1 Dear Editor,

Please find below a point by point answer to the comments provided by reviewer #2. In the following text, the comments of the reviewer are in written back and our answers are written in blue. All the modifications suggested by the reviewer have been carefully implemented into the manuscript. This updated version of the manuscript is available with the 'track changes' option at the end of this file, after our answers. In addition, following the reviewer's first request, the supplementary tables have also been modified and re-uploaded.

- 10 On behalf of all co-authors,
- 11 Goulven Laruelle
- 12

9

- 13 Overall statements
- 14 The revised manuscript "Air-water CO2 evasion from U.S. East Coast estuaries" by Goossens, N.,
- 15 Gildas, L.G., Arndt, S., Wei-Jun, C., Regnier, P. has improved substantially. The authors added several
- 16 sections and additional tables which improved the text. Unfortunately there are still a lot of flaws in
- the manuscript. After correcting these minor bugs I suggest to accept the manuscript for publishingin Biogeosciences.
- 19
- 20 Detailed statements
- 21 There is still some confusion on the number of estuaries (43) handled by the model. Table S2, for
- 22 example, includes 40 estuaries, Table 4 has 42. I know, the problem is that some rivers enter the
- same box. But anyway, this discrepancy in the presentation must be corrected within the entiremanuscript.
- 25 As the reviewer points out, there still were inconsistencies within the text with respect to the total
- 26 number of tidal estuaries simulated by the model. Table 2 is correct and the total number of systems
- 27 is 42. The entire manuscript has been updated accordingly and the supplementary tables (S1-S6)
- have been updated to match the systems reported in table 2.
- 30 In the following the line numbers refer to bg-2016-278-manuscript-version4.pdf.
- 31
- 32 L558 ff and your letter to the reviewer:
- 33 You discuss the outgassing of small and large estuaries saying that the surface area act as a limiting
- factor for gas exchange. Then I would expect smaller gas exchange per surface unit for smallerestuaries.
- 36 For very small estuarine systems (such as those referred to in the discussion about the NAR region),
- 37 the overall surface area in the system available for the exchange between air and water is not
- 38 sufficient to transfer all the oversaturated CO₂ from the estuarine water to the atmosphere. In that
- 39 sense, surface area is a limiting factor to CO₂ outgasing because this physical limitation of the
- 40 available surface for gas exchange hampers the overall amount of CO₂ emitted to the atmosphere
- 41 during its transit through the estuarine filter. The emission rates per surface area however, are high
- 42 compared to other larger estuaries because the magnitude of the pCO₂ gradient at the air-water
- 43 interface is larger in small systems which are largely oversaturated on their entire length compared
- 44 to larger system where most of the outgasing only occurs in the upstream section of the estuary and
- 45 where the average emission rate is distributed over a much larger surface area.
- 46
- 47 L169 NAR Fig. 1; Tab. 4 includes 11 estuaries .. 558 km2
- 48 L174 MAR (Tab. 4) 18 entries .. 9298 km2
- 49 L182 SAR (Tab. 4) 13 entries .. 959 km2

50 The numbers of estuaries per region as well as their associated surface areas have been updated to 51 match the value reported in table 4. In addition, the cumulated surface areas per regions are now 52 also included in table 5. L193 Friedrichs and Hofmann2001 : Reference missing 53 Both this reference and the one mentioned below were in the reference list but the line break 54 55 between them was missing, making the reference look like Fischer, 2001. This has been corrected in the revised manuscript. 56 57 58 L254 Fischer 1976: Reference missing Both this reference and the one mentioned above were in the reference list but the line break 59 between them was missing, making the reference look like Fischer, 2001. This has been corrected in 60 61 the revised manuscript. 62 63 L295 The primary production module does not include nutrients, grazing pressure, turbidity. The 64 only phytoplankton group is diatoms. Please comment on these shortenings. 65 The primary production module used in the model is described in extenso in Volta et al. (2014, 2016) 66 and does take into account nutrients limitations, grazing pressure and the effect of SPM 67 concentrations on water turbidity and, thus the extinction coefficient used to calculate the available 68 light in the water column. The brief description of the primary production module in the present 69 manuscript was only intended to explicit the numerical method used to integrate the light profile in 70 the water column. This short section has now been expended to clarify what processes are included 71 in the calculation of primary production in our model. 72 "The primary production dynamics, which takes into account the combined effects of nutrients 73 limitation and light attenuation in the water column induced by its background turbidity and SPM concentration, requires vertical resolution of the photic depth. The latter is calculated according to 74 the method described in Vanderborght et al. (2007). This method assumes an exponential decrease 75 76 of the light in the water column (Platt et al., 1980), which is solved using a Gamma function." 77 78 It is true however that our model only accounts for one phytoplankton group and that limitation as 79 well as potential future improvements are discussed in the 'Biogeochemical Model' paragraph of 80 section '3.4 Scope of applicability and model limitations'. 81 "Although the reaction network of C-GEM accounts for all processes that control estuarine FCO₂ 82 (Borges and Abril, 2012; Cai, 2011), several, potentially important processes, such as benthic-pelagic 83 exchange processes, phosphorous sorption/desorption and mineral precipitation, a more complex representation of the local phytoplankton community, grazing by higher trophic levels, or multiple 84 85 reactive organic carbon pools are not included. Although these processes are difficult to constrain 86 and their importance for FCO₂ is uncertain, the lack of their explicit representations induces 87 uncertainties in Cfilt." 88 89 L312 World Ocean Atlas, 2009: Reference missing 90 The data from the world ocean Atlas come from Antonov et al., 2010 and Locarini et al., 2010 for the 91 temperature and salinity, respectively. This has been clarified in the manuscript: 92 "Transient physical forcings are calculated for each season and grid cell using monthly mean values 93 of water temperature (World Ocean Atlas: Antonov et al. 2010; Locarini et al., 2010) ... " 94

95 L467 UNH/GRDC Database: give a reference

- 96 The following reference was added for the UNH/GRDC Database:
- 97 <u>"GRDC: Global Freshwater Fluxes into the World Oceans / Online provided by Global Runoff Data</u>
 98 <u>Centre. 2014 ed. Koblenz: Federal Institute of Hydrology (BfG), 2014."</u>
- 99
- 100 L468 Fekete et al 2000: Reference missing

101 The Fekete et al 2000 reference was removed and replaced by GRDC (2014) to refer to the 102 UNH/GRDC Database (see comment above). 103 104 L473 is it July 2003 or July 2013? Compare L487 The validation performed for the Delaware Bay relies on a pH longitudinal profile and boundary 105 106 conditions all sampled in 2003 (Sharp et al., 2009; Sharp, 2010) as stated in the manuscript. 107 However, for comparison's sake, a reference is also made to the recent work of Joesoef et al. (2015) 108 when discussing the pCO_2 profile because this study reports pCO_2 measurements performed in the 109 same estuary during the same month (July) but another year (2013). The fact that Joesoef et al. 110 (2015)'s data were not sampled the same year as the one simulated by the model was already mentioned in the text, but the following sentences have been modified to make this fact clearer and 111 112 avoid potential confusion: 113 "Overall, the longitudinal pCO2 profile of the Delaware estuary is characterized by values close to 114 equilibrium with the atmosphere in the widest section of the Delaware Bay (close to the estuarine 115 mouth and throughout the 40 first kilometers of the system) and values above 1200 µatm at kilometer 150 and beyond, where characteristic salinities are below 5. Although the profile 116 117 presented here is simulated using boundary conditions representative of July 2003 and no pCO₂ 118 data were available for validation for this period, a recent study by Joesoef et al. (2015) reports a 119 similar longitudinal pCO₂ profile in July 2013." 120 121 L481 I think you exchanged the display of pH upstream and downstream in the tables, as they do not 122 fit to Fig. 7 123 There was indeed in mistake in table S6 displaying the pH values used at the downstream boundary 124 condition, which are calculated from DIC and Alkalinity assuming CO₂ equilibrium between coastal 125 waters and the atmosphere (see section 2.4.4 of the manuscript). Table S6 was updated with the 126 proper values. Table S5, which provides the upstream boundary conditions, was correct however. 127 128 L490 Compare pCO2 along the salinity gradient, or change text here. 129 Panel c of figure 7 reports simulated pCO₂ values for the Delaware estuary against the distance from 130 the mouth of the system. When discussing this profile, we now refer the distance from the estuarine 131 mouth rather than to salinity to identify the different sections of the estuary: 132 "Overall, the longitudinal pCO2 profile of the Delaware estuary is characterized by values close to 133 equilibrium with the atmosphere in the widest section of the Delaware Bay (*near* the estuarine 134 mouth and throughout the 40 first kilometers of the system) and values above 1200 µatm at 135 kilometer 150 and beyond, where characteristic salinities are below 5." 136 137 L500 "Although ..." Improve grammar. 138 The sentence was rewritten as: 139 "Although *significant* discrepancies *are observed* at the level of individual systems, the model 140 captures remarkably well the overall behaviors of estuaries along the East coast of the US in term 141 of intensity of CO2 evasion rate." 142 143 L501 is it really a trend? 144 The use of the word tend was not really adequate in this sentence and it was removed in the 145 updated manuscript (see comment above). 146 L502 I see only 6 systems 147 148 If Florida Bay is removed from table 2, as suggested by the reviewer in his third to last comment, 149 there indeed will be only 6 systems with observed emission rates $< 5 \text{ mol C} \text{ m}^{-2} \text{ yr}^{-1}$. 150 151 L503 I see only 5 systems

152	Indeed, the reviewer is correct; there are only 5 systems with observed emission rates > 10 mol C m ⁻
153	² yr ⁻¹ . The sentence was corrected in the manuscript.
154	"The model simulates low CO ₂ efflux (< 5 mol C m ⁻² yr ⁻¹) for the 6 systems were such conditions have
155	been observed, while the <u>5</u> systems for which the CO_2 evasion exceeds 10 mol C m ⁻² yr ⁻¹ are the
156	same in the observations and in the model runs."
157	
158	L507 "local observations"
159	Corrected
160	
161	L544 "B0"
162	Corrected
163	Conceled
164	1468 Savanija 2000: Poforanco missing
165	L468 Savenije 2000: Reference missing The reference was intended to be Savenije (2005), which is in the reference list. This mistake was
166	corrected in the updated manuscript.
167	"A larger ratio of estuarine width <u>BO</u> and convergence length b corresponds to a more funnel shaped
168	estuary while a low ratio corresponds to a more prismatic geometry (Savenije, <u>2005</u> ; Volta et al.,
169	2014)."
170	
171	L564 "2013b"
172	Corrected
173	
174	L567 Zeebe and Wolf-Gladrow 2001: Reference missing
175	The reference has been added to the reference list:
176	<u> "Zeebe, R. E. and Wolf-Gladrow, D. (Eds.): CO2 in seawater: equilibrium, kinetics, isotopes,</u>
177	<u>Elsevier, Amsterdam, 2001."</u>
178	
179	L717 "discuss"
180	Corrected
181	
182	L721 "watersheds"
183	Corrected
184	
185	L723 "contained by" -> "covered by"
186	Corrected
187	
188	L730 (b, B0, H)
189	Corrected
190	
191	L772 omit "is"
192	Corrected
193	
194	L789 Antonov et al., 2014: Reference missing
195	Although the database has been updated in 2014, the recommended reference is Antonov et al.,
195	2010, which is in our reference list. The text was updated accordingly:
190	"At the lower boundary condition, direct observations for nutrients and oxygen are extracted from
197	databases such as the World Ocean Atlas (Antonov et al., <u>2010</u>)."
	ualabases such as the world ocean Atlas (Antonov et di., 2010).
199	1902 "Chlorophyll a"
200	L802 "Chlorophyll-a"
201	Corrected
202	

203	L802 omit "and" -> "For DIC and alkalinity boundary conditions"
204	Corrected
205	
206	L804 "are extracted"
207	Corrected
208	
209	L812-815 Improve grammar.
210	The sentence was rewritten as:
211	"The generic nature of the applied model approach <u>renders a direct validation of model results on</u>
212 213	<u>the basis of local and instantaneous observational data (e.g. longitudinal profiles) difficult.</u> In particular the applications of seasonally/annually averaged or model-deduced boundary conditions,
215 214	which are likely not representative of these long-term average conditions, <i>do not lend themselves</i>
214 215	which are likely not representative of these long-term average conditions, <i>do not rend themselves</i> well to comparison with punctual measurements."
215	wen to comparison with punctual measurements.
217	L841 Mayer and Eyre, 2012: Reference missing
218	The proper citation was Maher and Eyre, 2012. This typo was corrected in the manuscript and
219	Maher and Eyre (2012) is in the reference list.
220	
221	L897 "suggests"
222	Corrected
223	
224	L967 Abril 2002 does not fit to L39
225 226	Abril (2002) is not cited in L39, Borges and Abril (2012) is.
227	L998 Billen et al: Not called
228	The reference above was removed from the reference list.
229	
230	L1062 Hartmann 2012 does not fit to L165
231	Hartmann (2012) is not cited in L165, Hartmann et al. (2009) is.
232	
233	L1176 Paerl et al: Not called
234	L1262 Thieu et al: Not called
235	L1282 Van der Burgh: Not called
236	The three references above were removed from the reference list.
237	
238	L1306 Tab. 2 omit Florida Bay as this was not modeled.
239	Florida Bay has been removed from table 2 and the corresponding reference (Dufore et al., 2012)
240	has been removed from the reference list.
241	14252 la tha taut usu diasus Fig. 7h as Delauses (1400)
242	L1353 In the text you discuss Fig. 7b as Delaware (L486).
243	This is indeed a mistake, the pCO_2 profile for the Delaware estuary is represented in panel c. The text has been updated accordingly.
244 245	"Both processes lead to a well-developed pCO_2 increase in this area (Fig. <u>Zc</u>)."
245 246	Both processes lead to a well-developed pcO_2 increase in this area (Fig. $\underline{\mathcal{R}}$).
240 247	L1378 –FCO2 should be also at the y-axis
248	The caption is wrong and not the axis. Instead of referring to NEM and $-FCO_2$, the caption should
249	refer to $-NEM$ and FCO ₂ . It has been updated accordingly in the manuscript.
250	"Panels b, d and e represent <u>-NEM, FCO</u> 2 and CFilt, respectively. Panels a and c represent <u>-NEM,</u>
251	FCO ₂ normalized by a temperature Q10 function."
252	
253	

254	Air-water CO_2 evasion from U.S. East Coast estuaries
255	Goossens, Nicolas ¹ , Laruelle, Goulven Gildas ^{1*} , Arndt, Sandra ² , Cai, Wei-Jun ³ & Regnier, Pierre ¹
256	
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263	
264	

265 Abstract:

266 This study presents the first regional-scale assessment of estuarine CO₂ evasion along the East coast 267 of the US (25 - 45 °N). The focus is on <u>42</u> tidal estuaries, which together drain a catchment of 268 697000 km² or 76 % of the total area within this latitudinal band. The approach is based on the Carbon - Generic Estuarine Model (C-GEM) that allows simulating hydrodynamics, transport and 269 270 biogeochemistry for a wide range of estuarine systems using readily available geometric parameters 271 and global databases of seasonal climatic, hydraulic, and riverine biogeochemical information. Our 272 simulations, performed using conditions representative of the year 2000, suggest that, together, US East coast estuaries emit 1.9 TgC yr $^{-1}$ in the form of CO $_{2},$ which correspond to about 40 % of the 273 274 carbon inputs from rivers, marshes and mangroves. Carbon removal within estuaries results from a 275 combination of physical (outgassing of supersaturated riverine waters) and biogeochemical 276 processes (net heterotrophy and nitrification). The CO₂ evasion and its underlying drivers show 277 important variations across individual systems, but reveal a clear latitudinal pattern characterized by 278 a decrease in the relative importance of physical over biogeochemical processes along a North-South 279 gradient. Finally, the results reveal that the ratio of estuarine surface area to the river discharge, S/Q 280 (which has a scale of per meter discharged water per year), could be used as a predictor of the 281 estuarine carbon processing in future regional and global scale assessments.

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283 1 Introduction

284 Carbon fluxes along the land-ocean aquatic continuum are currently receiving increasing attention 285 because of their recently recognized role in the global carbon cycle and anthropogenic CO₂ budget 286 (Bauer et al., 2013; Regnier et al., 2013a; LeQuéré et al., 2014, 2015). Estuaries are important 287 reactive conduits along this continuum, which links the terrestrial and marine global carbon cycles 288 (Cai, 2011). Large amounts of terrestrial carbon transit through these systems, where they mix with 289 carbon from autochthonous, as well as marine sources. During estuarine transit, heterotrophic 290 processes degrade a fraction of the allochthonous and autochthonous organic carbon inputs, 291 supporting a potentially significant, yet poorly quantified CO₂ evasion flux to the atmosphere. Recent 292 estimates suggest that 0.15-0.25 PgC yr⁻¹ is emitted from estuarine systems worldwide (Borges and 293 Abril, 2012; Cai, 2011; Laruelle et al., 2010; Regnier et al., 2013a; Laruelle et al., 2013, Bauer et al., 294 2013). Thus, in absolute terms the global estuarine CO_2 evasion corresponds to about 15% of the 295 open ocean CO₂ uptake despite the much smaller total surface area.

296 Currently, estimates of regional and global estuarine CO₂ emissions are mainly derived on the basis 297 of data-driven approaches that rely on the extrapolation of a small number of local measurements 298 (Cai, 2011; Chen et al., 2013; Laruelle et al., 2013). These approaches fail to capture the spatial and 299 temporal heterogeneity of the estuarine environment (Bauer et al., 2013) and are biased towards 300 anthropogenically influenced estuarine systems located in industrialized countries (Regnier et al., 301 2013a). Even in the best surveyed regions of the world (e.g. Australia, Western Europe, North 302 America or China) observations are merely available for a small number of estuarine systems. In 303 addition, if available, data sets are generally of low spatial and temporal resolution. As a 304 consequence, data-driven approaches can only provide first-order estimates of regional and global 305 estuarine CO₂ emissions.

306 Integrated model-data approaches can help here, as models provide the means to extrapolate over 307 temporal and spatial scales and allow disentangling the complex and very dynamic network of 308 physical and biogeochemical processes that controls estuarine CO2 emissions. Over the past 309 decades, increasingly complex process-based models have been applied, in combination with local 310 data, to elucidate the coupled carbon-nutrient cycles on the scale of individual estuaries (e.g., 311 O'Kane, 1980; Soetaert and Herman, 1995; Vanderborght et al., 2002; Lin et al., 2007; Arndt et al., 312 2009; Cerco et al., 2010; Baklouti et al., 2011). However, the application of such model approaches 313 remains limited to the local scale due to their high data requirements for calibration and validation 314 (e.g. bathymetric and geometric information and boundary conditions), as well as the high 315 computational demand associated with resolving the complex interplay of physical and 316 biogeochemical processes on the relevant temporal and spatial scales (Regnier et al., 2013b). 317 Complex process-based models are thus not suitable for the application on a regional or global scale 318 and, as a consequence, the estuarine carbon filter is, despite its increasingly recognized role in 319 regional and global carbon cycling (e.g. Bauer et al., 2013), typically not taken into account in model-320 derived regional or global carbon budgets (Bauer et al., 2013). The lack of regional and global model 321 approaches that could be used as stand-alone applications or that could be coupled to regional 322 terrestrial river network models (e.g. GLOBALNEWS: Seitzinger et al., 2005; Mayorga et al., 2010; 323 SPARROW: Schwarz et al., 2006) and continental shelf models (e.g. Hofmann et al., 2011) is thus 324 critical.

325 The Carbon-Generic Estuary Model (C-GEM (v1.0); Volta et al., 2014) has been developed with the 326 aim of providing such a regional/global modeling tool that can help improve existing, observationally 327 derived first order estimates of estuarine CO₂ emissions. C-GEM (v1.0) has been specifically designed 328 to reduce data requirements and computational demand and, thus, tackles the main impediments 329 for the application of estuarine models on a regional or global scale. The approach takes advantage 330 of the mutual dependency between estuarine geometry and hydrodynamics in alluvial estuaries and uses an idealized representation of the estuarine geometry to support the hydrodynamic 331 332 calculations. It thus allows running steady state or fully transient annual to multi-decadal simulations 333 for a large number of estuarine systems, using geometric information readily available through maps

334 or remote sensing images. Although the development of such a regional/global tool inevitably 335 requires simplification, careful model evaluations have shown that, despite the geometric 336 simplification, C-GEM provides an accurate description of the hydrodynamics, transport and 337 biogeochemistry in tidal estuaries (Volta et al., 2014). In addition, the model approach was 338 successfully used to quantify the contribution of different biogeochemical processes for CO₂ air-339 water fluxes in an idealized, funnel-shaped estuary forced by typical summer conditions 340 characterizing a temperate Western European climate (Regnier et al., 2013b). Volta et al. (2016b) 341 further investigated the effect of estuarine geometry on the CO₂ outgassing using three idealized 342 systems and subsequently established the first regional carbon budget for estuaries surrounding the 343 North Sea by explicitly simulating the six largest systems of the area (Volta et al., 2016a), including 344 the Scheldt and the Elbe for which detailed validation was performed.

345 Here, we extend the domain of application of C-GEM (v1.0) to quantify CO_2 exchange fluxes, as well 346 as the overall organic and inorganic carbon budgets for the full suite of estuarine systems located 347 along the entire East coast of the United States, one of the most intensively monitored regions in the 348 world. A unique set of regional data, including partial pressure of CO_2 in riverine and continental 349 shelf waters (pCO₂; Signorini et al., 2013; Laruelle et al., 2015), riverine biogeochemical 350 characteristics (Lauerwald et al., 2013), estuarine eutrophication status (Bricker et al., 2007) and 351 estuarine morphology (NOAA, 1985) are available. These comprehensive data sets are 352 complemented by local observations of carbon cycling and CO_2 fluxes in selected, individual 353 estuarine systems (see Laruelle et al., 2013 for a review), making the East coast of the United States 354 an ideal region for a first, fully explicit regional evaluation of CO₂ evasion resolving every major tidal 355 estuary along the selected coastal segment. The scale addressed in the present study is 356 unprecedented so far (> 3000 km of coastline) and covers a wide range of estuarine morphological 357 features, climatic conditions, land-use and land cover types, as well as urbanization levels. The 358 presented study will not only allow a further evaluation of C-GEM (v1.0), but will also provide the 359 first regional-scale assessment of estuarine CO_2 evasion along the East coast of the US (25 – 45 °N)

and will help explore general relationships between carbon cycling and CO₂ evasion, and readily
 available estuarine geometrical parameters.

362 After a description of the model itself and of the dataset used to set up the simulations, a local 363 validation is presented which includes salinity, pCO₂ and pH longitudinal profiles for two well 364 monitored systems (the Delaware Bay and the Altamaha River Estuary). The yearly averaged rates of 365 CO₂ exchange at the air-water interface simulated by the model for 13 individual estuaries are also 366 compared with observed values reported in the literature. Next, regional scale simulations for 42 367 tidal estuaries of the eastern US coast provide seasonal and yearly integrated estimates of the Net 368 Ecosystem Metabolism (NEM), CO₂ evasion and carbon filtering capacity, CFilt. Model results are 369 then used to elucidate the estuarine biogeochemical behavior along the latitudinal transect 370 encompassed by the present study (30-45° N). Finally, our results are used to derive general 371 relationships between carbon cycling and CO₂ evasion, and readily available estuarine geometrical 372 parameters.

373

374 2. Regional description and model approach

375 **2.1 Observation-based carbon budget for the East coast of the United States**

376 The study area covers the Atlantic coast of the United States (Fig.1), from the southern tip of Florida 377 (25°N) to Cobscook Bay (45°N) at the US-Canada boundary. This area encompasses distinct climatic 378 zones and land cover types and exhibits a variety of morphologic features (Fig. 1). The region can be 379 subdivided into several sub-regions following a latitudinal gradient (Signorini et al., 2013). In this 380 study, we define three sub-regions following the boundaries suggested by the COSCAT segmentation 381 (Meybeck et al., 2006; Laruelle et al., 2013) and the further subdivision described in Laruelle et al. 382 (2015). From North to South, the regions are called North Atlantic, Mid Atlantic and South Atlantic 383 Regions (Fig. 1). Total carbon inputs from watersheds to US East coast estuaries (Tab. 1) have been Deleted: 3

estimated to range from 4.0 to 10.7 Tg C yr⁻¹ (Mayorga et al., 2010; Shih et al., 2010; Stets and Strieg, 2012; Tian et al., 2010; Tian et al., 2012), consisting of dissolved organic carbon (DOC; ~50%), dissolved inorganic carbon (DIC; ~40%) and particulate organic carbon (POC; ~10%). In addition, a statistical approach has been applied to estuaries of the region to quantify organic carbon budgets and Net Ecosystem Productivity (NEP) using empirical models (Herrmann et al., 2015).

390 Recent studies estimated that, along the East coast of the United States, rivers emit 11.4 TgC yr⁻¹ of 391 CO2 to the atmosphere (Raymond et al., 2013), while continental shelf waters absorb between 3.4 392 and 5.4 TgC yr⁻¹ of CO₂ from the atmosphere (Signorini et al., 2013). A total of thirteen local, annual 393 mean estuarine CO₂ flux estimates across the air-water interface based on measurements are also 394 reported in the literature and are grouped along a latitudinal gradient (Tab. 2). Four of these 395 estimates are located in the South Atlantic region (SAR): Sapelo Sound, Doboy Sound, Altamaha 396 Sound (Jiang et al., 2008), and the Satilla River estuary (Cai and Wang, 1998). Three studies 397 investigate CO₂ fluxes in the mid-Atlantic Region (MAR): the York River Estuary (Raymond et al., 398 2000) and the Hudson River (Raymond et al., 1997). There is also a comprehensive CO₂ flux study for 399 the Delaware Estuary published after the completion of this work (Joeseof et al., 2015). Six systems 400 are located in the North Atlantic region (NAR): The Great Bay, the Little Bay, the Oyster estuary, the 401 Bellamy estuary, the Cocheco estuary (Hunt et al., 2010; 2011), and the Parker River estuary 402 (Raymond and Hopkinson, 2003). The mean annual flux per unit area from these local studies is 11.7 \pm 13.1 mol C m⁻² yr⁻¹ and its extrapolation to the total estuarine surface leads to a regional CO₂ 403 404 evasion estimate of 3.8 Tg C y^{-1} . This estimate is in line with that of Laruelle et al. (2013) for the same region which proposes an average CO₂ emission rate of 10.8 mol C m⁻² yr⁻¹. Thus, CO₂ outgassing 405 406 could remove 35% to 95% of the riverine carbon loads during estuarine transit. About 75 % of the air-water exchange occurs in tidal estuaries (2.8 Tg C γ^{-1}) while lagoons and small deltas contribute to 407 408 the remaining 25 %. Although these simple extrapolations from limited observational data are 409 associated with large uncertainties, they highlight the potentially significant contribution of estuaries 410 to the CO₂ outgassing in the region. However, process-based quantifications of regional organic and 411 inorganic C budgets including air-water CO₂ fluxes for the estuarine systems along the East coast are
412 not available.

413 2.2 Selection of estuaries

414 The National Estuarine Eutrophication Assessment (NEAA) survey (Bricker et al., 2007), which uses 415 geospatial data from the National Oceanic and Atmospheric Administration (NOAA) Coastal Assessment Framework (CAF) (NOAA, 1985), was used to identify and characterize 58 estuarine 416 417 systems discharging along the Atlantic coast of the United States. From this set, <u>42</u> 'tidal' estuaries, 418 defined as a river stretch of water that is tidally influenced (Dürr et al., 2011), were retained (Fig. 1) 419 to be simulated by the C-GEM model, which is designed to represent such systems. Using outputs 420 from terrestrial models (Hartmann et al., 2009; Mayorga et al., 2010), the cumulated riverine carbon 421 loads for all the non-tidal estuaries that are excluded from the present study amount to 0.9 Tg C yr¹, which represents less than 15% of the total riverine carbon loads of the region. These 16 systems are 422 423 located in the SAR (10) and in the MAR (6).

The northeastern part of the domain (NAR, Fig. 1; Tab. 1) includes <u>11</u> estuaries along the Gulf of Maine and the Scotian shelf, covering a cumulative surface area of <u>558</u> km². It includes drowned valleys, rocky shores and a few tidal marshes. The climate is relatively cold (annual mean= 8°C) and the human influence is relatively limited because of low population density and low freshwater inputs. The mean estuarine water depth is 12.9 m and the mean tidal range is 2.8 m.

The central zone (MAR) includes <u>18 tidal estuaries accounting for a total surface area of <u>9298 km²</u>. The Chesapeake Bay and the Delaware estuaries alone contribute more than 60% to the surface area of the region. In this region, estuaries are drowned valleys with comparatively high river discharge and intense exchange with the ocean. Several coastal lagoons, characterized by a limited exchange with the ocean are located here, but are not included in our analysis. The Mid-Atlantic Region (MAR) is characterized by a mean annual temperature of 13°C and is strongly impacted by human activities,</u> Deleted: 43

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due to the presence of several large cities (e.g. New York, Washington, Philadelphia, Baltimore) and
intense agriculture. The mean water depth is about 4.7 m and the tidal range is 0.8 m.

The southern Atlantic region (SAR) includes <u>13 tidal estuaries covering a total surface area of <u>959</u> km². These systems are generally dendritic and surrounded by extensive salt marshes. The climate is subtropical with an average annual temperature of 19°C. Land use includes agriculture and industry, but the population density is generally low. Estuarine systems in the SAR are characterized by a shallow mean water depth of 2.9 m and a tidal range of 1.2 m.</u>

449 2.3 Model set-up

450 The generic 1D Reactive-Transport Model (RTM) C-GEM (Volta et al., 2014) is used to quantify the 451 estuarine carbon cycling in the <u>42</u> systems considered in this study. The approach is based on 452 idealized geometries (Savenije, 2005; Volta et al., 2014) and is designed for regional and global scale applications (Regnier et al., 2013b; Volta et al., 2014, 2016a). The model approach builds on the 453 premise that hydrodynamics exerts a first-order control on estuarine biogeochemistry (Arndt et al., 454 455 2007; Friedrichs and Hofmann, 2001) and CO₂ fluxes (Regnier et al., 2013a). The method takes 456 advantage of the mutual dependence between geometry and hydrodynamics in tidal estuaries 457 (Savenije, 1992) and the fact that, as a consequence, transport and mixing can be easily quantified from readily available geometric data (Regnier et al., 2013a; Savenije, 2005; Volta et al., 2016b). 458

459 **2.3.1 Description of idealized geometries for tidally-averaged conditions**

Although tidal estuaries display a wide variety of shapes, they nevertheless share common geometric characteristics that are compatible with an idealized representation (Fig. 2, Savenije, 1986; Savenije, 2005). For tidally-averaged conditions, their width B (or cross-sectional area A) can be described by an exponential decrease as a function of distance, *x*, from the mouth (Savenije, 1986; Savenije, 2005): **Deleted:** 10 **Deleted:** 12182

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$$B = B0 * \exp\left(-\frac{x}{b}\right) \tag{1}$$

where B (m) is the tidally averaged width, B0 (m) the width at the mouth, x (m) the distance from the mouth (x=0) and b (m) the width convergence length (Fig. 2). The width convergence length, b, is defined as the distance between the mouth and the point at which the width is reduced to B0 e⁻¹. It is directly related to the dominant hydrodynamic forcing. A high river discharge typically results in a prismatic channel with long convergence length (river dominated estuary), while a large tidal range results in a funnel-shaped estuary with short convergence length (marine dominated estuary). At the upstream boundary, the estuarine width is given by:

$$B_L = B0 * \exp\left(-\frac{L}{b}\right) \tag{2}$$

475 Where L denotes the total estuarine length (m) along the estuarine longitudinal axis.

The total estuarine surface S (m²) can be estimated by integrating equation (1) over the estuarine
length:

$$S = \int_{0}^{L} B \, dx = b * B0 * \left(1 - \exp\left(-\frac{L}{b}\right) \right)$$
(3)

478

479 The width convergence length is then calculated from B0, B_L , L and the real estuarine surface area 480 (SR) by inserting equation (2) in equation (3):

$$b = \frac{SR}{B0 - BL} \tag{4}$$

SR is calculated for each system using the SRTM water body data (Fig. 3a), a geographical dataset encoding high-resolution worldwide coastal outlines in a vector format (NASA/NGA, 2003). While such a database exists for a well monitored region such as the East coast of the US, resorting to using the idealized estuarine surface area (S) is necessary in many other regions. The longitudinal

485 mean, tidally averaged, depth h (m), is obtained from the National Estuarine Eutrophication
486 Assessment database (Bricker et al., 2007).

Using this idealized representation, the estuarine geometry can be defined by a limited number of parameters: the width at the mouth (B₀), the estuarine length (L), the estuarine width at the upstream limit (B₁) and the mean depth h. These parameters can be easily determined from local maps or Google Earth using Geographic Information Systems (GIS) or obtained from databases (NASA/NGA, 2003).

492 2.3.2 Hydrodynamics, transport and biogeochemistry

493 Estuarine hydrodynamics are described by the one-dimensional barotropic, cross-sectionally
494 integrated mass and momentum conservation equations for a channel with arbitrary geometry
495 (Nihoul and Ronday, 1976; Regnier et al., 1998; Regnier and Steefel, 1999):

496
$$r_s \frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = 0$$
 (5)

497
$$\frac{\partial U}{\partial t} + U \frac{\partial U}{\partial x} = -g \frac{\partial \zeta}{\partial x} - g \frac{U|U|}{C_z^2 H}$$
(6)

498 where:

499	t	time	[s]
500	x	distance along the longitudinal axis	[m]
501	A	cross-section area $A = H \cdot B$	[m ²]
502	Q	cross-sectional discharge $Q = A \cdot U$	[m ³ s ⁻¹]
503	U	flow velocity Q/A	[m s ⁻¹]
504	r _s	storage ratio $r_s = B_s / B$	[-]

505	B _s	storage width	[m]
506	g	gravitational acceleration	[m s ⁻²]
507	ξ	elevation	[m]
508	Н	total water depth $H = h + \xi(x,t)$	[m]
509	Cz	Chézy coefficient	[m ^{1/2} s ⁻¹]

510 The coupled partial differential equations (Eqs. (5) and (6)) are solved by specifying the elevation

511 $\xi_0(t)$ at the estuarine mouth and the river discharge $Q_r(t)$ at the upstream limit of the model domain.

512 The one-dimensional, tidally-resolved, advection-dispersion equation for a constituent of

513 concentration *C*(*x*,*t*) in an estuary can be written as (e.g. Pritchard, 1958):

514
$$\frac{\partial C}{\partial t} + \frac{Q}{A}\frac{\partial C}{\partial x} = \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + P \tag{7}$$

515 where Q(x,t) and A(x,t) denote the cross-sectional discharge and area, respectively and are provided 516 by the hydrodynamic model (eq. 5 and 6). P(x,t) is the sum of all production and consumption 517 process rates affection the concentration of the constituent. The effective dispersion coefficient D 518 (m² s⁻¹) implicitly accounts for dispersion mechanisms associated to sub-grid scale processes (Fischer, 519 1976; Regnier et al., 1998). In general, D is maximal near the sea, decreases upstream and becomes 520 virtually zero near the tail of the salt intrusion curve (Preddy, 1954; Kent, 1958; Ippen and Harleman, 521 1961; Stigter and Siemons, 1967). The effective dispersion at the estuarine mouth can be quantified 522 by the following relation (Savenije, 1986):

523
$$D_0 = 26 \cdot (h_0)^{1.5} \cdot (N \cdot g)^{0.5}$$
(8)

where h_0 (m) is the tidally-averaged water depth at the estuarine mouth and *N* is the dimensionless Canter Cremers' estuary number defined as the ratio of the freshwater entering the estuary during a 526 tidal cycle to the volume of salt water entering the estuary over a tidal cycle (Simmons, 1955).

$$527 \qquad N = \frac{Q_b \cdot T}{P} \tag{9}$$

In this equation, Q_b is the bankfull discharge (m³ s⁻¹), T is the tidal period (s) and P is the tidal prism
(m³). For each estuary, N can thus be calculated directly from the hydrodynamic model. The
variation in *D* along the estuarine gradient can be described by Van der Burgh's equation (Savenije,
1986):

532
$$\frac{\partial D}{\partial x} = -K \frac{Q_r}{A} \tag{10}$$

where *K* is the dimensionless Van der Burgh's coefficient and the minus sign indicates that *D* increases in downstream direction (Savenije, 2012). The Van der Burgh's coefficient is a shape factor that has values between 0 and 1 (Savenije, 2012), and is a function of estuarine geometry for tidally average conditions. Therefore, each estuarine system has its own characteristic *K* value, which correlates with geometric and hydraulic scales (Savenije, 2005). Based on a regression analysis covering a set of 15 estuaries, it has been proposed to constrain *K* from the estuarine geometry (Savenije, 1992):

540
$$K = 4.32 \cdot \frac{h_0^{0.36}}{B_0^{0.21} \cdot b^{0.14}} \quad \text{with} \quad 0 < K < 1 \tag{11}$$

Reaction processes *P* considered in C-GEM comprise aerobic degradation, denitrification, nitrification, primary production, phytoplankton mortality and air-water gas exchange for O_2 and CO_2 (Fig. 4 and Tab. 3). These processes and their mathematical formulation are described in detail in Volta et al. (2014) and Volta et al. (2016a).

The non-linear partial differential equations for the hydrodynamics are solved by a finite difference scheme following the approach of (Regnier et al., 1997; Regnier and Steefel, 1999) and (Vanderborght et al., 2002). The timestep Δt is 150s and the grid size Δx is constant along the 548 longitudinal axis of the estuary. The grid size default value is 2000 m, but can be smaller for short 549 length estuaries to guarantee a minimum of 20 grid points within the computational domain. 550 Transport and reaction terms are solved in sequence within a single timestep using an operator 551 splitting approach (Regnier et al., 1997). The advection term in the transport equation is integrated 552 using a third-order accurate total variation diminishing (TVD) algorithm with flux limiters (Regnier et 553 al., 1998), ensuring monotonicity (Leonard, 1984), while a semi-implicit Crank-Nicholson algorithm is 554 used for the dispersion term (Press et al., 1992). These schemes have been extensively tested using 555 the CONTRASTE estuarine model (e.g. Regnier et al., 1998; Regnier and Steefel, 1999; Vanderborght 556 et al., 2002) and guarantee mass conservation to within <1%. The reaction network (including 557 erosion-deposition terms when the constituent is a solid species), is numerically integrated using the 558 Euler method (Press et al., 1992). The primary production dynamics, which takes into account the 559 combined effects of nutrients limitation and light attenuation in the water column induced by its 560 background turbidity and SPM concentration, requires vertical resolution of the photic depth. The 561 latter is calculated according to the method described in Vanderborght et al. (2007). This method 562 assumes an exponential decrease of the light in the water column (Platt et al., 1980), which is solved 563 using a Gamma function.

564 **2.4 Boundary and forcing conditions**

Boundary and forcing conditions are extracted from global databases and global model outputs that are available at 0.5° resolution. Therefore, C-GEM simulations are performed at the same resolution according to the following procedure. First, <u>42</u> coastal cells corresponding to tidal estuaries are identified in the studied area (Fig. 1). If the mouth of an estuary is spread over several 0.5° grid cells, those cells are regrouped in order to represent a single estuary (e.g. Delaware estuary), and subsequently, a single idealized geometry is defined as described above. The model outputs (Hartmann et al. , 2009; Mayorga et al., 2010) and databases (Antonov et al., 2010; Garcia et al., Deleted: , Deleted: is

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575 2010a; Garcia et al., 2010b) used to constrain our boundary conditions are representative of the576 year 2000.

For each resulting cell, boundary and forcing conditions are calculated for the following periods:
January-March; April-June; July-September and October-December. This allows for an explicit
representation of the seasonal variability in the simulations.

580 2.4.1 External forcings

Transient physical forcings are calculated for each season and grid cell using monthly mean values of water temperature (World Ocean Atlas: Antonov et al. 2010; Locarini et al., 2010) and seasonal averaged values for wind speed (Cross-Calibrated-Multi-Platform (CCMP) Ocean Surface Wind Vector Analyses project (Atlas et al., 2011)). Mean daily solar radiation and photoperiods (corrected for cloud coverage using the ISCCP Cloud Data Products, Rossow and Schiffer, 1999) are calculated depending on latitude and day of the year using a simple model (Brock, 1981).

587 2.4.2 Riverine discharge, concentrations and fluxes

588 River discharges are extracted from the UNH/GRDC runoff dataset (Fekete et al., 2002). These 589 discharges represent long-term averages (1960-1990) of monthly and annual runoff at 0.5 degree 590 resolution. The dataset is a composite of long-term gauging data, which provides average runoff for 591 the largest river basins, and a climate driven water balance model (Fekete et al., 2002). Total runoff 592 values are then aggregated for each watershed at the coarser 0.5 degree resolution (Fig. 3b). Next, seasonal mean values (in m³ s⁻¹) are derived in order to account for the intra-annual variability in 593 594 water fluxes. Based on annual carbon and nutrients inputs from the watersheds (Mg y^{-1}), mean annual concentrations (mmol m⁻³) are estimated for each watershed using the UNH/GRDC annual 595 runoff (km³ y⁻¹). Mean seasonal concentrations are then calculated from the seasonally resolved 596 597 river water fluxes of a given sub-region.

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599 Annual inputs of dissolved organic carbon (DOC), particulate organic carbon (POC) and inorganic 600 nutrients are derived from the globalNEWS2 model (Mayorga et al., 2010). Global NEWS is a spatially 601 explicit, multi-element (N, P, Si, C) and multi-form global model of nutrient exports by rivers. In a 602 nutshell, DOC exports are a function of runoff, wetland area, and consumptive water use (Harrison 603 et al., 2005). No distinction is made between agricultural and natural landscapes, since they appear 604 to have similar DOC export coefficients (Harrison et al., 2005). Sewage inputs of OC are ignored in 605 GlobalNEWS, because their inclusion did not improve model fit to data (Harrison et al., 2005). POC 606 exports from watersheds are estimated using an empirical relationship with Suspended Particulate 607 Matter (SPM; Ludwig et al., 1996). Inorganic nitrogen (DIN) and phosphorus (DIP) fluxes calculated 608 by GlobalNEWS depend on agriculture and tropical forest coverage, fertilizer application, animal 609 grazing, sewage input, atmospheric N deposition and biological N fixation (Mayorga et al., 2010). The 610 inputs of dissolved silica (DSi) are controlled by soil bulk density, precipitation, slope, and presence 611 of volcanic lithology (Beusen et al., 2009).

The DIN speciation is not provided by the GlobalNEWS2 model. The NH₄ and NO₃ concentrations are therefore determined independently on the basis of an empirical relationship between ammonium fraction (NH4/DIN ratio) and DIN loads (Meybeck, 1982). Dissolved Oxygen (DO) concentrations are extracted from the water quality criteria recommendations published by the United States Environmental Protection Agency (EPA, 2009). The same source is used for phytoplankton concentrations, using a chlorophyll-a to phytoplankton carbon ratio of 50 gC (gChla)⁻¹ (Riemann et al., 1989) to convert the EPA values to carbon units used in the present study.

Inputs of dissolved inorganic carbon (DIC) and total Alkalinity (ALK) are calculated from values reported in the GLORICH database (Hartmann et al., 2009). For each watershed, seasonal mean values of DIC and ALK concentrations are estimated from measurements performed at the sampling locations that are closest to the river-estuary boundary. The spatial distribution of annual inputs of TOC=DOC+POC, DIC, and TC=TOC+DIC from continental watersheds to estuaries are reported in Fig.

5a, 5c and 5d, respectively. The contribution of tidal wetlands to the TOC inputs is also shown (Fig.
5b). Overall, the TC input over the entire model domain is estimated at 4.6 Tg C yr⁻¹, which falls in
the lower end of previous reported estimations (Najjar et al. 2012).

627

628 2.4.3 Inputs from tidal wetlands

The DOC input of estuarine wetlands (Fig. 5b) scales to their fraction, W, of the total estuarine and iscalculated using the GlobalNEWS parameterization:

$$Y_{DOC} = \frac{\left[(E_{C_{wet}} * W) + E_{C_{dry}} * (1 - W) \right] * R^{a} * Q_{act}}{Q_{nat}}$$
(12)

631

$$\frac{Y_DOC_{wet}}{Y_DOC} = \frac{E_C_{wet} * W}{E_C_{wet} * W + E_C_{dry} * (1 - W)}$$
(13)

632

633 where Y_DOC is the DOC yield (kg C km⁻² y⁻¹) calculated for the entire watershed, Y_DOC_{wet} is the estimated DOC yield from wetland areas (kg C km⁻² y⁻¹), Q_{act}/Q_{nat} is the ratio between the measured 634 discharge after dam construction and before dam construction, E_{wet} and E_{dry} (kg C km⁻² y⁻¹) are 635 636 the export coefficients of DOC from wetland and non-wetland soils, respectively. W is the 637 percentage of the land area within a watershed that is covered by wetlands, R is the runoff (m y⁻¹) 638 and a is a unit-less calibration coefficient defining how non-point source DOC export responds to 639 runoff. The value of a is set to 0.95, consistent with the original GlobalNEWS -DOC model of Harrison 640 et al. (2005). The carbon load Y_DOC_{wet} is then exported as a diffuse source along the relevant 641 portions of estuary. The estuarine segments receiving carbon inputs from tidal wetlands are 642 identified using the National Wetlands Inventory of the U.S. Fish and Wildlife Service (U.S. Fish and 643 Wildlife Service, 2014). The inputs from those systems are then allocated to the appropriate grid cell

644 of the model domain using GIS. The flux calculated is an annual average that is subsequently 645 partitioned between the four seasons as a function of the mean seasonal temperature, assumed to 646 be the main control of the wetland-estuarine exchange. This procedure reflects the observation that 647 in spring and early summer, DOC export is small as a result of its accumulation in the salt marshes 648 induced by the high productivity (Dai and Wiegert, 1996), (Jiang et al., 2008). In late summer and fall, 649 the higher water temperature and greater availability of labile DOC contribute to higher bacterial 650 remineralization rates in the intertidal marshes (Cai et al., 1999; Middelburg et al., 1996; Wang and 651 Cai, 2004), which induce an important export. This marsh production-recycle-export pattern is 652 consistent with the observed excess DIC signal in the offshore water (Jiang et al. 2013). DIC export 653 from tidal wetlands is neglected here because it is assumed that OC is not degraded before reaching 654 the estuarine realm. Although this assumption may lead to an overestimation of OC export from 655 marshes and respiration in estuarine water, it will not significantly affect the water pCO₂ and 656 degassing in the estuarine waters because mixing is faster than respiration.

657 **2.4.4 Concentrations at the estuarine mouth**

658 For each estuary, the downstream boundary is located 20 km beyond the mouth to minimize the 659 bias introduced by the choice of a fixed concentration boundary condition to characterize the ocean 660 water masses (e.g. Regnier et al., 1998). This approach also reduces the influence of marine 661 boundary conditions on the simulated estuarine dynamics, especially for all organic carbon species 662 whose concentrations are fixed at zero at the marine boundary. This assumption ignores the 663 intrusion of marine organic carbon into the estuary during the tidal cycle but allows focusing on the 664 fate of terrigenous material and its transit through the estuarine filter. DIC concentrations are 665 extracted from the GLODAP dataset (Key et al., 2004), from which ALK and pH are calculated 666 assuming CO₂ equilibrium between coastal waters and the atmosphere. The equilibrium value is computed using temperature (WOA2009, Locarnini et al., 2010) and salinity (WOA2009, Antonov et 667 668 al. (2010)) data which vary both spatially and temporally. The equilibrium approach is a reasonable assumption because differences in partial pressure ΔpCO_2 between coastal waters and the atmosphere are generally much smaller (0-250 µatm (Signorini et al., 2013)) than those reported for estuaries (ΔpCO_2 in the range 0-10000 µatm (Borges and Abril, 2012)). Salinity, DO, NO₃, DIP and DSi concentrations are derived from the World Ocean Atlas (Antonov et al., 2010; Garcia et al., 2010a; Garcia et al., 2010b). NH₄ concentrations are set to zero in marine waters. For all variables, seasonal means are calculated for each grid cell of the boundary.

675

676 2.5 Biogeochemical indicators

The model outputs (longitudinal profiles of concentration and reaction rates) are integrated in time over the entire volume or surface of each estuary to produce the following indicators of the estuarine biogeochemical functioning (Regnier et al., 2013b): the mean annual Net Ecosystem Metabolism (*NEM*), the air-water CO_2 flux (*FCO*₂), the carbon and nitrogen filtering capacity (*CFilt* and *NFilt*) and their corresponding element budgets. The *NEM* (molC y⁻¹) (Caffrey, 2004; Odum, 1956) is defined as the difference between net primary production (*NPP*) and total heterotrophic respiration (*HR*) at the system scale:

$$NEM = \int_{0}^{365} \int_{0}^{L} [NPP(x,t) - R_{aer}(x,t) - R_{den}(x,t)] * B(x) * H(x,t) dx dt$$
(14)

684

where *NPP* is the Net Primary Production (mol C m⁻³ y⁻¹), R_{aer} the aerobic degradation of organic matter (in mol C m⁻³ y⁻¹) and R_{den} the denitrification (in mol C m⁻³ y⁻¹) (see Volta et al., 2014 for detailed formulations). *NEM* is thus controlled by the production and decomposition of autochthonous organic matter, by the amount and degradability of organic carbon delivered by rivers and tidal wetlands and by the export of terrestrial and in-situ produced organic matter to the adjacent coastal zone. Following the definition of *NEM*, the trophic status of estuaries can be net heterotrophic (NEM<0) when *HR* exceeds *NPP* or net autotrophic (NEM>0), when *NPP* is larger than *HR* because the burial and export of autochthonous organic matter exceeds the decomposition of
river-borne material.

694 The FCO_2 (mol C y⁻¹) is defined as:

$$FCO_2 = \int_0^{365} \int_0^L RCO_2(x,t) * B(x) \, dx \, dt \tag{15}$$

695

$$RCO_{2}(x,t) = -v_{p}(x,t) \left(\left[CO_{2(aq)} \right](x,t) - K_{0}(x,t) * P_{CO2}(x,t) \right)$$
(16)

696

where RCO_2 (molC m⁻² y⁻¹) is the rate of exchange in CO₂ at the air-water interface per unit surface area, v_p is the piston velocity (m y⁻¹) and is calculated according to Regnier et al. (2002) to account for the effect of current velocity and wind speed, [CO2(aq)] is the concentration of CO₂ in the estuary (mol m⁻³), K_0 is Henry's constant of CO₂ in sea water (mol m⁻³ atm⁻¹) and P_{cO2} is the atmospheric partial pressure in CO₂ (atm).

The carbon filtering capacity (in %) corresponds to the fraction of the river-borne supply that is lost to the atmosphere and is defined here as the ratio of the net outgassing flux of CO_2 and the total inputs of C, e.g. total carbon expressed as the sum of inorganic and organic carbon species, both in the dissolved and particulate phases.

706
$$CFilt = \frac{FCO_2}{\int_0^{365} Q*[TC]_{riv} dt} * 100$$
 (17)

where [*TC*]_{*riv*} denote the total concentrations of C in the riverine inputs.

Fluxes per unit area for FCO_2 and NEM, noted $\overline{FCO_2}$ and \overline{NEM} , respectively, are defined in mol C m⁻² y⁻¹ and are calculated by dividing the integrated values calculated above by the (idealized) estuarine surface *S*:

711
$$\overline{NEM} = \frac{NEM}{c} * 1000$$

712 $\overline{FCO_2} = \frac{FCO_2}{S} * 1000$

2.6 Model-data comparison

Seasonal values for the biogeochemical indicators are calculated using the same formula as above,
but calculate the integral over a seasonal rather than annual timescale (i.e. 3 months).

715

716

717 C-GEM has been specifically designed for an application on a global/regional scale requiring the 718 representation of a large number of individual and often data-poor systems. Maximum model 719 transferability and minimum validation requirements were thus central to the model design process 720 and the ability of the underlying approach in reproducing observed dynamics with minimal 721 calibration effort has been extensively tested. The performance C-GEM's one-dimensional 722 hydrodynamic and transport models using idealized geometries have been evaluated for a number 723 of estuarine systems exhibiting a wide variety of shapes (Savenije, 2012). In particular, it has been 724 shown that the estuarine salt intrusion can be successfully reproduced using the proposed modeling 725 approach (Savenije 2005; Volta et al., 2014; 2016b). In addition, C-GEM's biogeochemistry has also 726 been carefully validated for geometrically contrasting estuarine system in temperate climate zones. 727 Simulations for the Scheldt Estuary (Belgium and the Netherlands), a typical funnel-shaped estuary, 728 were validated through model-data and model-model comparison (Volta et al., 2014; Volta et al., 729 2016a). Furthermore, simulations for the Elbe estuary (Germany), a typical prismatic shape estuary 730 that drains carbonate terrains and, thus, exhibits very high pH was validated against field data (Volta 731 et al., 2016a). In addition, C-GEM carbon budgets have been compared budget derived from 732 observations for 6 European estuaries discharging in the North Sea (Volta et al., 2016a). Although C-733 GEM has been specifically designed and tested for the type of regional application presented here, 734 its transferability from North Sea to US East Coast estuaries was further evaluated by assessing its

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736	performance in two East Coast estuaries. First, the hydrodynamic and transport model was tested
737	for the Delaware Bay (MAR). The model was forced with the monthly, minimal and maximal
738	observed discharge at Trenton over the period between 1912 and 1985 (UNH/GRDC Database,
739	GRDC, 2014). Simulated salinity profiles are compared with salinity observations from January,
740	February, May and June (the months with the highest number of data entries), which were extracted
741	from the UNH/GRDC Database. Figure 6 shows that the model captures both the salinity intrusion
742	length and the overall shape of the salinity profile well. In addition, the performance of the
743	biogeochemical model and specifically its ability to reproduce pH and pCO ₂ profiles was evaluated by
744	a model-data comparison for both the Delaware Bay (MAR) in July 2003 and the Altamaha river
745	estuary (SAR) in October 1995. Similar to Volta et al., 2016a, the test systems were chosen due to
746	their contrasting geometries. The Delaware Bay is a marine dominated system characterized by a
747	pronounced funnel shape, while the Altamaha River has a prismatic estuary characteristic of river
748	dominated systems (Jiang et al., 2008). Monthly upstream boundary conditions for nutrients, as well
749	as observed pH data and calculated pCO_2 are extracted from datasets described in (Sharp, 2010) and
750	(Sharp et al., 2009) for the Delaware and in Cai and Wang (1998), Jiang et al. (2008) and (Cai et al.,
751	1998) for the Altamaha river estuary. The additional forcings and boundary conditions are set
752	similarly to the simulation for 2000 (see Tab. 2, 3, 4, 5, 6 in SI). Figure 7 shows that measured and
753	simulated pH values are in good agreement with observed pH and observation-derived calculations
754	of pCO_2 . In the Delaware Bay, a pH minimum is located around km 140 and is mainly caused by
755	intense nitrification sustained by large inputs of NH ₄ from the Philadelphia urban area, coupled to an
756	intense heterotrophic activity. Both processes lead to a well-developed pCO_2 increase in this area
757	(Fig. 7 <u>c</u>). <u>Overall, the longitudinal pCO₂ profile of the Delaware estuary is characterized by</u> values
758	close to equilibrium with the atmosphere in the widest section of the Delaware Bay (<u>near</u> the
759	estuarine mouth and throughout the 40 first kilometers of the system) and values above 1200 µatm
760	at kilometer 150 and beyond, where characteristic salinities are below 5. Although the profile
761	presented here is simulated using boundary conditions representative of July 2003 and no pCO ₂ data

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were available for validation for this period, a recent study by Joesoef et al. (2015) reports a similar 780 longitudinal pCO₂ profile in July 2013. For the Altamaha river estuary, pH steadily increases from 781 typical river to typical coastal ocean values (Fig. 7b). In addition, both observations and model 782 results reveal that outgassing is very intense in the low-salinity region with more than a 5 fold 783 decrease in pCO₂ between salinity 0 and 5 (Fig. 7d).

784 While such local validations allow assessing the performance of the model for a specific set of 785 conditions, the purpose of this study is to capture the average biogeochemical behavior of the 786 estuaries of the eastern coast of the US. Therefore, in addition to the system-specific validation, 787 published annually averaged FCO₂ estimates for <u>12</u> tidal systems located within the study area 788 collected over the 1994-2006 period are compared to simulated FCO₂ for conditions representative 789 of the year 2000. Overall, simulated FCO_2 are comparable to values reported in the literature (Tab. 790 2). Although significant discrepancies are observed at the level of individual systems, the model 791 captures remarkably well the overall behaviors of estuaries along the East coast of the US in term of 792 intensity of CO₂ evasion rate. The model simulates low CO₂ efflux (< 5 mol C m⁻² yr⁻¹) for the 6 systems were such conditions have been observed, while the 5 systems for which the CO₂ evasion 793 exceeds 10 mol C m⁻² yr⁻¹ are the same in the observations and in the model runs. The discrepancies 794 795 at the individual system level likely result from a combination of factors, including the choice of 796 model processes and there parametrization, the uncertainties in constraining boundary conditions 797 and the limited representability of instantaneous and local observations.

798 **3** Results and discussion

799 3.1 Spatial variability of estuarine carbon dynamics

Figure 8 presents the spatial distribution of simulated mean annual $\overline{FCO_2}$ and \overline{NEM} (Fig. 8a), as well 800 as FCO_2 and -NEM (Fig. 8b). In general, mean annual $\overline{FCO_2}$ are about 30% larger than mean annual 801 802 \overline{NEM} , with the exception of six estuaries situated in the North of the coastal segment. Overall, the

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 \overline{NEM} is characterized by smaller system to system variability compared to the $\overline{FCO_2}$ in all regions. In addition, Fig. 8 reveals distinct differences across the three coastal segments and highlights the important influence of the estuarine geometry and residence time, as well as the latitudinal temperature gradient on estuarine carbon cycling.

Overall, $\overline{FCO_2}$ values are the lowest in the NAR (mean flux = 17.3 ± 16.4 mol C m⁻² y⁻¹; surface 824 weighted average = 23.1 mol C m⁻² y⁻¹), consistent with previously reported very low values for small 825 826 estuaries surrounding the Gulf of Maine (Hunt et al., 2010; 2011; Tab. 2). In contrast, \overline{NEM} reveals a regional minimum in the NAR (-51.2 \pm 16.6 mol C m⁻² y⁻¹; surface weighted average = -52.8 mol C m⁻² 827 y⁻¹). The MAR is characterized by intermediate values for $\overline{FCO_2}$, with a mean flux of 26.3 ± 34.6 mol 828 C m⁻² y⁻¹ (surface weighted average =11.1 mol C m⁻² y⁻¹) and lowest values for \overline{NEM} (-15.1 ± 14.2 mol 829 C m⁻² y⁻¹; surface weighted average =-7.4 mol C m⁻² y⁻¹). This region also shows the largest variability 830 831 in CO2 outgassing compared to the NAR and SAR, with the standard deviation exceeding the mean $\overline{FCO_2}$, and individual estimates ranging from 3.9 mol C m⁻² y⁻¹ to 150.8 mol C m⁻² y⁻¹. This variability 832 833 is mainly the result of largely variable estuarine surface areas and volumes. Some of the largest East 834 coast estuaries (e.g. Chesapeake and Delaware Bays), as well as some of smallest estuaries (e.g. York River and Hudson River estuaries, Raymond et al., 1997; 2000), are located in this region (Tab. 2 and 835 4). The maximum values of 150.8 mol C m⁻² y⁻¹ simulated in the MAR are similar to the highest FCO₂ 836 reported in the literature (132.3 mol C m^{-2} y⁻¹ for the Tapti estuary in India; Sarma et al., 2012). The 837 SAR is characterized by the highest mean $\overline{FCO_2}$ (46.7 ± 33.0 mol C m⁻² y⁻¹; surface weighted average 838 = 40.0 mol C m⁻² y⁻¹) and intermediate \overline{NEM} (-36.8 ± 24.7 mol C m⁻² y⁻¹; surface weighted average = -839 31.2 mol C m⁻² y⁻¹). 840

The NAR is characterized by a regional minimum in $\overline{FCO_2}$, and only contributes 4.6% to the total *FCO*₂ of the East coast of the US, owing to the small cumulative surface area available for gas exchange in its 10 estuarine systems. In contrast, the 18 MAR estuaries, with their large relative contribution to the total regional estuarine surface area, account for as much as 70.1% of the total

845 outgassing. Because of their smaller cumulated surface area compared to those of the MAR, the 14 846 SAR estuaries account for merely 25.3% of the total outgassing despite their regional maximal $\overline{FCO_2}$. A similar, yet slightly less pronounced pattern emerges for the \overline{NEM} . The NAR, MAR and SAR 847 respectively contribute 13.7%, 60.7% and 25.6% to the total regional net ecosystem metabolism. The 848 comparatively larger relative contribution of the NAR to the total NEM as compared to the total 849 850 FCO_2 can be explained by the importance of the specific aspect ratio for NEM. A larger ratio of 851 estuarine width <u>B0</u> and convergence length b corresponds to a more funnel shaped estuary while a 852 low ratio corresponds to a more prismatic geometry (Savenije, 2005; Volta et al., 2014). In the NAR, 853 estuaries are generally characterized by relatively narrow widths and deep-water depths, thus 854 limiting the potential surface area for gas exchange with the atmosphere. However, the relative contribution of each region to the total regional NEM and FCO₂ is largely controlled by estuarine 855 surface area. Figure 9 illustrates the cumulative NEM (a) and FCO_2 (b) as a function of the cumulative 856 857 estuarine surface areas. The disproportionate contribution of large estuaries from the MAR 858 translates into a handful of systems (Chesapeake and Delaware Bays and the main tributaries of the 859 former, in particular) contributing to roughly half of the regional NEM and FCO2, in spite of relatively 860 low individual rates per unit surface area. However, the smallest systems (mostly located in the NAR 861 and SAR) nevertheless still contribute a significant fraction to the total regional NEM and FCO_2 . The 862 27 smallest systems merely account for less than 10% of the total regional estuarine surface area, yet contribute 38% and 29% to the total regional NEM and FCO2, respectively (Fig. 9). This 863 disproportioned contribution can be mainly attributed to their high individual $\overline{FCO_2}$ and \overline{NEM} . This 864 is illustrated by the average simulated $\overline{FCO_2}$ for all 27 smallest systems (calculated as the sum of 865 866 each estuarine CO₂ outgassing per unit surface area divided by the total number of estuarine systems) which is significantly higher (30.2 mol C m^{-2} y⁻¹) than its surface weighted average (14 mol C 867 868 m^{-2} y⁻¹). Thereby accounting for the disproportionate contribution of very large systems (calculated 869 as the sum of each estuarine CO₂ outgassing divided by the total estuarine surface area across the 870 region).

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873	Following the approach used in Regnier et al. (2013 <u>b</u>), the contribution of each biogeochemical
874	process to FCO ₂ is assessed by evaluating their individual contribution to DIC and ALK changes taking
875	into account the local buffering capacity of an ionic solution when TA and DIC are changing due to
876	internal processes, but ignoring advection and mixing (Zeebe and Wolf-Gladrow 2001). In the
877	present study, we quantify the effect of the NEM on the $\rm CO_2$ balance, which is almost exclusively
878	controlled by aerobic degradation rates because the contributions of denitrification and NPP to the
879	net ecosystem balance are small. Nitrification, a process triggered by the transport and/or
880	production of NH_4 in oxygenated waters, favors outgassing through its effect on pH, which shifts the
881	acid-base equilibrium of carbonate species and increases the $\rm CO_2$ concentration. The contribution of
882	supersaturated riverine waters to the overall estuarine CO_2 dynamics is calculated as difference
883	between all the other processes creating or consuming CO ₂ Figure 10a presents the contribution of
884	the annually integrated NEM, nitrification and evasion of supersaturated, DIC enriched riverine
885	waters to the total outgassing for each system, as well as for individual regions of the domain. The
886	calculation of these annual values is based on the sum of the seasonal fluxes. Model results reveal
887	that, regionally, the NEM supports about 50% of the estuarine CO_2 outgassing, while nitrification and
888	riverine DIC inputs sustain about 17% and 33% of the \mbox{CO}_2 emissions, respectively. The relative
889	significance of the three processes described above shows important spatial variability. In the NAR,
890	oversaturated riverine waters and NEM respectively sustain 50% and 44% of the outgassing within
891	the sub-region, while nitrification is of minor importance (6%). In the MAR, the contribution of
892	riverine DIC inputs is significantly lower (~30%) and the main contribution to the outgassing is NEM
893	(~50%); nitrification accounting for slightly less than 20% of the outgassing. In the SAR, the riverine
894	contribution is even lower (~20%), and the outgassing is mainly attributed to the NEM (~55%) and
895	nitrification (~25%). Therefore, although the model results reveal significant variability across
896	individual systems, a clear latitudinal trend in the contribution to the total FCO_2 emerge from the
897	analysis; the importance of oversaturated riverine water decreasing from North to South, while NEM
898	and nitrification increase along the same latitudinal gradient. The increasing relative importance of

estuarine biogeochemical processes over riverine DIC inputs as drivers of FCO_2 along the North-South gradient is largely driven by increasing temperatures from North to South, especially in the SAR region (Tab. SI 1).

902 Contrasting patterns across the 3 regions can also be observed with respect to carbon filtering 903 capacities, CFilt (Fig. 10b). In the NAR, over 90% of the riverine carbon flux is exported to the coastal 904 ocean. However, in the MAR, the high efficiency of the largest systems in processing organic carbon 905 results in a regional CFilt that exceeds 50%. This contrast between the NAR and the MAR and its 906 potential implication for the carbon dynamics of the adjacent continental shelf waters has already 907 been discussed by Laruelle et al. (2015). In the NAR, short estuarine residence results in a much 908 lower removal of riverine carbon by degassing compared to the MAR. Laruelle et al. (2015) 909 suggested that this process could contribute to the weaker continental shelf carbon sink adjacent to 910 the NAR, compared to the MAR. In the SAR, most estuaries remove between 40% and 65% of the 911 carbon inputs. The high temperatures observed and resulting accelerated biogeochemical process 912 rates in this region favor the degradation of organic matter and contribute to increase the estuarine 913 filtering capacity for carbon. However, in the SAR, a large fraction of the OC loads is derived from 914 adjacent salt marshes located along the estuarine salinity gradients, thereby reducing the overall 915 residence time of OC within the systems. The filtering capacity of the riverine OC alone, which 916 transits through the entire estuary, would thus be higher than the one calculated here. As a 917 consequence, highest C retention rates are expected in warm tidal estuaries devoid of salt marshes 918 or mangroves (Cai, 2011).

919 3.2 Seasonal variability of estuarine carbon dynamics

Carbon dynamics in estuaries of the US East coast not only show a marked spatial variability, but also vary on the seasonal timescale. Table 5 presents the seasonal distribution of *NEM* and *FCO*₂ for each sub-region. In the NAR, a strong seasonality is simulated for the *NEM* and the summer period contributes more than a third to the annually integrated value. The outgassing reveals a lower

924 seasonal variability and is only slightly higher than summer outgassing during fall and lower during 925 spring. In the MAR, summer contributes more to the NEM (>28% of the yearly total) than any other 926 season, but seasonality is less pronounced than in the NAR. Here, FCO_2 is largest in winter and 927 particularly low during summer. In the SAR, summer accounts for 30 % of the NEM, while spring 928 contributes 21 %. FCO₂ is relatively constant throughout the year suggesting that seasonal variations 929 in carbon processing decrease towards the lower latitudes in the SAR. This is partly related to the 930 low variability in river discharge throughout the year in lower latitudes (Tab. SI1). In riverine 931 dominated systems with low residence times, such as, for instance, the Altamaha River estuary, the 932 CO₂ exchange at the air-water interface is mainly controlled by the river discharge because the time 933 required to degrade the entire riverine organic matter flux exceeds the transit time of OC through 934 the estuary. Therefore, the riverine sustained outgassing is highest during the spring peak discharge 935 periods. In contrast, the seasonal variability in FCO₂ in long-residence, marine-dominated systems 936 with large marsh areas (e.g. Sapelo and Doboy Sound) is essentially controlled by seasonal 937 temperature variations. Its maximum is reached during summer when marsh plants are dying and 938 decomposing, as opposed to spring when marshes are in their productive stage (Jiang et al., 2008). 939 These contrasting seasonal trends have already been reported for different estuarine systems in 940 Georgia, such as the Altamaha Sound, the Sapelo Sound and the Doboy Sound (Cai, 2011). At the 941 scale of the entire East coast of the US, the seasonal trends in NEM reveal a clear maximum in 942 summer and minimal values during autumn and winter. The seasonality of FCO_2 is much less 943 pronounced because the outgassing of oversaturated riverine waters throughout the year 944 contributes to a large fraction of the FCO_2 and dampens the effect of the temperature dependent 945 processes (NEM and denitrification). In our simulations, the competition between temperature and river discharge is the main driver of the seasonal estuarine carbon dynamics is. When discharge 946 947 increases, the carbon loads increase proportionally and the residence time within the system 948 decreases, consequently limiting an efficient degradation of organic carbon input fluxes. In warm

949 regions like the SAR, the temperature is sufficiently high all year round to sustain high C processing950 rates and this explains the reduced seasonal variability in NEM.

951

952 3.3 Regional carbon budget: a comparative analysis

953 The annual carbon budget for the entire East coast of the US is summarized in Fig. 11a. The total carbon input to estuaries along the East coast of the US is 4.6 Tg C y^{-1} , of which 42% arrives in 954 955 organic form and 58% in inorganic form. Of this total input, saltmarshes contribute 0.6 Tg C yr $^{-1}$, 956 which corresponds to about 14% of the total carbon loads and 32% of the organic loads in the 957 region. The relative contribution of the saltmarshes to the total carbon input increases towards low latitudes and is as high as 60% in the SAR region. Model results suggest that 2.7 Tg C y⁻¹ is exported 958 to the continental shelf (25% as TOC and 75% as DIC), while 1.9 Tg C y⁻¹ is emitted to the 959 960 atmosphere. The overall carbon filtering capacity of the region thus equals 41% of the total carbon 961 entering the 42 estuarine systems (river + saltmarshes). Because of the current lack of a benthic 962 module in C-GEM, the water column carbon removal occurs entirely in the form of CO₂ outgassing 963 and does not account for the potential contribution of carbon burial in sediments. The estimated 964 estuarine carbon retention presented here is thus likely a lower bound estimate. Reported to the modeled surface area of the region, the total FCO_2 of 1.9 Tg C y⁻¹ translates into a mean air water 965 CO_2 flux of about 14 mol C m⁻² y⁻¹. This value is slightly higher than the estimate of 10.8 mol C m⁻² y⁻¹ 966 calculated by Laruelle et al., (2013) on the basis of local $\overline{FCO_2}$ estimates assumed to be 967 968 representative of yearly averaged conditions (see section 2.1). The latter was calculated as the average of 13 annual $\overline{FCO_2}$ values reported in the literature (Tab. 2), irrespective of the size of the 969 970 systems. This approach is useful and widely used to derive regional and global carbon budgets 971 (Borges et al., 2005; Laruelle et al., 2010; Chen et al., 2013). However, it may lead to potentially 972 significant errors (Volta et al., 2016a) due to the uncertainty introduced by the spatial interpolation

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974 of local measurements to large regional surface areas, while useful and widely used to derive975 regional and global carbon budgets.

976 Regional C budgets are sparse. To our knowledge, the only other published regional assessment of 977 the estuarine carbon and CO_2 dynamics comes from a relatively well studied region: the estuaries 978 flowing into the North Sea in Western Europe (Fig. 11b). This budget was calculated using a similar 979 approach (Volta 2016a) and thus provides an ideal opportunity for a comparative assessment of C 980 cycling in these regions. However, it is important to note that there are also important differences in 981 the applied model approaches and those differences should be taken into account when comparing 982 the derived budgets. In particular, the NW European study is based on a simulation of the 6 largest 983 systems only (Elbe, Scheldt, Thames, Ems, Humber and Weser), accounting for about 40% for the 984 riverine carbon loads of the region. It assumes that the intensity of carbon processing and evasion in 985 all other smaller estuaries discharging into the North Sea (16 % of the carbon loads) can be 986 represented by the average of the 6 largest system simulation results. In addition, the Rhine-Meuse 987 system, which alone accounts for 44% of the carbon riverine inputs of the region, was treated as a 988 passive conduit with respect to carbon due to its very short freshwater residence time (Abril et al., 989 2002). The contribution of saltmarshes to the regional carbon budget was also ignored because their 990 total surface area is much smaller than along the US East coast (Regnier et al., 2013b). Another 991 important difference is the inclusion of seasonality in the present study while the budget calculated 992 for the North Sea is derived from yearly average conditions (Volta et al., 2016a).

993 Overall, although both regions receive similar amounts of C from rivers (4.6 Tg C y^{-1} and 5.9 Tg C y^{-1} 994 for the East coast of the US and the North Sea, respectively), they reveal significantly different C 995 filtering capacities. While the estuaries of the East coast of the US filter 41% of the riverine TC loads, 996 those from the North Sea only remove 8% of the terrestrial-derived material. This is partly due to the 997 large amounts of carbon transiting through the 'passive' Rhine-Meuse system. The regional filtering 998 capacity is higher (15%) when this system is excluded from the analysis. However, even when

999 neglecting this system, significant differences in filtering efficiencies between both regions remain. 1000 FCO₂ from the North Sea estuaries (0.5 Tg C y^{-1}) is significantly lower than the 1.9 Tg C y^{-1} computed 1001 for the East coast of the US. The reason for the lower evasion rate in NW European estuaries is 1002 essentially twofold. First, the total cumulative surface area available for gas exchange is significantly 1003 lower along the North Sea, in spite of comparable flux densities calculated using the entire estuarine surface areas of both regions (14 mol C m⁻² y⁻¹ and 23 mol C m⁻² y⁻¹ for the East coast of the US and 1004 1005 the North Sea, respectively). Second, although the overall riverine carbon loads are comparable in 1006 both regions (Fig. 11), the ratio of organic to inorganic matter input is much lower in the North Sea 1007 area because of the regional lithology is dominated by carbonate rocks and mixed sediments that 1008 contain carbonates (Dürr et al., 2005; Hartmann et al., 2012). As a consequence, TOC represents less 1009 than 20% of the riverine loads and only 10% of the carbon exported to the North Sea. In both 1010 regions, however, the increase of the inorganic to organic carbon ratio between input and output is 1011 sustained by a negative NEM (Fig. 11). Although the ratios themselves may significantly vary from a 1012 region of the world to the other as evidenced by these two studies, a NEM driven increase of the 1013 inorganic fraction within carbon load along the estuarine axis is consistent with the global estuarine 1014 carbon budget proposed by Bauer et al. (2013). In the East coast of the US, the respiration of riverine 1015 OC within the estuarine filter is partly compensated by OC inputs from marshes and mangroves in 1016 such a way that the input and export IC/OC ratios are closer than in the North Sea region.

1017 **3.4 Scope of applicability and model limitations**

1018 Complex multidimensional models are now increasingly applied to quantitatively explore carbon and 1019 nutrient dynamics along the land-ocean transition zone over seasonal and even annual timescales 1020 (Garnier et al., 2001; Arndt et al., 2007, 2009; Arndt and Regnier, 2007; Mateus et al., 2012). 1021 However, the application of such complex models remains limited to individual, well-constrained 1022 systems due their high data requirements and computational demand resulting from the need to 1023 resolve important physical, biogeochemical and geological processes on relevant temporal and

spatial scales. The one-dimensional, computationally efficient model C-GEM has been specifically designed to reduce data requirements and computational demand and to enable regional/global scale applications (Volta et al., 2014, 2016a). However, such a low data demand and computational efficiency inevitably requires simplification. The following paragraphs critically discus<u>s</u> these simplifications and their implications.

1029 Spatial resolution

Here, C-GEM is used with a 0.5° spatial resolution. While this resolution captures the features of large systems, it is still very coarse for relatively small watersheds, such as those of the St. Francis River, Piscataqua River, May River or the Sapelo River. For instance, the 5 estuaries reported by Hunt et al. (2010, 2011, see section 2.6) are all small systems <u>covered</u>, by the same watershed at a 0.5° resolution. Only watersheds whose area spans several grid cells can be properly identified and represented (i.e. Merrimack or Penobscot with 6 and 9 cells, respectively).

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1037 Hydrodynamic and Transport Model

1038 C-GEM is based on a theoretical framework that uses idealized geometries and significantly reduces 1039 data requirements. These idealized geometries are fully described by three, easily obtainable 1040 geometrical parameters (B, BO, H). The model thus approximates the variability of estuarine width 1041 and cross-section along the longitudinal axis through a set of exponential functions. A 1042 comprehensive sensitivity study (Volta et al., 2014) has shown that integrated process rates are 1043 generally sensitive to changes in these geometrical parameters because of their control on estuarine 1044 residence times. For instance, Volta et al. (2014) demonstrated that the NEM, is particularly sensitive 1045 to the convergence length. Similarly, the use of constant depth profile may lead to variations of 1046 about 10% in NEM (Volta et al., 2014). Nevertheless, geometrical parameters are generally easy to 1047 constrain, especially well-monitored regions such as the US east coast. Here, all geometrical 1048 parameters are constrained on the basis of observed estuarine surface areas and average water Deleted: contained

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depths. In addition, the model also accounts for the slope of the estuarine channel. This approach
ensures that simulated estuarine surface areas, volumes and, thus, residence times are in good
agreement with those of the real systems and minimizes uncertainties associated to the physical setup.

1055 In addition, the one-dimensional representation of the idealized estuarine systems does not resolve 1056 two- or three-dimensional circulation features induced by complex topography and density driven 1057 circulation. While C-GEM performs well in representing the dominant longitudional gradients, its 1058 applicability to branched systems or those with aspect ratios for which a dominant axis is difficult to 1059 identify (e.g. Blackwater estuary, UK; Pearl River estuary, China; Tagus estuary, Portugal; Bay of 1060 Brest, France) is limited.

1061 Biogeochemical Model

1062 Although the reaction network of C-GEM accounts for all processes that control estuarine FCO_2 1063 (Borges and Abril, 2012; Cai, 2011), several, potentially important processes, such as benthic-pelagic 1064 exchange processes, phosphorous sorption/desorption and mineral precipitation, a more complex representation of the local phytoplankton community, grazing by higher trophic levels, or multiple 1065 1066 reactive organic carbon pools are not included. Although these processes are difficult to constrain 1067 and their importance for FCO_2 is uncertain, the lack of their explicit representations induces 1068 uncertainties in Cfilt. In particular, the exclusion of benthic processes such as organic matter 1069 degradation and burial in estuarine sediments could result in an underestimation of Cfilt. However, 1070 because very little is known on the long term fate of organic carbon in estuarine sediments, setting 1071 up and calibrating a benthic module proves a difficult task. Furthermore, to a certain degree model 1072 parameters (such as organic matter degradation and denitrification rate constant) implicitly account 1073 for benthic dynamics. We nonetheless acknowledge that, by ignoring benthic processes and burial in 1074 particular, our estimates for the estuarine carbon filtering may be underestimated, particularly in 1075 the shallow systems of the SAR.

1076 Biogeochemical model parameters for regional and global applications are notoriously difficult to 1077 constrain (Volta et al., 2016b). Model parameters implicitly account for processes that are not 1078 explicitly resolved and their transferability between systems is thus limited. In addition, published 1079 parameter values are generally biased towards temperate regions in industrialized countries (Volta 1080 et al., 2016b). A first order estimation of the parameter uncertainty associated to the estuarine 1081 carbon removal efficiency (CFilt) can be extrapolated from the extensive parameter sensitivity 1082 analyses carried out by Volta et al. (2014, 2016b). These comprehensive sensitivity studies on end-1083 member systems have shown that the relative variation in Cfilt when a number of key 1084 biogeochemical parameters are varied by two orders of magnitude varies by ±15 % in prismatic 1085 (short residence time on order of days) to ±25 % in funnel-shaped (long residence time) systems. 1086 Thus, assuming that uncertainty increases linearly between those bounds as a function of residence 1087 time, an uncertainty estimate can be obtained for each of our modelled estuary. With this simple 1088 method, the simulated regional Cfilt of 1.9 Tg C yr-1 would be associated with an uncertainty range 1089 comprised between 1.5 and 2.2 Tg C yr⁻¹. Our regional estuarine CO_2 evasion estimate is thus 1090 reported with moderate confidence. Furthermore, in the future, this uncertainty range could be 1091 further constrained using statistical methods such as Monte Carlo simulations (e.g. Lauerwald et al., 1092 2015).

1093 Boundary Conditions and Forcings

1094 In addition, simulations are only performed for climatological means over the period 1990-2010 1095 without resolving interannual and secular variability. Boundary conditions and forcings are critical as 1096 they place the modelled system in its environmental context and drive transient dynamics. However, 1097 for regional applications, temporally resolved boundary conditions and forcings are difficult to 1098 constrain. C-GEM places the lower boundary condition 20 km from the estuarine mouth into the 1099 coastal ocean and the influence of this boundary condition on simulated biogeochemical dynamics is 1100 thus limited. At the lower boundary condition, direct observations for nutrients and oxygen are Deleted: is

extracted from databases such as the World Ocean Atlas (Antonov et al., 2010). However, lower boundary conditions for OC and pCO₂ (zero concentration for OC and assumption of pCO₂ equilibrium at the sea side) are simplified. This approach does not allow addressing the additional complexity introduced by biogeochemical dynamics in the estuarine plume (see Arndt et al., 2011). Yet, these dynamics only play a secondary role in the presented study that focuses on the role of the estuarine transition zone in processing terrestrial-derived carbon.

1108 Constraining upper boundary conditions and forcings is thus more critical. Here, C-GEM is forced by 1109 seasonally-averaged conditions for Q, T, and radiation. To date, GlobalNEWS only provide yearly-1110 averaged conditions for a number of upper boundary conditions (Seitzinger et al., 2005; Mayorga et 1111 al., 2010), representative of the year 2000. Simulations are thus only partly transient (induced by 1112 seasonality in Q, T and radiation) and do not resolve short-lived events such as storms or extreme 1113 drought conditions. In addition, direct observations of upper boundary conditions are rarely 1114 available, in particular over seasonal or annual timescales. For the US East Coast estuaries, direct 1115 observations are only available for O₂, <u>Chlorophyll-a</u>, DIC and Alk. For DIC and alkalinity boundary 1116 conditions are constrained by calculating the average concentration over a period of about three 1117 decades. In addition, observational data are extracted at the station closest to the model's upper 1118 boundary, which might be still located several kilometres upstream or downstream of the model 1119 boundary. Upper boundary conditions of POC, DOC, DIN, DIP, DSi are extracted from GlobalNews 1120 and thus model-derived. As a consequence, our results are thus intimately dependent on the 1121 robustness of the GlobalNEWS predictions. These values are usually only considered robust estimates for watersheds larger than ~10 cells (Beusen et al., 2005), which only correspond to 13 of 1122 1123 the <u>42</u> estuaries modelled in this study.

1124 Model-data comparison

The generic nature of the applied model approach <u>renders a direct validation of model results on the</u>
 <u>basis of local and instantaneous observational data (e.g. longitudinal profiles) difficult.</u>

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1134 the <u>applications</u> of seasonally/annually averaged or model-deduced boundary conditions, which <u>are</u> 1135 likely not representative of these long-term average conditions, do not lend themselves well to comparison with punctual measurements, Therefore, model performance is evaluated on the basis 1136 1137 of spatially aggregated estimates (e.g. regional FCO₂ estimates based on local measurements) rather 1138 than system-to-system comparisons with longitudinal profile from specific days. However, note that 1139 the performance of C-GEM has been intensively tested by specific model-data comparisons for a number of different systems (e.g. Volta et al., 2014, 2016a) and we are thus confident of its 1140 1141 predictive capabilities.

1142 Despite the numerous simplifying assumptions inevitably required for such a regional assessment of 1143 carbon fluxes along the land-ocean continuum, the presented approach does nevertheless provide 1144 an important step forward in evaluating the role of land-ocean transition systems in the global 1145 carbon cycle. It provides a first robust estimate of carbon dynamics based on a theoretically well-1146 founded and carefully tested, spatially and temporally resolved model approach. This approach 1147 provides novel insights that go beyond those gained through traditionally applied zero-salinity 1148 method or box model approaches. In addition, it also highlights critical variables and data gaps and 1149 thus helps guide efficient monitoring strategies.

1150 **3.5** Towards predictors of the estuarine carbon processing

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1151 The mutual dependence between geometry and transport in tidal estuaries and, ultimately, their 1152 biogeochemical functioning (Savenije, 1992; Volta et al., 2014) allows relating easily extractable 1153 parameters linked to their shape or their hydraulic properties to biogeochemical indicators. In this 1154 section, we explore the relationships between such simple physical parameters and indicators of the estuarine carbon processing \overline{NEM} , $\overline{FCO_2}$ and CFilt. In order to account for the effect of temperature 1155 on C dynamics, $-\overline{NEM}$ and $\overline{FCO_2}$ are also normalized to the same temperature (arbitrarily chosen to 1156 be 0 degree). These normalized values are obtained by dividing $-\overline{NEM}$ and $\overline{FCO_2}$ by a Q₁₀ function 1157 1158 f(T) (see Volta et al., 2014). This procedure allows accounting for the exponential increase in the rate

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1166 of several temperature dependent processes contributing to the NEM (i.e. photosynthesis, organic 1167 carbon degradation...). Applying the same normalization to $-\overline{NEM}$ and $\overline{FCO_2}$ is a way of testing how 1168 intimately linked NEM and FCO2 are in estuarine systems. Indeed linear relationships relating one to 1169 the other have been reported (Mayer and Eyre, 2012). The three indicators are then investigated as 1170 a function of the ratio between the estuarine surface S and the seasonal river discharge Q. The 1171 surface area is calculated from the estuarine width and length, as described by equation 2, in order 1172 to use a parameter which is potentially applicable to other regions for which direct estimates of the 1173 real estuarine surface area is not available. Since the fresh water residence time of a system is 1174 obtained by dividing volume by river discharge, the S/Q ratio is also intimately linked to residence 1175 time. Here, we choose to exclude the estuarine depth from the analysis because this variable cannot 1176 be easily quantified from maps or remote sensing images and would thus compromise the 1177 applicability of a predictive relationship on the global scale. However, from dimensional analysis, S/Q can be viewed as a water residence time normalized to meter depth of water. As shown by equation 1178 3, S only requires constraining BO and width convergence length b, two parameters that can readily 1179 1180 be extracted from the Google Earth engine. Global database of river discharges, as for instance 1181 RivDIS (Vörösmarty et al., 1996) are also available in such a way that the S/Q ratio can potentially be 1182 extracted for all estuaries around the globe.

1183 Figure 12a reveals that small values of S/Q are associated with the most negative NEM / f(T). The 1184 magnitude of the \overline{NEM} then exponentially decreases with increasing values of S/Q. Estuaries 1185 characterized by small values of S/Q are mainly located in the NAR sub-region and correspond to small surface area, and thus short residence time systems. It is possible to quantitatively relate -1186 \overline{NEM} / f(T) and S/Q through a power law function (y = 25.85 x^{-0.64} with a r² = 0.82). The coefficient 1187 1188 of determination remains the same when excluding estuaries from the NAR region and the equation 1189 itself is not significantly different, although those estuaries on their own do not display any 1190 statistically significant trend (Tab. 6). The decrease in the intensity of the net ecosystem metabolism

in larger estuaries (Fig 8), characterized by high S/Q ratios, can be related to the extensive consumption of the organic matter pool during its transit through the estuarine filter. However, when reported to the entire surface area of the estuary, larger systems (with high values of S/Q) still reveal the most negative surface integrated *NEM* (Fig. 12b). It can also be noted that some estuaries from the NAR region display very low values of *–NEM*. These data points correspond to fall and winter simulations for which the temperature was relatively cold (<5 °C) and biogeochemical processing was very low.

The overall response of $\overline{FCO_2}/f(T)$ to S/Q is comparable to that of $\overline{NEM}/f(T)$ (Fig. 12c), with 1198 lower values of $\overline{FCO_2}$ observed for high values of S/Q. However, for S/Q < 3 days m⁻¹, the $\overline{FCO_2}$ 1199 values are very heterogeneous and contain many, low $\overline{FCO_2}$ outliers from the NAR region. These 1200 1201 data points generally correspond to low water temperature conditions which keep pCO₂ low, even if 1202 the system generates enough CO_2 internally via NEM. Thus, the well-documented correlation between \overline{NEM} and $\overline{FCO_2}$ (Maher and Eyre, 2012) does not seem to hold for systems with very short 1203 1204 residence times. For systems with S/Q > 3 days m⁻¹, we obtain a regression $FCO_2 = -0.64 \times NEM + 5.96$ 1205 with a r^2 of 0.46, which compares well with the relation $FCO_2 = -0.42 \times NEM + 12$ proposed by Maher 1206 and Eyre (2012) who used 24 seasonal estimates from small Australian estuaries. However, our 1207 results suggest that this relationship cannot be extrapolated to small systems such as those located 1208 in the NAR. Figure 12d, which reports non-normalized FCO₂ reveals a monotonous increase of FCO₂ 1209 with S/Q. This suggests that, unlike the NEM for which the normalization by a temperature function 1210 allowed explaining most of the variability; FCO2 is mostly controlled by the water residence time 1211 within the system. Discharge is the main FCO₂ driver in riverine dominated systems, while 1212 interactions with marshes are driving the outgassing in marine dominated systems surrounded by 1213 marshes. Net aquatic biological production (NEM being negative or near 0) in large estuaries (with 1214 large S/Q) is another important reason for low FCO₂ in such systems. For example, despite the higher 1215 CO₂ degassing flux in the upper estuary of the Delaware, strong biological CO₂ uptake in the mid-bay

1216 and near zero NEM in the lower bay result in a much lower FCO₂ for the entire estuary (Joesoef et al. 2015). In systems with S/Q < 3 days m⁻¹, the short residence time prevents the excess CO₂ of 1217 oversaturated water from being entirely exchanged with the atmosphere and simulations reveal that 1218 1219 the estuarine waters are still oversaturated in CO_2 at the estuarine mouth. Thus, the inorganic 1220 carbon, produced by the decomposition of organic matter, is not outgassed within the estuary but 1221 exported to the adjacent continental shelf waters. This result is consistent with the observation-1222 based hypothesis of Laruelle et al. (2015) for the NAR estuaries. As a consequence of the distinct 1223 behavior of short residence time systems, the coefficient of determination of the best-fitted power law function relating $\overline{FCO_2}$ and S/Q is only significant if NAR systems are excluded (y = 31.64 x^{-0.58} 1224 with a $r^2 = 0.70$). This thus suggests that such relationships (as well as that proposed by Maher and 1225 1226 Eyre, 2012) cannot be applied to any system but only those for which S/Q>3 day m⁻¹.

1227 Finally, Fig. 12e reports the simulated mean seasonal carbon filtering capacities as a function of the 1228 depth normalized residence time. Not surprisingly, and in overall agreement with previous studies 1229 on nutrient dynamics in estuaries (Nixon et al., 1996), the carbon filtering capacity increases with 1230 S/Q. The best statistical relation between CFilt and S/Q is obtained when including all 3 regions, resulting in $r^2 = 0.70$ (y = 40.64 log₁₀(x) + 11.84). Very little C removal occurs in systems with S/Q < 1 1231 1232 day m⁻¹. For systems characterized by longer depth-normalized residence times, CFilt increases regularly, and reaches 100% for S/Q > 100 day m⁻¹. Such high values are only observed for very large 1233 1234 estuaries from the MAR region (Delaware and Chesapeake Bays); the majority of our systems had an 1235 S/Q range between 1 and 100 day m⁻¹. The quantitative assessment of estuarine filtering capacities 1236 is further complicated by the complex interplay of estuarine and coastal processes. Episodically, 1237 marked spatial variability in concentration gradients near the estuarine mouth may lead to a reversal 1238 of net material fluxes from coastal waters into the estuary (Regnier at al., 1998; Arndt et al. 2011). 1239 Our results show that this feature is particularly significant for estuaries with a large width at the 1240 mouth and short convergence length (funnel shaped or 'Bay type' systems). These coastal nutrient 1241 and carbon inputs influence the internal estuarine C dynamics and lead to filtering capacities that 1242 can exceed 100%. This feature is particularly significant in summer, when riverine inputs are low and1243 the marine material is intensively processed inside the estuary.

1244 Previous work investigated the relationship between fresh water residence time and nutrient 1245 retention (Nixon et al., 1996; Arndt et al., 2011; Laruelle, 2009). These studies, however, were 1246 constrained by the scarcity of data. For instance, the pioneering work of Nixon et al. (1996) only 1247 relied on a very limited number (<10) of quite heterogeneous coastal systems, all located along the 1248 North Atlantic. Here, our modeling approach allows us to generate $\frac{168}{42}$ x 4) data points, each 1249 representing a system-scale biogeochemical behavior. Together, this database spans the entire 1250 spectrum of estuarine settings and climatic conditions found along the East coast of the US. In 1251 addition, the ratio S/Q used as master variable for predicting temperature normalized \overline{NEM} , $\overline{FCO_2}$ 1252 and CFilt only requires a few easily accessible geometric parameters (B0, b and L) and an estimate of the river discharge. While it is difficult to accurately predict $\overline{FCO_2}$ for small systems such as those 1253 1254 located in the NAR region, the relationships found are quite robust for systems in which S/Q > 3 days 1255 m⁻¹. Most interestingly, *CFilt* values reveal a significant correlation with S/Q and could be used in 1256 combination with global riverine carbon delivery estimates such as GlobalNews 2 (Mayorga et al., 1257 2010) to constrain the estuarine CO_2 evasion and the carbon export to the coastal ocean at the 1258 continental and global scales.

1259 4. Conclusions

This study presents the first complete estuarine carbon budget for the East coast of the US using a modeling approach. The structure of the model C-GEM relies on a restricted number of readily available global datasets to constrain boundary conditions and limits the number of geometrical and physical parameters to be constrained. Our simulations predict a total CO₂ outgassing of 1.9 Tg C y⁻¹ for all tidal estuaries of the East coast of the US. This quantification accounts for the seasonality in estuarine carbon processing as well as for distinct individual behaviors among estuarine types (marine or river dominated). The total carbon output to the coastal ocean is estimated at 2.7 TgC y⁻¹, **Deleted:** 172 **Deleted:** 43 1269 and the carbon filtering capacity with respect to riverine, marshes and mangrove inputs is thus on 1270 the order of 40%. This value is significantly higher than the recently estimated C filtering capacity for 1271 estuaries surrounding the North Sea using a similar approach (Volta et al., 2016a), mainly because 1272 the surface area available for gas exchange and the draining lithology limits the CO₂ evasion in the 1273 NW European systems. At the regional scale of the US East coast estuaries, net heterotrophy is the 1274 main driver (50%) of the CO_2 outgassing, followed by the ventilation of riverine supersaturated 1275 waters entering the estuarine systems (32%) and nitrification (18%). The dominant mechanisms for 1276 the gas exchange and the resulting carbon filtering capacities nevertheless reveal a clear latitudinal 1277 pattern, which reflects the shapes of estuarine systems, climatic conditions and dominant land-use 1278 characteristics.

1279 Our model results are used to derive predictive relationships relating the intensity of the area-based Net Ecosystem Metabolism (\overline{NEM}), air-water CO₂ exchange ($\overline{FCO_2}$) and the carbon filtering capacity 1280 1281 (CFilt) to the depth normalized residence time, expressed as the ratio of the estuarine surface area 1282 to the river discharge. In the future, such simple relationships relying on readily available geometric 1283 and hydraulic parameters could be used to quantify carbon processing in areas of the world devoid 1284 of direct measurements. However, it is important to note that such simple relationships are only 1285 valid over the range of boundary conditions and forcings explored and may not be applicable to 1286 conditions that fall outside of this range. In regions with better data coverage, such as the one 1287 investigated here, our study highlights that the regional-scale quantification, attribution, and 1288 projection of estuarine biogeochemical cycling are now at reach.

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1649	Table 1: Estimates of total annual riverine input from wa	atersheds to estuaries (Tg C yr ⁻¹). The ranges

are based on Stets and Striegl (2012), Global NEWS (Mayorga et al. 2010), Hartmann et al. (2009),

1651 SPARROW (Shih et al. 2010) and DLEM (Tian et al. 2010, 2012). Modified from Najjar et al. 2012.

	DIC	DOC	POC	TOTAL
NAR	0.2-0.8	0.3-2.1	0.1-0.2	0.6-3.1
MAR	1.4-1.8	0.5-2.3	0.1-0.3	2.0-4.4
SAR	0.4-1.4	0.9-1.6	0.1-0.2	1.4-3.2
TOTAL	2.0-4.0	1.7-6.0	0.3-0.7	4.0-10.7

1655	Table 2 : Published local annually averaged estimates of $\overline{FCO_2}$ in mol C m ⁻² yr ⁻¹ for estuaries along the	
1656	East coast of the US."	

Name	Lon	Lat	FCO ₂		Reference
			Observed.	Modeled	
Altamaha Sound	-81.3	31.3	32.4	72.7	Jiang et al. (2008)
Bellamy	-70.9	43.2	3.6	3.9	Hunt et al. (2010)
Cocheco	-70.9	43.2	3.1	3.9	Hunt et al. (2010)
Doboy Sound	-81.3	31.4	13.9	25.7	Jiang et al. (2008)
Great Bay	-70.9	43.1	3.6	3.9	Hunt et al. (2011)
Little Bay	-70.9	43.1	2.4	3.9	Hunt et al. (2011)
Oyster Bay	-70.9	43.1	4	3.9	Hunt et al. (2011)
Parker River estuary	-70.8	42.8	1.1	3.9	Raymond and Hopkinson (2003)
Sapelo Sound	-81.3	31.6	13.5	20.6	Jiang et al. (2008)
Satilla River	-81.5	31	42.5	25.7	Cai and Wang (1998)
York River	-76.4	37.2	6.2	8.1	Raymond et al. (2000)
Hudson River	-74	40.6	13.5	15.5	Raymond et al. (1997)

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Table 3: State variables and processes explicitly implemented in CGEM.

State variables		
Name	Symbol	Unit
Suspended Particulate Mater	SPM	gL⁻¹
Total Organic Carbon	TOC	μΜ C
Nitrate	NO₃	μΜ Ν
Ammonium	NH_4	μΜ Ν
Phosphate	DIP	μΜ Ρ
Dissolved Oxygen	DO	$\mu M O_2$
Phytoplankton	Phy	μΜ C
Dissolved Silica	dSi	μM Si
Dissolved Inorganic Carbon	DIC	μΜ C
Biogeochemical reactions		
Name	Symbol	Unit
Gross primary production	GPP	μM C s⁻¹
Net primary production	NPP	μM C s⁻¹
Phytoplankton mortality	М	μM C s ⁻¹
Aerobic degradation	R	μM C s⁻¹
Denitrification	D	μM C s⁻¹
Nitrification	Ν	μM N s⁻¹
O ₂ exchange with the atmosphere	FO ₂	μM O₂ s⁻¹
CO ₂ exchange with the atmosphere	FCO ₂	μM C s⁻¹
SPM erosion	E _{SPM}	gL ⁻¹ s ⁻¹
SPM deposition	D _{SPM}	gL ⁻¹ s ⁻¹

long	lat	S	0	Rt	FCO	NEM	FCO ₂	NEM
degrees	degrees	km ²	Q m ³ s ⁻¹	days	FCO ₂ mol C m ⁻² yr ⁻¹	mol C m ⁻² yr ⁻¹	10 ⁶ mol C yr ⁻¹	10 ⁶ mol C yr ⁻¹
NAR						,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		
-67.25	44.75	7	38.5	15	3.7	-37.4	27	-270
-67.25	45.25	12	73.6	15	6.0	-56.7	71	-666
-67.25	45.25	12	73.6	15	13.8	-56.6	162	-666
-67.75	44.75	3	68.5	4	6.7	-63.5	23	-221
-68.25	44.75	14	69.5	19	4.1	-56.2	58	-791
-68.75	44.75	89	309.9	23	27.4	-58.2	2431	-5163
-69.75	44.25	50	626.6	5	32.3	-74.4	1607	-3703
-70.25	43.75	3	25.8	10	2.1	-21.0	7	-71
-70.75	41.75	288	103.6	958	5.0	-4.0	1428	-1146
-70.75	42.25	63	210.7	40	16.2	-32.9	1025	-2081
-70.75	42.75	17	105.8	3	56.3	-69.0	943	-1155
MAR								
-70.75	43.25	31	29.9	11	21.6	-37.4	662	-1146
-71.25	41.75	257	28.2	808	3.9	-2.5	997	-650
-71.75	41.25	21	112.4	4	35.2	-32.6	726	-672
-72.75	40.75	20	25.4	62	30.7	-21.1	623	-430
-72.75	41.25	10	142.5	2	150.8	-36.9	1578	-386
-72.75	41.75	55	476.6	3	55.9	-45.7	3088	-2523
-73.25	40.75	19	26.8	56	31.4	-28.4	608	-550
-74.25	40.75	1192	608.2	126	15.5	-11.8	18432	-14047
-75.25	38.25	399	80.5	172	13.9	-5.0	5558	-2016
-75.25	38.75	354	31.8	357	7.5	-3.0	2659	-1076
-75.25	39.75	1716	499.0	221	10.0	-7.8	17072	-13439
-75.75	39.25	224	18.3	434	7.5	-2.9	1685	-640
-76.25	39.25	3427	717.1	352	8.1	-5.1	27646	-17352
-76.75	37.25	586	272.3	74	15.0	-10.4	8810	-6084
-76.75	37.75	154	36.3	163	10.7	-6.6	1654	-1023
-76.75	39.25	59	71.2	29	48.6	-34.6	2862	-2038
-77.25	38.25	206	30.2	268	6.1	-3.3	1265	-676
-77.25	38.75	568	259.2	118	16.7	-10.8	9488	-6134
SAR -78.25	34.25	48	167.4	7	122.5	-62.4	5916	-3015
-78.25	33.25	48	56.3	42	43.4	-36.5	2056	-1728
-79.25	33.75	47	291.4	42 8	43.4 85.1	-78.7	3843	-3551
-79.75	33.25	25	33.8	15	37.9	-32.8	956	-828
-80.25	32.75	25	31.0	50	48.8	-42.5	1214	-1057
-80.25	33.25	92	75.5	61	62.7	-61.2	5769	-5625
-80.25	32.25	71	21.1	182	12.9	-7.0	918	-5025
-80.75	32.75	164	63.1	95	20.6	-11.5	3372	-1879
-81.25	31.75	92	71.7	45	25.7	-20.9	2361	-1926
-81.25	32.25	130	379.8	11	51.7	-39.2	6732	-5097
-81.75	30.75	34	18.7	61	17.5	-14.7	602	-505
-81.75	31.25	130	17.7	294	5.5	-4.0	713	-523
-81.75	31.75	56	350.5	4	72.7	-67.4	4068	-3770
				•				

Table 4: Yearly averaged surface area (*S*), fresh water discharge (*Q*), residence time (*Rt*), *FCO*₂ and
 NEM of all simulated estuaries.

Region	<u>s</u>	NEM	winter	spring	summer	fall	FCO ₂	winter	spring	summer	fall 🔸
	<u>km</u> ²	mol C y ⁻¹	%	%	%	%	mol C y ⁻¹	%	%	%	%
NAR	<u>558</u>	-16.3 10 ⁹	14.7	21.2	37.0	27.2	7.2 10 ⁹	26.3	18.9	26.5	28.3
MAR	<u>9298</u>	-72.2 10 ⁹	21.9	25.9	28.8	23.4	108.3 10 ⁹	29.8	23.3	20.7	26.2
SAR	<u>959</u>	-30.5 10 ⁹	24.6	20.9	30.3	24.2	39.2 10 ⁹	26	23.4	27	23.6

Table 5: Seasonal contribution to *FCO*₂ and *NEM* in each the sub-region. The seasons displaying the
 highest percentages are indicated in bold. Winter is defined as January, February and March, Spring
 as April, May and June and so on...

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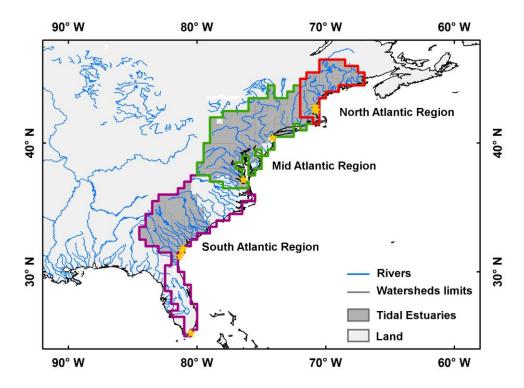
1670

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Region	$-\overline{NEM}/f(T)$	$\overline{FCO_2}/f(T)$	CFilt
NAR	$y = 27.84 x^{-0.17}$	$y = 6.07 x^{0.00}$	y = 15.08 log ₁₀ (x) + 4.86
	$r^2 = 0.11$	$r^2 = 0.00$	$r^2 = 0.40$
MAR	y = 26.03 x ^{-0.63}	y = 34.36 x ^{-0.58}	$y = 40.46 \log_{10}(x) + 9.60$
	r ² = 0.86	r ² = 0.68	$r^2 = 0.70$
SAR	$y = 28.36 x^{-0.71}$	y = 32.82 x ^{-0.66}	$y = 23.19 \log_{10}(x) + 43.71$
	r ² = 0.76	$r^2 = 0.80$	$r^2 = 0.46$
MAR + SAR	y = 25.85 x ^{-0.64}	y = 31.64 x ^{-0.58}	$y = 33.30 \log_{10}(x) + 24.88$
	r ² = 0.82	r ² = 0.70	r ² = 0.57
NAR + MAR + SAR	y = 28.98 x ^{-0.66}	y = 12.98 x ^{-0.33}	$y = 40.64 \log_{10}(x) + 11.84$
	$r^2 = 0.82$	$r^2 = 0.30$	$r^2 = 0.70$

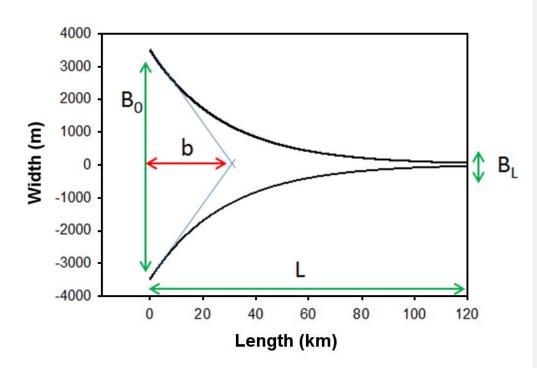
Table 6: Regressions and associated coefficient of determination between the depth normalized1672residence time (S/Q) and $-\overline{NEM} / f(T)$, $\overline{FCO_2} / f(T)$ and CFilt.



1675

1676 Figure 1: Limits of the 0.5 degrees resolution watersheds corresponding to tidal estuaries of the East
 1677 coast of the US. 3 sub-regions are delimited with colors and orange stars represent the location of

1678 previous studies.



1681 Figure 2: Idealized estuarine geometry and main parameters. Parameters indicated by green arrows1682 are measured, b is calculated. See section 2.3.1 for further details.

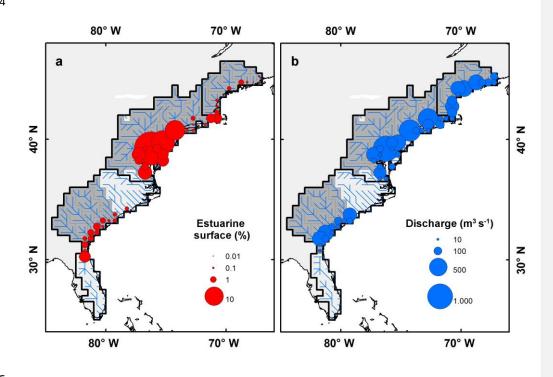


Figure 3: Estuarine surface area (a) and mean annual freshwater discharge (b) for each tidal estuary
 of the East coast of the US. Estuarine surface area are expressed as percentage of the entire surface

1688 area of the region (19830 km²)

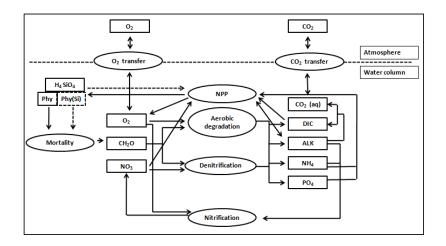


Figure 4: Conceptual scheme of the biogeochemical module of C-GEM used in this study. State-1692 variables and processes are represented by boxes and oval shapes, respectively. Modified from Volta

1693 et al., 2014.

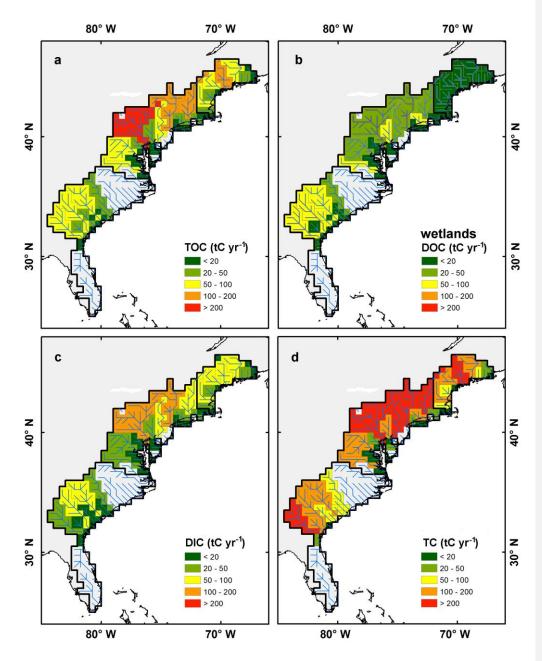
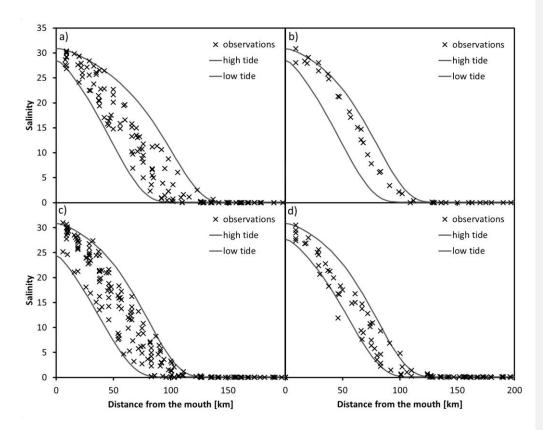
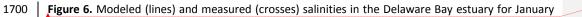




Figure 5: Annual river carbon loads of TOC (a), annual DOC fluxes from wetlands (b), annual river
 carbon loads of DIC (c) and annual TC fluxes (d). All fluxes are indicated per watershed.



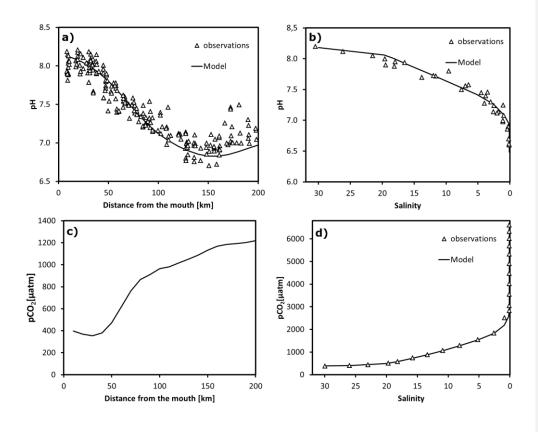




(a), February (b), May (c), June (d). The two lines correspond to high and low tides.

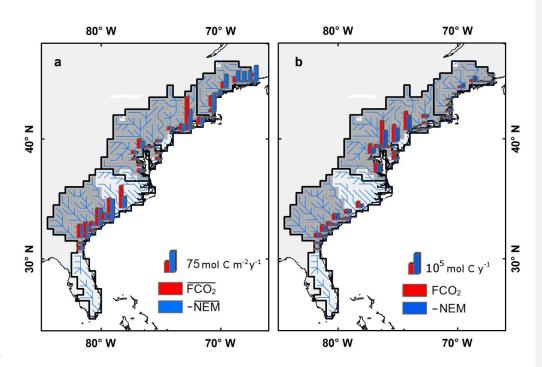
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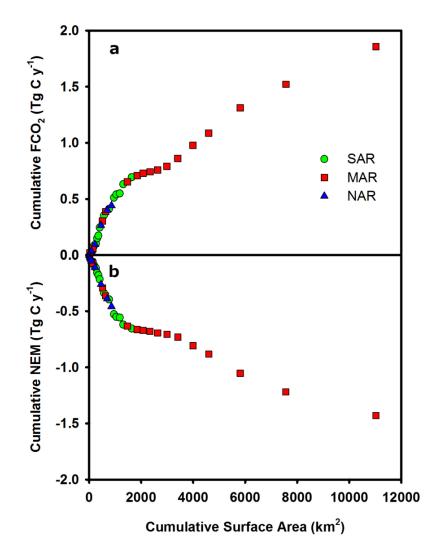
1704 Figure 7. Longitudinal profiles of pH (top) and pCO₂ (bottom) for the Delaware Bay (left) and

1705 Altamaha river estuary (right).

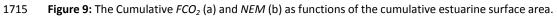




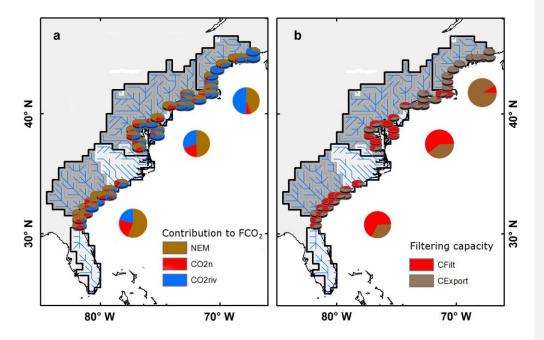
1709Figure 8: Spatial distribution of spatially averaged value (a) and integrated value (b) of mean annual1710 FCO_2 (red) and -NEM (blue) along the East coast of the US. On panel a, the notation with overbars1711 $(\overline{FCO_2} \text{ and } -\overline{NEM})$ represents rates per unit surface. For the sake of the comparison with $\overline{FCO_2}$, Fig.17128 displays $-\overline{NEM}$ because the model predicts that all estuaries in this region are net heterotrophic.







1716 Systems are sorted by increasing surface area.

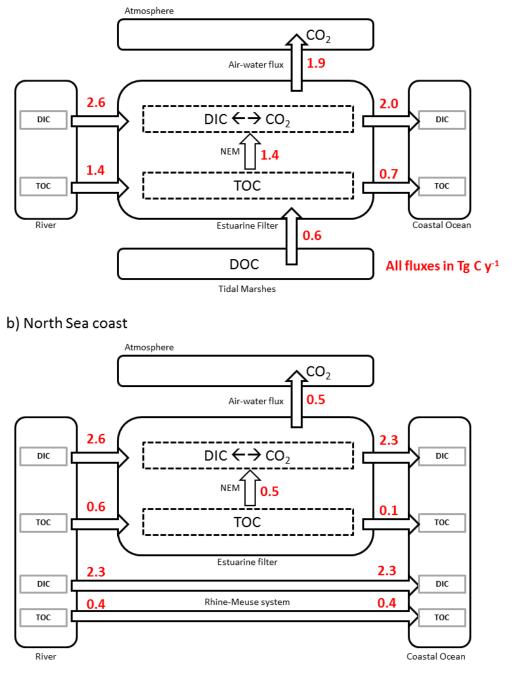


1719 Figure 10: Contribution of *NEM*, nitrification and riverine waters super-saturated waters to the mean

annual *FCO*₂ (a). Spatial distribution of mean annual carbon filtration capacities (*CFilt*) and export

1721 (CExport) along the East coast of the US (b).

a) Eastern US coast



All fluxes in Tg C y⁻¹

1723

1724 Figure 11: Annual carbon budget of the estuaries of the East coast of the US (a) and of the coast of1725 the North Sea (b, modified from Volta et al., 2016a).

