matter and the salinity gradient were assumed to be homogeneously distributed (see also Garnier et al. 2008). Instead, the present study takes into account realistic 3D morphological features and sedimentary dynamics.

Similar assessments have been done for estuaries in the Atlantic coast of Europe (Soetaert et al. 2006; Canton et al. 2012) and elsewhere (e.g., Nixon et al. 1996; Jickells et al. 2014; Sin et al. 2015; Xu et al. 2015) that can be compared to our retention estimates.

In the Scheldt, which is about 100 km north of the Seine, Soetaert and Herman (1995) calculated N removal values of −22%. Changes in the buffer capacity of the Scheldt estuary

were later exhaustively described by Soetaert et al. (2006). Like the Seine, the Scheldt estuary has greatly reduced its nutrient load and improved its oxic conditions in the past few decades. Changes in water quality have modified the behavior of the estuary, and current patterns for P, N, and Si retention along the estuary are similar to those observed in the Seine: a net removal of N and Si and a net production of P, mostly desorbed from the relic high-phosphate sediments. In the North Atlantic, Nixon et al. (1996) studied several locations and estimated that estuarine processes removed 30–65% of the total N and 10–55% of the total P, higher than our Seine estimates. Retention figures were much lower in the temperate and tropical estuaries reviewed by Tappin (2002): from −15% to −33%, closer to the range here found for the Seine.

The main retention mechanisms may also differ from those found in the Seine and in similar macrotidal estuaries. In small, highly flushed estuarine systems, sediment desorption is not a source of phosphorus. In the Leyre, a much smaller temperate estuary with a steep salinity gradient and residence times of just a few days, phytoplankton uptake and deposition during productive periods constitutes the main removal process, and the filtering capacity varies widely throughout the year: the estuary is a net sink of P, N, and Si in spring, but nutrient variations are minor in the summer and the passive transport with conservative mixing is observed in autumn and winter (Canton et al. 2012).

Difference between wet and dry years

One surprising result obtained with the simulations is the little difference in the percentage of nutrient retention between wet and dry years, winter and summer values. We expected to find larger retention values during dry years, notably under summer conditions. Higher retention values during dry years can be intuitively explained by the longer residence—and therefore, reaction—times. However, the trade-off between long residence times in dry years and high fluxes in wet years results in similar annual percentages of nutrient reduction. This does not mean, however, that the filter effect is equivalent between the two conditions. In absolute values, differences are large: during wet years, the retention of N is three-fold that of dry years, the retention of P is twice as high, and the retention of silica is seven-fold the value of dry years. In addition, longer water residence times allow for higher algal growth and higher consumption of nutrients, but if residence times are too long, they also allow for the growth of heterotrophic organisms feeding on alive phytoplankton cells or on detrital algal material and releasing part of the consumed nutrients, which eventually reduces the net nutrient removal percentage during dry periods.

Another important result with regard to the filter effect is the ascertainment that the upper fluvial estuary, and not the TMZ, is responsible for the largest nutrient drops. This was unexpected, as the TMZ plays a very important role in many biogeochemical processes, including the C metabolism (Garnier et al. 2008), and previous efforts had shown that this was an active section of the estuary for the transformation of nutrients. However, the longer residence time of the upstream segment and the better light conditions due to lower turbidity favor primary production processes, nutrient uptake, and subsequent deposition of organic material in the benthic compartment, thus enhancing retention processes. The increasing importance of biological processes in the upper reaches may be related to the progressive amelioration in water quality, which has led to lower organic matter inputs, higher transparency and oxygen concentrations, and a decrease in the nitrification and the heterotrophic mineralization processes that prevailed in the past.

The biological response in marine waters

The reservoir of nutrients that is not retained or removed in the estuary is transferred downstream to the marine section and the nearby bay, where algal blooms may develop intensely. According to Passy et al. (2016), algal blooms within the Seine Bight are generally observed in the plume of the river, just downstream from the TMZ. This is also what we observe in our model simulations, with maximum chlorophyll values concentrated in the outer estuary and the adjacent coastal waters.

The ECO-MARS3D model results also emphasize that dry years are particularly risky in terms of high phytoplankton biomass in marine waters. This may seem paradoxical, because during dry years, riverine nutrient inputs are lower. Higher biomass values, however, can be linked to physical features: under low river discharge, the freshwater plume is confined into a shallower water layer and often within a smaller area of the bay, close to the coastline, where nutrients are concentrated and phytoplankton can thrive, whereas the rapid flush of water during wet years dilutes the plume into a much larger volume.

Besides excessive phytoplankton growth, the occurrence of nondiatoms, often harmful algal blooms (HABs) is a matter of concern in the Seine Bight. HABs can cause severe economic losses in the region, where shellfish farming brings in a substantial income. The main HAB-forming species are paralytic shellfish poisoning Dinophyceae, including *Dinophysis* and *Alexandrium* spp. (Cugier et al. 2005*b*). These species are present throughout the year but tend to form large populations after the diatom spring bloom, when silica is depleted. Our model shows that both diatoms and dinoflagellates reach higher numbers under dry conditions; diatoms spread east and west from the river mouth and occupy a large part of the bay, while dinoflagellates extend along the Normandy coast. Cugier et al. (2005*b*) also found that summer blooms of dinoflagellates were particularly pronounced during dry years; besides plume dispersion and stratification issues, these authors argued that the silica

deficit with regard to N and P was a major cause underpinning their large proliferations. Sustained high values of N after a strong reduction of P may still foster the emergence of nuisance blooms (Passy et al. 2013; Glibert 2017). Romero et al. (2013) reported a general phytoplankton decrease, but an increase in the summer abundance of dinoflagellates within the bay, again largely attributed to the imbalanced N : P : Si molar ratios and the nutrient leftovers.

The N-ICEP and P-ICEP values here calculated at the outlet of the estuary indeed show N fluxes in excess over Si fluxes, but a deficit of P, particularly pronounced during wet years. The stronger limitation of P during wet years may support the lower growth of phytoplankton in the bay at high discharges, especially dinoflagellates. In contrast, the release of P from the sediment in the TMZ during the summer period alleviates the P limitation and balances the ratios (summer P-ICEPs are only slightly negative, and even 0 during the dry year), while N remains in excess (N-ICEPs systematically > 0). This allows disproportionate growth of dinoflagellates vs. diatoms on unconsumed nutrients. P release is therefore crucial, because it may sustain the growth of organisms that would otherwise be limited by P. Moreover, as discussed by Billen and Garnier (2007) and Romero et al. (2013), P remineralization processes in marine waters happen at a fast pace; so provided there is available N (and current N inputs are large throughout the year), blooms can develop even in the presence of apparently low concentrations of P.

Conclusions

The buffer role of the Seine estuary has long been considered as minor, and several studies have even successfully addressed the impact of the river on the adjacent coastal waters bypassing the estuarine transformations (e.g., Lancelot et al. 2007, 2011; Passy et al. 2013). Garnier et al. (2010) provided an estimate on N, P, and Si retention in the TMZ, but an actual quantification of the filtering role for the whole estuary, from Poses down to Le Havre, was missing from the literature. Here, we present for the first time a coupled model of the river–estuary–bay continuum, considering biogeochemical processes in the sediment and the water column and using an updated realistic morphology of the estuarine stretches. The model provides information on the nutrient fluxes per estuarine section, so we could assess what parts of the estuary are the most efficient for nutrient removal. This result can therefore serve as a guide for Seine estuary restoration.

Our results point out that biological activity in the upper part of the estuary largely determines the overall estuarine retention, with an additional retention of nutrients in the most downstream marine section and very little variation in the middle reaches. The model also stresses the importance of hydrological conditions. Low river flows during dry periods allow for longer residence times and favor nutrient

transformations within the estuary, but the resulting N : P : Si ratios and the fact that the plume is later confined into a shallower water layer can lead to a higher risk of coastal eutrophication.

The present study thus delivers a new vision of the complex biogeochemical behavior of the estuary. The modeling tool developed here will be useful in combination with the formulation of future scenarios, with different degrees of human impact on the upstream watershed, to assess how the estuary may respond to forthcoming perturbations.

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Conflict of Interest

None declared

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