

# Role of Riverine Dissolved Organic and Inorganic Carbon and Nutrients in Global-ocean Air-sea CO<sub>2</sub> Fluxes

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## Key Points:

- We assess how global lateral exports impact air-sea CO<sub>2</sub> flux and carbon cycling in ECCO-Darwin ocean biogeochemistry simulations
- Near river mouths, changes in CO<sub>2</sub> flux are dominated by the solubility pump and lead to outgassing
- Further offshore, riverine nitrogen leads to increased CO<sub>2</sub> uptake via phytoplankton fertilization

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## Abstract

While the preindustrial ocean was assumed to be in equilibrium with the atmosphere, the modern ocean is a carbon sink, resulting from natural variability and anthropogenic perturbations, such as fossil fuel emissions and changes in riverine exports over the past two centuries. Here we use a suite of sensitivity experiments based on the ECCO-Darwin global-ocean biogeochemistry model to evaluate the response of air-sea CO<sub>2</sub> flux and carbon cycling to present-day lateral fluxes of carbon, nitrogen, and silica. We generate a daily export product by combining point-source freshwater discharge from JRA55-do with the Global NEWS 2 watershed model, accounting for lateral fluxes from 5171 watersheds worldwide. From 2000 to 2019, carbon exports increase CO<sub>2</sub> outgassing by 0.22 Pg C yr<sup>-1</sup> via the solubility pump, while nitrogen exports increase the ocean sink by 0.17 Pg C yr<sup>-1</sup> due to phytoplankton fertilization. On regional scales, exports to the Tropical Atlantic and Arctic Ocean are dominated by organic carbon, which originates from terrestrial vegetation and peats and increases CO<sub>2</sub> outgassing (+10 and +20%, respectively). In contrast, Southeast Asia is dominated by nitrogen from anthropogenic sources, such as agriculture and pollution, leading to increased CO<sub>2</sub> uptake (+7%). Our results demonstrate that the magnitude and composition of riverine exports, which are determined in part from upstream watersheds and anthropogenic perturbations, substantially impact present-day regional-to-global-ocean carbon cycling. Ultimately, this work stresses that lateral fluxes must be included in ocean biogeochemistry and Earth System Models to better constrain the transport of carbon, nutrients, and metals across the land-ocean-aquatic-continuum.

## Plain Language Summary

Due to ongoing climate change and human activities, the transport of carbon and nutrients from rivers to the ocean has changed, with rivers now contributing to the modern ocean's sequestration of atmospheric carbon dioxide (CO<sub>2</sub>). In this study, we add the effect of present-day rivers to a numerical model of the ocean carbon cycle (ECCO-Darwin) and then estimate their impact on air-sea CO<sub>2</sub> exchange and ocean biogeochemistry. Over a 20-year period, riverine carbon saturates the surface ocean and increases the amount of CO<sub>2</sub> released to the atmosphere, while nitrogen fertilizes phytoplankton and increases the capture of atmospheric CO<sub>2</sub> via photosynthesis. In the Tropical Atlantic and Arctic Oceans, organic carbon drained from vegetation and peats causes outgassing of ocean carbon. In Southeast Asia, the large amount of riverine nitrogen originating from human activities, such as agriculture or waste water, increases ocean CO<sub>2</sub> sequestration. Our work highlights how rivers, which are affected by present-day human actions and climate change, impacts the ocean's carbon cycle across regional-to-global scales.

## 1 Introduction

Globally, shelf and marginal seas are typically sinks of CO<sub>2</sub>, where uptake driven by strong biological productivity exceeds outgassing from organic matter degradation and carbon enrichment by river runoff and coastal upwelling (Ianson et al., 2009; W.-J. Cai, 2011; W. Cai et al., 2013; Laruelle et al., 2017; Bertin et al., 2023). Rivers transport roughly 0.8–0.9 Pg C yr<sup>-1</sup> from land to coastal regions as dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), particulate organic carbon (POC), and particulate inorganic carbon (PIC); a third of the aforementioned total riverine export of carbon is buried in coastal sediments (Regnier et al., 2022; Battin et al., 2023). Nutrients such as phosphorus, nitrogen, and silica are also conveyed by rivers along with carbon. Terrestrial inorganic carbon and nutrients in streams originate from weathering of the lithosphere and the associated sink of atmospheric CO<sub>2</sub>, along with the remineralization of organic matter in streams and/or on land (Suchet & Probst, 1995; Battin et

al., 2023). Riverine organic carbon and nutrients are further supplemented by primary production from land vegetation and organic matter mobilized through direct litterfall, runoff, leaching, and erosion into rivers (Meybeck & Vörösmarty, 1999; Seitzinger et al., 2010; Regnier et al., 2013; Battin et al., 2023).

Once injected into the coastal ocean, riverine carbon is generally outgassed back to the atmosphere in the form of  $\text{CO}_2$ , due to the saturation of surface-ocean waters by terrestrial DIC and remineralization of terrestrial organic matter (Hartmann et al., 2009; Lacroix et al., 2020; Bertin et al., 2023) in shallow, well-mixed water columns. The natural transport of carbon from terrestrial ecosystems to ocean outgassing, the so-called “river loop”, is estimated to be  $0.65 \pm 0.3 \text{ Pg C yr}^{-1}$  (Regnier et al., 2022; Friedlingstein et al., 2023). With respect to inorganic nutrients, their injection into the surface ocean can fertilize growth of photosynthetic organisms in nutrient-limited regions. Globally, this lateral flux increases ocean primary productivity and contributes to a coastal-ocean sink of  $\sim 0.25 \text{ Pg C yr}^{-1}$ , which is roughly 17% of the global-ocean sink (W.-J. Cai, 2011; Lacroix et al., 2021; S. Gao et al., 2023).

Over the past two centuries, terrestrial anthropogenic perturbations have led to a substantial increase in the load of nitrogen and phosphorus through agricultural fertilization, leaked sewage, and land-use change (Smith et al., 2003; Lee et al., 2016; Lacroix et al., 2021). Projections of the historical riverine dissolved nitrogen and phosphorus load depict a three- to four-fold increase over the period 1900–2019 (Lacroix et al., 2021). When delivered in excessive amounts, these nutrients can alter aquatic and ocean ecosystems, resulting in eutrophication, hypoxia, and acidification in coastal waters (Laurent et al., 2017; Fennel & Testa, 2019). Dissolved and particulate carbon are also affected regionally by agricultural liming, the addition of sulfuric acid to watersheds, changes in erosion patterns, and river management (Monteith et al., 2007; Raymond et al., 2008; Calmels et al., 2007; Regnier et al., 2013; Maavara et al., 2017). Projected trends for river biogeochemical loads remain uncertain and exhibit disparate regional responses over the 21<sup>st</sup> century depending on the chosen shared socioeconomic pathway (Beusen et al., 2022; Beusen & Bouwman, 2022; Vishwakarma et al., 2022; Zhang et al., 2022).

While present estimates of riverine freshwater and biogeochemical fluxes are poorly sampled in space and time, land surface and watershed models can provide spatiotemporally-resolved lateral exports at global scales (Mayorga et al., 2010; Krinner et al., 2005; Hagemann & Dümenil, 1997; Hagemann & Gates, 2003; M. Li et al., 2017; Bloom et al., 2020). Coupled with ocean biogeochemical models, it is thus possible to quantify the response of the coastal and open-ocean carbon cycle to lateral fluxes (Lacroix et al., 2020, 2021; Mathis et al., 2022; Louchard et al., 2021; da Cunha & Buitenhuis, 2013; Le Fouest et al., 2013; S. Gao et al., 2023; Bertin et al., 2023). Regarding the importance of lateral exports in ocean carbon cycling, it is critical that ocean biogeochemical models better account for coastal mechanisms occurring across the land-ocean-aquatic-continuum (LOAC) (Ward et al., 2020; Mathis et al., 2022). Such improvements will come from 1) finer horizontal and vertical grid resolution to resolve small-scale ocean physics (vertical mixing, submesoscale processes) and associated biology (hypoxia, phytoplankton blooms) and 2) improved representation of LOAC components (river and groundwater discharge, bottom sediment diagenesis, and estuarine biogeochemical filtering) (Ward et al., 2020; Sharples et al., 2017). While recent modeling efforts have made improvements in this regard (Volta et al., 2016; Laruelle et al., 2017; Mathis et al., 2022, 2024), the respective contribution of riverine exports to air-sea  $\text{CO}_2$  fluxes across the global ocean remains to be assessed.

In this study, we add lateral fluxes of carbon and nutrients to the ECCO-Darwin global-ocean biogeochemistry state estimate (Carroll et al., 2020, 2022) and evaluate the response of air-sea  $\text{CO}_2$  flux and ocean biogeochemistry to daily point-source river forcing from 2000–2019. We compute daily riverine biogeochemical export by combining point-source freshwater discharge from the JRA55-do atmospheric reanalysis with the Global NEWS 2 watershed model (Mayorga et al., 2010; Suzuki et al., 2018; Tsujino et al., 2018;

Feng et al., 2021). We then investigate the respective contribution of dissolved organic and inorganic carbon, nitrogen, and silica to air-sea CO<sub>2</sub> fluxes at coastal, basin, and global scales, as performed in Lacroix et al. (2020). This paper provides new tools and methods for improved estimates of how riverine biogeochemical exports impact ocean carbon cycling, which is pivotal for understanding the response of ocean biogeochemistry to anthropogenic perturbations on land.

## 2 Methods

### 2.1 The ECCO-Darwin Ocean Biogeochemistry State Estimate

The ECCO-Darwin ocean biogeochemistry state estimate is extensively described in Brix et al. (2015), Manizza et al. (2019) and Carroll et al. (2020, 2022, 2024). For the ECCO-Darwin solution presented in this paper, ocean physics (circulation, temperature, salinity, and sea ice) are provided by the Estimating the Circulation and Climate of the Ocean (ECCO) global-ocean and sea-ice data synthesis version 4 release 5 (V4r5) (Forget et al., 2015).

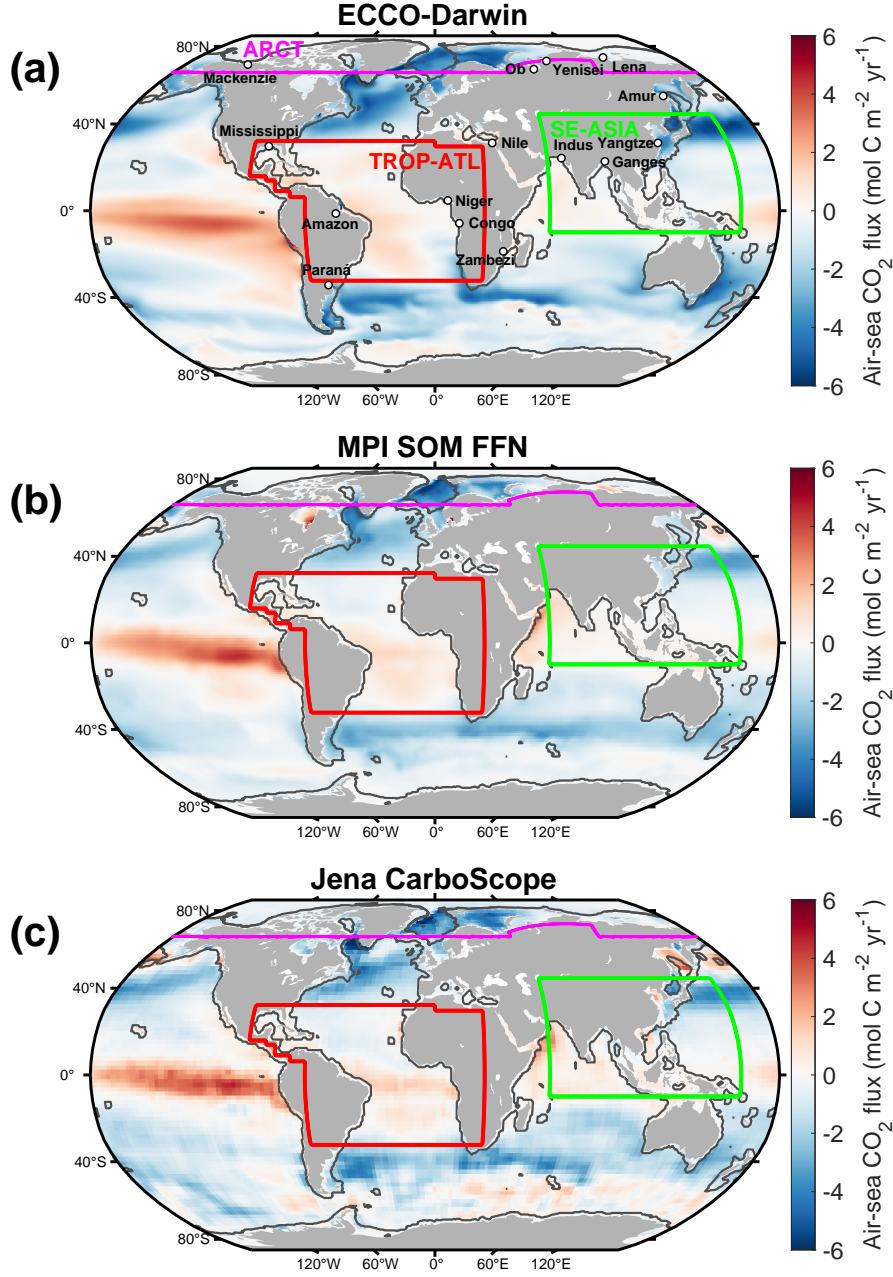
The horizontal grid is based on the LLC90 (Lat-Lon-Cap 90) grid, which is described in detail in (Forget et al., 2015). The nominal horizontal grid resolution in ECCO v4 LLC90 is 1° (~55 km at high latitudes). The vertical discretization consists of 50 z-levels, ranging from 10-m thickness in the top 7 levels to 450 m at depth. ECCO v4 uses a third-order, direct-space-time tracer advection scheme in the horizontal and an implicit third-order upwind scheme in the vertical; a time step of 3600 s is used. Vertical mixing is parameterized using the Gaspar–Grégoris–Lefevre (GGL) mixing-layer turbulence closure and convective adjustment scheme (Gaspar et al., 1990). ECCO v4 assimilates physical observations via the 4-D adjoint method (Wunsch et al., 2009; Wunsch & Heimbach, 2013).

Daily river runoff in the present configuration is based on the Japanese 55-year atmospheric reanalysis (JRA55-do) river forcing dataset, which uses the CaMa-Flood global river routing model and adjusted runoff from the land component of JRA-55 (Suzuki et al., 2018; Tsujino et al., 2018; Feng et al., 2021). Point source JRA55-do freshwater runoff (m s<sup>-1</sup>) was added to ECCO v4 as a real freshwater flux in the surface ocean (first vertical level) at the closest ECCO v4 LLC90 grid cell along the coastal periphery. The freshwater flux was adjusted according to the difference in grid cell area between JRA55-do (0.25°x 0.25°) and ECCO v4 LLC90. A full evaluation of ocean physics from ECCO v4 LLC90 compared to observations can be found in the Supporting Information and Feng et al. (2021).

ECCO v4 LLC90 ocean physics was coupled online with the Massachusetts Institute of Technology Darwin Project ecosystem model described in Brix et al. (2015). The ecosystem model solves 39 prognostic variables such as carbon, nitrogen, phosphorus, iron, silica, oxygen, and alkalinity. The model simulates their respective cycle from inorganic pools to living/dead matter of plankton organisms and the subsequent remineralization, all driven by the ocean physics. The carbonate chemistry is solved by the method in Follows et al. (2006). Plankton species consist of five large-to-small functional phytoplankton types (diatoms, other large eukaryotes, *Synechococcus*, and low- and high-light adapted *Prochlorococcus*), and two zooplankton types. Atmospheric CO<sub>2</sub> partial pressure at sea level (apCO<sub>2</sub>) from the National Oceanic and Atmospheric Administration Marine Boundary Layer Reference product (Andrews et al., 2014) was used to drive air-sea CO<sub>2</sub> fluxes computed by the model according to Wanninkhof (1992). Atmospheric iron dust is deposited at the ocean surface based on the monthly climatology of Mahowald et al. (2009). Once at the ocean bottom, particulate inorganic and organic matter is removed at the sinking rate to limit the accumulation of particulates on the seafloor. Biogeochemical observations were used to optimize the biogeochemical model using a Green’s



176 Functions approach (Menemenlis et al., 2005); the optimization methodology and asso-  
177 ciated data are fully described in Carroll et al. (2020). The ECCO-Darwin solution was  
178 previously published using monthly climatological freshwater runoff forcing from Fekete  
179 et al. (2002). Here, the Baseline simulation consists of the same ocean biogeochemistry  
180 simulation as Carroll et al. (2020), but with daily point-source freshwater runoff from  
181 January 1992 to December 2019. To allow partial adjustment to these new boundary con-  
182 ditions, the analysis period hereinbelow spans the last 20 years of the simulation, Jan-  
183 uary 2000 to December 2019. Figure 1 shows the general match-up between time-mean  
184 ECCO-Darwin air-sea CO<sub>2</sub> fluxes and the MPI SOM FFN v2022 (Landschützer et al.,  
185 2016; Jersild et al., 2023) and Jena CarboScope v2023 (Rödenbeck et al., 2013) prod-  
186 ucts for the 2000–2019 study period.



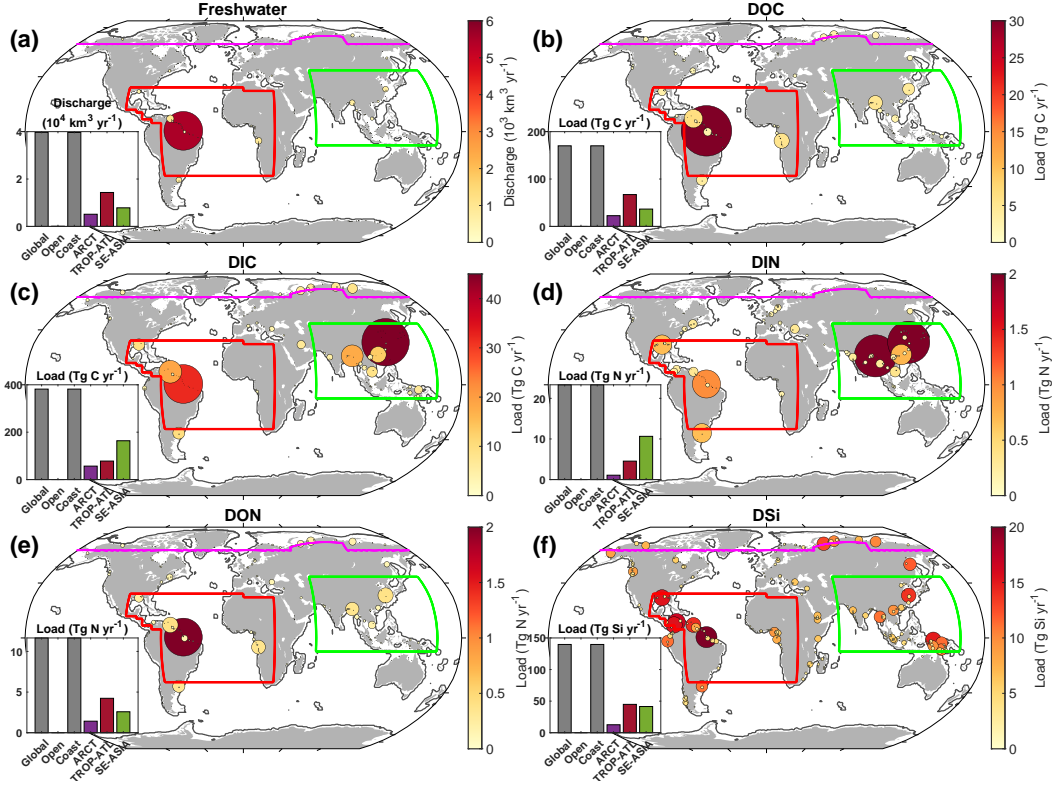
**Figure 1.** Climatological global-ocean air-sea CO<sub>2</sub> flux for (a) ECCO-Darwin Baseline, (b) MPI SOM FFN, and (c) Jena CarboScope. Positive values represent CO<sub>2</sub> outgassing (red colors); negative values are uptake (blue colors). All fields shown are time means from January 2000 to December 2019. Colored boundary lines correspond to domains used for regional analysis of the Arctic Ocean (ARCT, violet line), the Tropical Atlantic (TROP-ATL, red line), and Southeast Asia (SE-ASIA, green line). The black line delineates the coastal ocean from the open ocean, which is set by the furthest point from the coastline of either a 300-km distance or the 1000-m isobath. White points show river mouth locations for the top-15 global rivers in terms of watershed area. MPI SOM FFN v2022 and Jena CarboScope v2023 products were interpolated on the ECCO v4 LLC90 grid.

## 2.2 Biogeochemical River Runoff

In addition to the Baseline simulation, we conducted a suite of sensitivity experiments where we added terrestrial DOC ( $t_{DOC}$ ), DIC ( $t_{DIC}$ ), total alkalinity ( $t_{ALK}$ ), dissolved inorganic nitrogen ( $t_{DIN}$ ), dissolved organic nitrogen ( $t_{DON}$ ), and dissolved silica ( $t_{DSi}$ ), henceforth referred to as riverine exports in this study. We excluded phosphorus and iron due to the complexity of their reactions when entering the marine environment (i.e., absorption, bio-availability). Except for  $t_{DIC}$  and  $t_{ALK}$ , riverine exports are provided by the Global NEWS 2 (Global Nutrient Export from WaterSheds) model (Mayorga et al., 2010).

Global NEWS 2 uses statistical and mechanistic relations at the watershed scale to compute annual-mean freshwater discharge and riverine loads based on natural and anthropogenic sources, with 6292 individual watersheds delineated according to the global river systems dataset from Vörösmarty et al. (2000).  $t_{DIN}$  was partitioned into nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), and ammonium ( $\text{NH}_4^+$ ), according to the mean fraction of each species concentration relative to the total DIN concentration from the GLObal RIver CHEmistry Database (GLORICH) (Hartmann et al., 2014). The  $\text{NO}_2^-$ :DIN,  $\text{NO}_3^-$ :DIN, and  $\text{NH}_4^+$ :DIN ratios were estimated to be 0.02, 0.65, and 0.33, respectively. Riverine  $t_{DIC}$  loads were computed using an empirical relation between freshwater discharge and gross  $\text{CO}_2$  consumption from rock weathering as described in M. Li et al. (2017, equation 9).  $\text{CO}_2$  consumption by rock weathering over each Global NEWS 2 watershed was estimated based on the freshwater discharge and the basin-dominant lithology (Amiotte Suchet et al., 2003).  $t_{ALK}$  loads were computed using an ALK:DIC ratio (0.98) based on the mean total ALK compared to DIC from GLORICH.  $t_{DOC}$  was not considered to be more refractory than marine DOC; the DOC remineralization rate is set to 1 over 100 days. We used Global NEWS 2 outputs for year 2000 as representative of present-day carbon and nutrient loads (Mayorga et al., 2010).

Global NEWS 2 river mouth locations were associated with JRA55-do grid points exhibiting the closest annual-mean freshwater discharge in 2000 within a euclidean distance of  $5^\circ$ . The top-100 largest rivers (by watershed extent) from Global NEWS 2 were imposed on JRA55-do grid points as a function of distance only. In total, 5171 river mouths were associated with JRA55-do grid points. For each discharge point, export concentrations from the associated river were estimated by dividing the load by the annual volume of freshwater from Global NEWS 2; the concentration was then converted to a daily flux using the corresponding daily-mean freshwater flux from JRA55-do. Exports were adjusted according to the grid cell area difference between JRA55-do and ECCO v4 LLC90. These biogeochemical exports were then added as point-source discharge along riverine freshwater flux (Figure 2). Due to extreme values in our automated Global-NEWS-2-derived computation for the Amazon River, the DIC load for this system was set to a more-realistic, literature-mean of  $2.54 \text{ Tmol yr}^{-1}$  (da Cunha & Buitenhuis, 2013; Probst et al., 1994; M. Li et al., 2017) (for more details see Supporting Information Text S1).



**Figure 2.** Riverine freshwater discharge and biogeochemical exports resulting from the association of Global NEWS 2 and JRA55-do on the ECCO v4 LLC90 grid. Domain-scale freshwater discharge and load is relative to the respective domain area. Insets show corresponding year-2000 discharge/load for various regions. The size of circles represents magnitude of loads. Colored boundaries correspond to domains used for regional analysis. The black line delineates the coastal ocean from the open ocean. Only rivers with annual discharge over  $10 \text{ km}^3 \text{ yr}^{-1}$  are shown.

As riverine  $t_{DOC}$ ,  $t_{DIN}$ ,  $t_{DON}$ , and  $t_{DSi}$  were computed from Global NEWS 2 concentration and modulated with JRA55-do freshwater runoff, our fluxes agree well with existing estimates based on the NEWS 2 database (Mayorga et al., 2010; Frings et al., 2016; Sharples et al., 2017; Lacroix et al., 2020; Tivig et al., 2021; Tian et al., 2023).  $t_{DIC}$  lateral export from rivers was estimated according to Amiotte Suchet et al. (2003); Mayorga et al. (2010); M. Li et al. (2017), resulting in a  $t_{DIC}$  load of  $381.81 \text{ Tg C yr}^{-1}$  to the ocean, which is in general agreement with recent studies (Drake et al., 2018; M. Li et al., 2017; Lacroix et al., 2020; Battin et al., 2023; Tian et al., 2023).

### 2.3 Sensitivity Experiments and Analysis

Sensitivity experiments consisted of adding riverine exports separately or together along with freshwater runoff (Table 1).  $t_{ALK}$  was always added along with  $t_{DIC}$  in relevant experiments. Moreover, we ran additional sensitivity experiments using all riverine exports (Table 1,  $ALL_{run}$ ) for each of the top-15 global rivers in terms of watersheds extent (Mayorga et al., 2010). Ancient river systems and rivers terminating in enclosed basins or on land were discarded from our analysis. The locations of the corresponding top-15 river mouths are shown in Figure 1.

**Table 1.** Annual carbon and nutrient loads in runoff sensitivity experiments.

Experiment Name	$t_{DOC}$ (Tg C yr <sup>-1</sup> )	$t_{DIC}$ (Tg C yr <sup>-1</sup> )	$t_{DON}$ (Tg N yr <sup>-1</sup> )	$t_{DIN}$ (Tg N yr <sup>-1</sup> )	$t_{DSi}$ (Tg Si yr <sup>-1</sup> )
Baseline	0	0	0	0	0
DC <sub>run</sub>	170.1	381.8	0	0	0
DIC <sub>run</sub>	0	381.8	0	0	0
DN <sub>run</sub>	0	0	11.7	23.3	0
DIN <sub>run</sub>	0	0	0	23.3	0
DSi <sub>run</sub>	0	0	0	0	139.7
ALL <sub>run</sub>	170.1	381.8	11.7	23.3	139.7

We analyzed monthly-mean model fields along the coastal ocean (limits set by the furthest point from the coastline, either the 1000-m isobath or a distance of 300 km; 58 x 10<sup>6</sup> km<sup>2</sup>) and the open ocean (300 x 10<sup>6</sup> km<sup>2</sup>) during 2000–2019. In addition to the global ocean, we also evaluated the sensitivity of ocean carbon cycling in three specific regions that receive large volumes of freshwater from major river systems: the Arctic Ocean (ARCT, 22 x 10<sup>6</sup> km<sup>2</sup>), Tropical Atlantic (TROP-ATL, 77 x 10<sup>6</sup> km<sup>2</sup>), and Southeast Asia (SE-ASIA, 62 x 10<sup>6</sup> km<sup>2</sup>). Coastal and open ocean boundaries are delineated by the black line in Figure 1. Monthly-mean net primary production (NPP) was integrated over the upper 100 m.

Furthermore, we separated the respective contributions of 1) the solubility pump and 2) primary production resulting from river-driven changes in climatological air-sea CO<sub>2</sub> flux ( $\Delta\text{CO}_2$ ) in the ALL<sub>run</sub> as:

$$\Delta\text{CO}_2_{ALL_{run}} = \Delta\text{CO}_2^{\text{solub}^C} + \Delta\text{CO}_2^{\text{solub}^{N,Si}} + \Delta\text{CO}_2^{\text{NPP}^{N,Si}}, \quad (1)$$

where  $\Delta\text{CO}_2^{\text{solub}^C}$  and  $\Delta\text{CO}_2^{\text{solub}^{N,Si}}$  are the changes in air-sea CO<sub>2</sub> flux associated with the solubility pump due to the addition of terrestrial carbon and nitrogen/silica, respectively.  $\Delta\text{CO}_2^{\text{NPP}^{N,Si}}$  is the change in air-sea CO<sub>2</sub> flux driven by NPP in response to terrestrial nitrogen and silica.

In DC<sub>run</sub>, changes in air-sea CO<sub>2</sub> flux are only associated with the solubility pump:

$$\Delta\text{CO}_2^{\text{solub}^C} = \Delta\text{CO}_2_{DC_{run}}. \quad (2)$$

We then associated the change in surface-ocean DIC concentration with  $\Delta\text{CO}_2$  driven by the solubility pump in DC<sub>run</sub> to isolate  $\Delta\text{CO}_2$  due to the solubility pump relative to changes in surface-ocean DIC concentration in DN and DSi<sub>runs</sub>:

$$\Delta\text{CO}_2^{\text{solub}^{N,Si}} = \frac{\Delta\text{CO}_2^{\text{solub}^C}}{[DIC]_{surf}^C} \times [DIC]_{surf}^{N,Si}. \quad (3)$$

The change in  $\Delta\text{CO}_2$  due to changes in NPP in DN and DSi<sub>runs</sub> was then estimated by subtracting  $\Delta\text{CO}_2$  due to the solubility pump from the total  $\Delta\text{CO}_2$ :

$$\Delta\text{CO}_2^{\text{NPP}^{N,Si}} = \Delta\text{CO}_2_{DN,DSi_{runs}} - \Delta\text{CO}_2^{\text{solub}^{N,Si}}. \quad (4)$$

### 3 Results

#### 3.1 Climatological Global Analysis

Along with  $39,687 \text{ km}^3 \text{ yr}^{-1}$  of riverine freshwater, total loads of  $551.9 \text{ Tg C yr}^{-1}$ ,  $35 \text{ Tg N yr}^{-1}$ , and  $139.7 \text{ Tg Si yr}^{-1}$  were exported into the global ocean in  $\text{ALL}_{run}$  (Table 1). The addition of dissolved carbon, nitrogen, and silica in  $\text{ALL}_{run}$  led to an increase in  $\text{CO}_2$  outgassing of  $0.03 \text{ Pg C yr}^{-1}$  compared to the Baseline, globally (Figure 3a and Figure 4a, Table 2). The majority of  $\text{CO}_2$  outgassing ( $0.04 \text{ Pg C yr}^{-1}$ ) occurs in the coastal ocean (Figure 3a and Table 2). In the open ocean, riverine exports slightly increased  $\text{CO}_2$  uptake by  $0.01 \text{ Pg C yr}^{-1}$  (Figure 3a and Table 2).

In  $\text{ALL}_{run}$ , changes in air-sea  $\text{CO}_2$  flux resulted from compensation between the effects of riverine carbon and nitrogen, as  $\text{DC}_{run}$  and  $\text{DN}_{run}$  experiments result in elevated  $\text{CO}_2$  outgassing and uptake, respectively (Table 2). In  $\text{DC}_{run}$ , the increase in ocean carbon due to riverine exports diminished the ocean's capacity to take up atmospheric  $\text{CO}_2$ , resulting in a net  $\text{CO}_2$  outgassing of  $0.22 \text{ Pg C yr}^{-1}$  (Table 2). In  $\text{DN}_{run}$ , the increase in nutrients to the euphotic zone led to increased phytoplankton productivity. The additional uptake of carbon by phytoplankton decreased surface-ocean DIC, resulting in an additional  $\text{CO}_2$  sink of  $0.17 \text{ Pg C yr}^{-1}$  (Table 2).

$\text{CO}_2$  outgassing driven by riverine carbon ( $\text{DC}_{run}$ ) was dominated by  $t_{DOC}$  (70%), with a smaller contribution from  $t_{DIC}$  (30%) (Figure 4a). While outgassing driven by riverine carbon was compensated by uptake due to nitrogen in the open ocean,  $\text{CO}_2$  uptake due to nitrogen was 36% lower than riverine-carbon-driven coastal outgassing, leading to global-ocean net  $\text{CO}_2$  outgassing in  $\text{ALL}_{run}$  (Table 2).

Riverine dissolved carbon, nitrogen, and silica also resulted in a NPP increase of  $0.6 \text{ Pg C yr}^{-1}$  (+2%) compared to Baseline (Figure 3b and Figure 4b, Table 2). Riverine  $t_{DIN}$  ( $\text{DIN}_{run}$ ) contributed to 70% and 86% of the  $\text{CO}_2$  uptake and NPP increase simulated in  $\text{DN}_{run}$ , respectively (Figure 4b). The total increase of NPP in  $\text{ALL}_{run}$  from riverine exports was equally distributed between the coastal and open ocean ( $0.3 \text{ Pg C yr}^{-1}$  for each) (Figure 4b). However, the increase of NPP was stronger in the coastal ocean ( $+5.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ , +7%) compared to the open ocean ( $+1 \text{ g C m}^{-2} \text{ yr}^{-1}$ , +1%) relative to their surface area.



**Table 2.** Air-sea CO<sub>2</sub> flux and NPP for each experiment in the coastal ocean, open ocean, and global ocean. Positive values represent CO<sub>2</sub> outgassing; negative values are uptake.

Domain	Experiment	CO <sub>2</sub> Flux (Pg C yr <sup>-1</sup> )	NPP (Pg C yr <sup>-1</sup> )
<b>Coastal Ocean</b>	Baseline	-0.68	3.8
	ALL <sub>run</sub> - Baseline	+0.04	+0.3
	DC <sub>run</sub> - Baseline	+0.1	0.0
	DN <sub>run</sub> - Baseline	-0.07	+0.3
	DSi <sub>run</sub> - Baseline	-0.01	+0.01
<b>Open Ocean</b>	Baseline	-1.90	20.6
	ALL <sub>run</sub> - Baseline	-0.01	+0.3
	DC <sub>run</sub> - Baseline	+0.1	0.0
	DN <sub>run</sub> - Baseline	-0.1	+0.3
	DSi <sub>run</sub> - Baseline	-0.01	+0.01
<b>Global Ocean</b>	Baseline	-2.58	24.4
	ALL <sub>run</sub> - Baseline	+0.03	+0.6
	DC <sub>run</sub> - Baseline	+0.22	0.0
	DN <sub>run</sub> - Baseline	-0.17	+0.6
	DSi <sub>run</sub> - Baseline	-0.01	+0.01

### 3.2 Climatological Regional Analysis

The Arctic Ocean region (Figure 1, ARCT) received 5,138 km<sup>3</sup> yr<sup>-1</sup> of freshwater from rivers in Baseline, which is roughly 13% of global freshwater discharge. In ALL<sub>run</sub>, freshwater discharge was supplemented with 22.6 and 56.8 Tg C yr<sup>-1</sup> of t<sub>DOC</sub> and t<sub>DIC</sub>, respectively (Figure 2). The river load of carbon and t<sub>DOC</sub> into ARCT represented 15% and 12% of their associated global loads, respectively. ARCT also received 2.5 Tg N yr<sup>-1</sup> as t<sub>DON</sub> (56%) and t<sub>DIN</sub> (44%) in ALL<sub>run</sub>. The t<sub>DSi</sub> river load was 12.6 Tg Si yr<sup>-1</sup> (Figure 2) in this region. Riverine export loads were primarily from the Ob, Yenisei, Lena, and Mackenzie Rivers (Figure 2 and Supporting Information Table S1).

In Baseline, ARCT produced a CO<sub>2</sub> uptake of roughly 0.21 Pg C yr<sup>-1</sup>. When riverine carbon, nitrogen, and silica were added in ALL<sub>run</sub>, ARCT CO<sub>2</sub> uptake was reduced by 0.02 Pg C yr<sup>-1</sup>, with the majority of the response (80%) in the coastal ocean (Figure 3a and Figure 4a). Riverine-induced CO<sub>2</sub> outgassing was dominated by the input of t<sub>DOC</sub> in ARCT (Figure 4a). 50% of the riverine-induced CO<sub>2</sub> outgassing was due to the Ob, Yenisei, Lena, and Mackenzie Rivers (Table 3). In the Baseline experiment, NPP was 0.22 Pg C yr<sup>-1</sup>, with a similar magnitude in the coastal and open ocean. The addition of riverine nitrogen into ARCT increased coastal NPP by 40% (Figure 3b and Figure 4b).

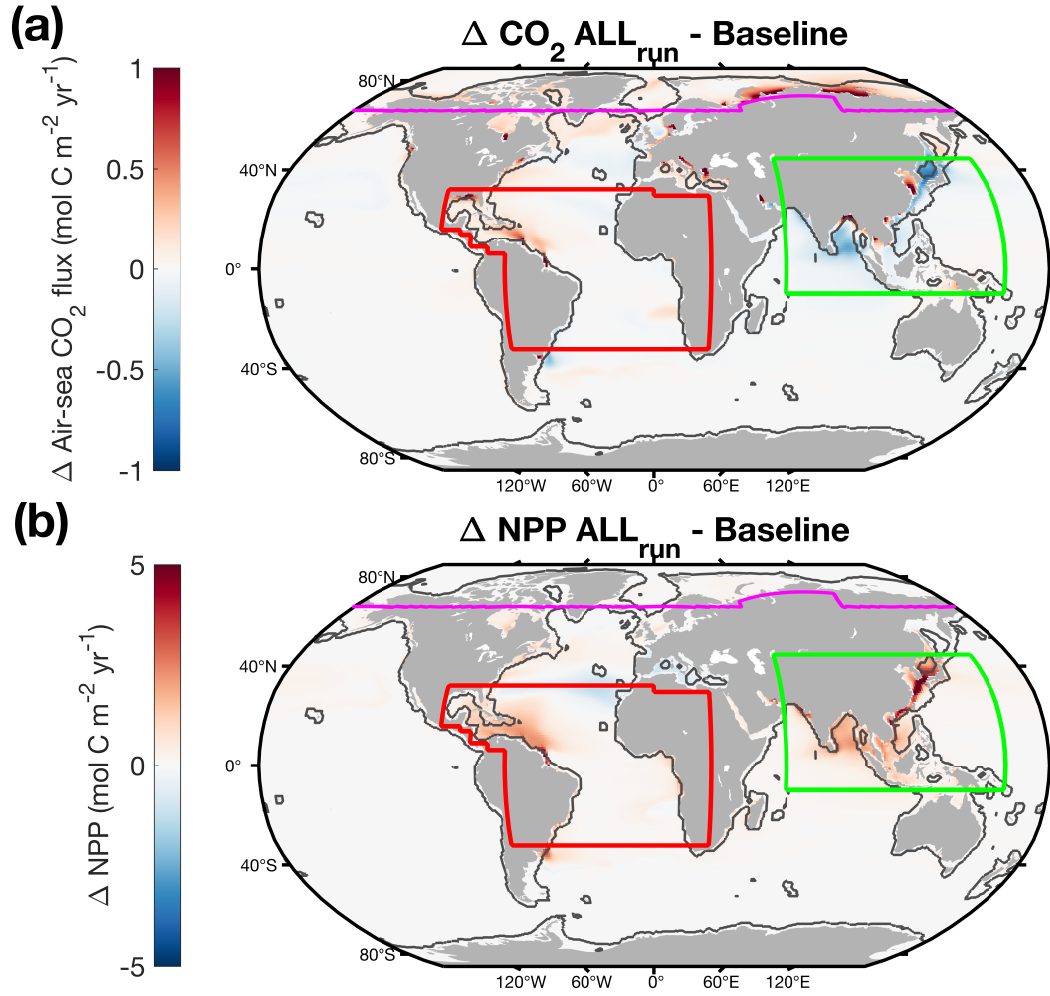
The Tropical Atlantic (Figure 1, TROP-ATL) received 36% of global freshwater discharge (14,228 km<sup>3</sup> yr<sup>-1</sup>) and 35% of the global t<sub>DOC</sub> load from rivers (67.2 Tg C yr<sup>-1</sup>). Combined with t<sub>DIC</sub>, the net carbon load was 145.3 Tg C yr<sup>-1</sup> (Figure 2). Roughly 30% of the global dissolved nitrogen and silica river load was delivered to TROP-ATL, with river loads dominated by the Amazon River (Figure 2 and Supporting Information Table S1).

Riverine carbon, nitrogen, and silica resulted in a TROP-ATL CO<sub>2</sub> outgassing of 0.02 Pg C yr<sup>-1</sup> compared to Baseline (0.10 Pg C yr<sup>-1</sup>). This imbalance resulted from CO<sub>2</sub> outgassing driven by carbon, which was 30% larger than uptake due to increased phytoplankton productivity from riverine nitrogen (Figure 4a). 85% of CO<sub>2</sub> outgassing in DC<sub>run</sub> was driven by riverine  $t_{DOC}$  (Figure 4a). Riverine  $t_{DOC}$  indirectly drives CO<sub>2</sub> outgassing by first being remineralized to DIC, which increases DIC concentration in the ocean and thus limits the ocean's capacity to take up atmospheric CO<sub>2</sub>. Most of the CO<sub>2</sub> outgassing driven by  $t_{DOC}$  occurs in the open ocean (Figure 3a and Figure 4a). The Amazon River drove 70% of riverine-induced CO<sub>2</sub> outgassing in TROP-ATL (Table 3). In Baseline, NPP in TROP-ATL was 3.18 Pg C yr<sup>-1</sup>. The increase in NPP driven by riverine  $t_{DIN}$  occurred predominantly in the open ocean (~60%) compared to the coastal (~40%) zone (Figure 4b). The Amazon River was responsible for 65% of the NPP increase driven by riverine exports (Figure 4b).

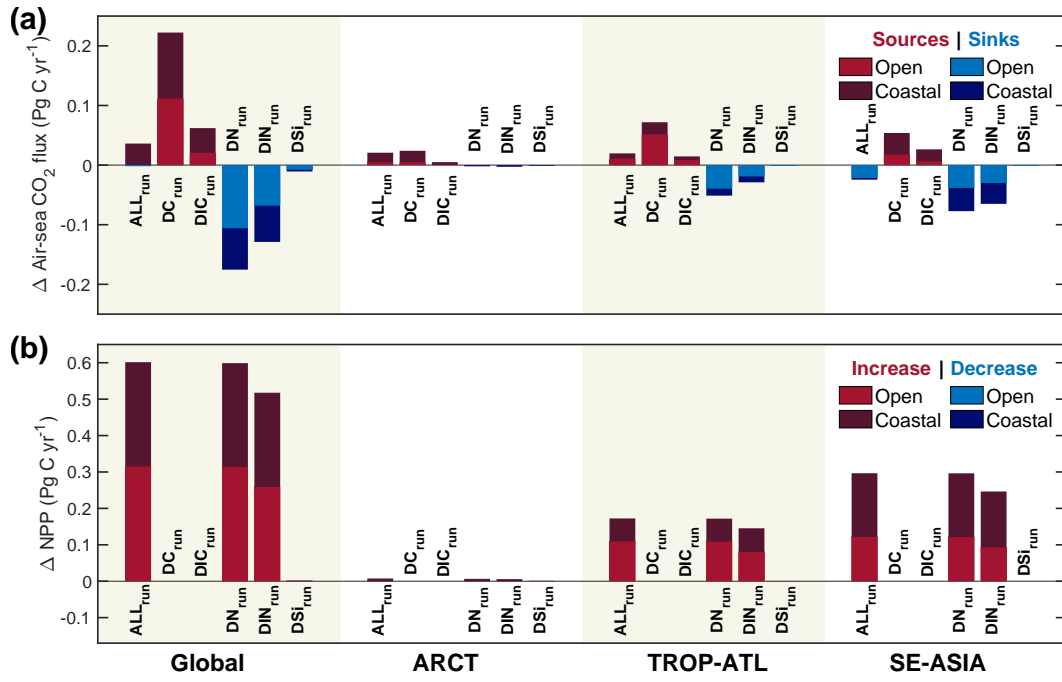
In Baseline, the freshwater discharge into SE-ASIA was 7,841 km<sup>3</sup> yr<sup>-1</sup>, roughly 20% of global discharge. In ALL<sub>run</sub>, SE-ASIA received 38% of dissolved carbon from rivers, globally (207.39 Tg C yr<sup>-1</sup>). 81% of dissolved carbon delivered into SE-ASIA was inorganic, representing 42% of the global  $t_{DIC}$  river load (Figure 2). SE-ASIA also received 45% (10.6 Tg N yr<sup>-1</sup>) of the global  $t_{DIN}$  load from rivers (Figure 2). 41.5 Tg Si yr<sup>-1</sup> was discharged into SE-ASIA (Figure 2). Nutrient loads into SE-ASIA were dominated by high riverine  $t_{DIC}$  and  $t_{DIN}$  from the Ganges and Yangtze Rivers (Figure 2 and Supporting Information Table S1). The Yangtze river contributed 12% of  $t_{DIC}$  river loads, globally (Figure 2 and Supporting Information Table S1). Taken together, the Yangtze and Ganges Rivers delivered 20% of the global  $t_{DIN}$  river load (Figure 2 and Supporting Information Table S1).

SE-ASIA had a CO<sub>2</sub> sink of 0.30 Pg C yr<sup>-1</sup> in Baseline, while CO<sub>2</sub> uptake increased by 0.02 Pg C yr<sup>-1</sup> in ALL<sub>run</sub> (Figure 4a). Riverine carbon- and nitrogen-driven air-sea CO<sub>2</sub> flux was compensated in the coastal ocean ( $\pm 0.03$  Pg C yr<sup>-1</sup>). However, in the open ocean, the riverine nitrogen-driven increase in NPP and associated CO<sub>2</sub> uptake was two times higher than carbon-driven outgassing — leading to an overall imbalance and resulting in net CO<sub>2</sub> uptake in the domain (Figure 4a).

$t_{DIN}$  was responsible for 85% of biological CO<sub>2</sub> uptake (Figure 4a). The Ganges River (58%), combined with the Indus and Yangtze Rivers, were responsible for 77% of CO<sub>2</sub> uptake in SE-ASIA (Table 3). NPP in SE-ASIA without the addition of riverine exports was 3.3 Pg C yr<sup>-1</sup>. In ALL<sub>run</sub>, NPP increased by 0.30 Pg C yr<sup>-1</sup> due to elevated  $t_{DIN}$  in both the open and coastal ocean (Figure 4b). The Ganges and Yangtze Rivers caused roughly 40% of the NPP increase in SE-ASIA (Table 3).



**Figure 3.** Global-ocean (a) air-sea CO<sub>2</sub> flux and (b) NPP driven by riverine exports in ALL<sub>run</sub>. Fields represent time-mean values from January 2000 to December 2019. Colored lines on maps show domains used for regional analysis. The black line delineates the coastal ocean from the open ocean.



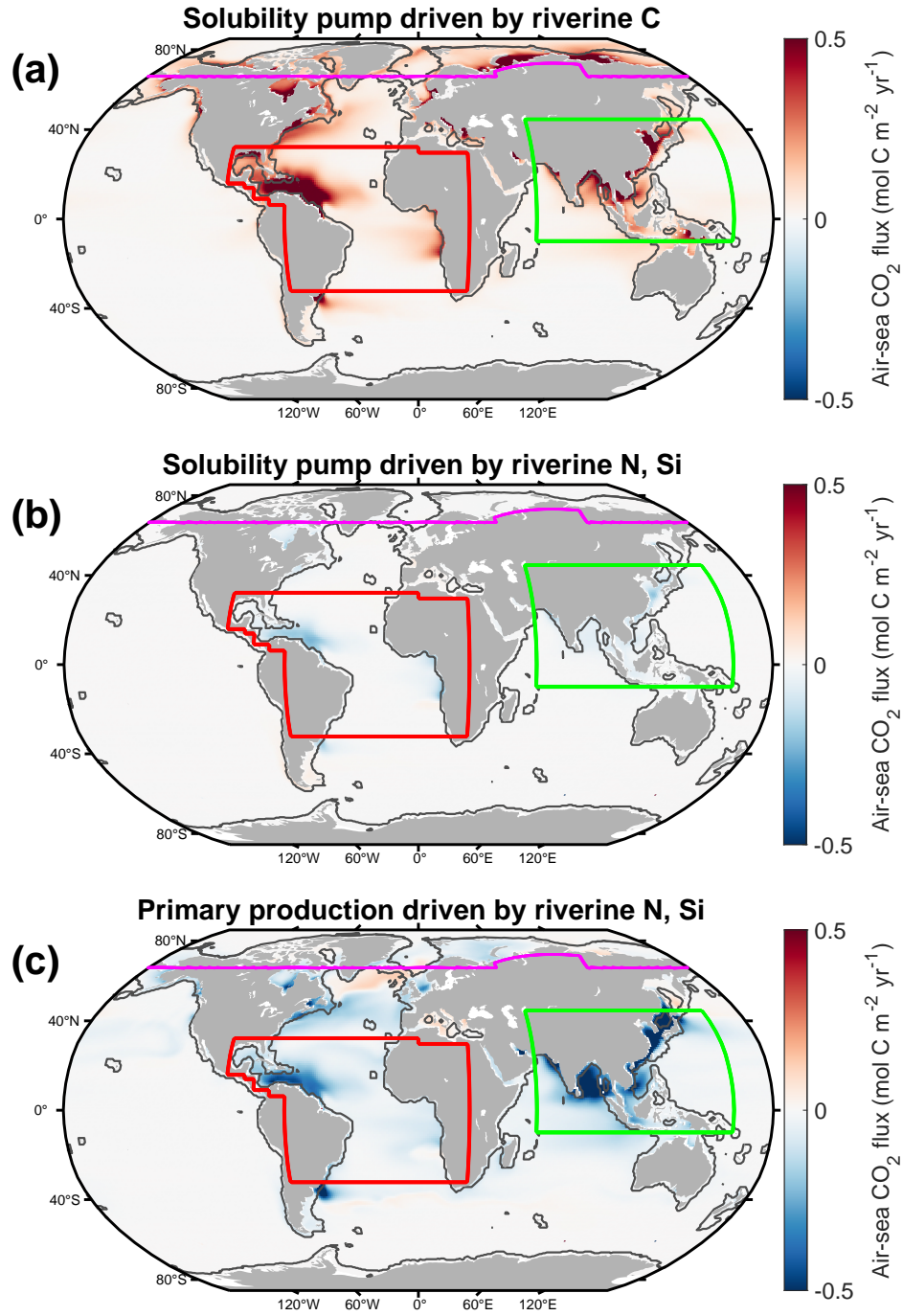
**Figure 4.** Domain-integrated differences in (a) air-sea  $\text{CO}_2$  flux and (b) NPP driven by riverine exports in each sensitivity experiment. Differences were computed from time-mean fields from January 2000 to December 2019. The black line delineates the coastal ocean from the open ocean.

**Table 3.** Contribution of the global top-15 rivers in terms of watershed area to changes in air-sea CO<sub>2</sub> flux and NPP. Positive values represent CO<sub>2</sub> outgassing driven by the corresponding river; negative values are uptake. The respective river contribution is estimated from the difference between Baseline and a modified ALL<sub>run</sub>, where only the corresponding river was included. Locations of river mouths are shown in Figure 1.

Rank	River	$\Delta \text{CO}_2 \text{ Flux}$ (Tg C yr <sup>-1</sup> )	$\Delta \text{NPP}$ (Tg C yr <sup>-1</sup> )
1	Amazon	+14.3	+113.6
2	Nile	+0.3	-0.1
3	Congo	+1.3	+12.4
4	Mississippi	-1.3	+26.4
5	Ob	+2	+2.2
6	Paraná	+0.5	+13.5
7	Yenisei	+2.6	+1.5
8	Lena	+2.8	+1.1
9	Niger	-0.1	+3
10	Yangtze	-3	+57.3
11	Amur	+0.7	+1.7
12	Mackenzie	+1.7	+0.6
13	Ganges	-11.7	+64.5
14	Zambezi	+0.1	+1
15	Indus	-0.7	+3.7
N/A	Total	+9.5	+302.4

### 3.3 Mechanisms of River-driven Air-sea CO<sub>2</sub> Flux

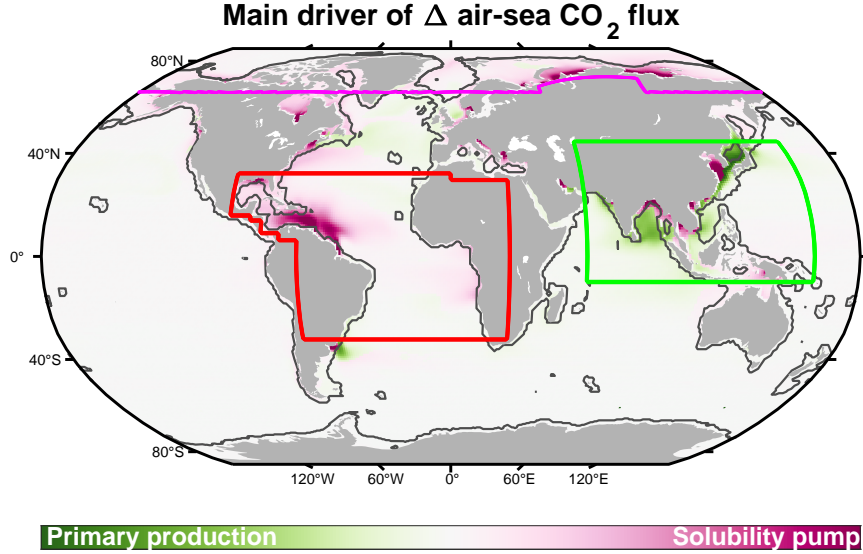
From January 2000 to December 2019, the time-mean surface-ocean DIC mass in DC<sub>run</sub> increased by 370.7 Tg C. This triggered a solubility-pump-driven outgassing of 222.4 Tg C yr<sup>-1</sup> (Figure 4a). Over the same period, the addition of terrestrial nitrogen and silica, the sum of DN<sub>run</sub> and DSi<sub>run</sub>, drove a reduction of 21.5 Tg C in the surface-ocean DIC mass. Assuming the same ratio of surface-ocean DIC and air-sea CO<sub>2</sub> flux as in DC<sub>run</sub>, the input of terrestrial nitrogen and silica will cause a CO<sub>2</sub> uptake of 12.9 Tg C yr<sup>-1</sup> (Figure 4b). Since the net ocean CO<sub>2</sub> uptake increased by 186.2 Tg C yr<sup>-1</sup> in response to terrestrial nitrogen and silica fertilization of NPP, the net increase in global CO<sub>2</sub> uptake is 173.3 Tg C yr<sup>-1</sup> (Figure 4c).



**Figure 5.** Climatological (January 2000 to December 2019) air-sea CO<sub>2</sub> flux associated with (a) change in the solubility pump driven by riverine carbon, (b) change in the solubility pump driven by riverine nitrogen and silica, and (c) NPP driven by riverine nitrogen and silica. Colored lines on maps show domains used for regional analysis. The black line delineates the coastal ocean from the open ocean.



Overall, the change in air-sea CO<sub>2</sub> flux driven by riverine exports was dominated 1) by the solubility pump near river mouths in response to terrestrial carbon and 2) by NPP in the open ocean where CO<sub>2</sub> uptake from nitrogen- and silica-driven phytoplankton blooms exceeded riverine carbon-driven outgassing (Figure 4 and Figure 6). TROP-ATL and ARCT were dominated by riverine-driven CO<sub>2</sub> outgassing (71.9 and 24 Tg C yr<sup>-1</sup>, respectively) and CO<sub>2</sub> uptake due to NPP fertilization in TROP-ATL and ARCT was minor (44.4 and 3.3 Tg C yr<sup>-1</sup>, respectively). In SE-ASIA, the increase of CO<sub>2</sub> uptake due to enhanced NPP (69.6 Tg C yr<sup>-1</sup>) exceeded CO<sub>2</sub> outgassing driven by riverine carbon (53.9 Tg C yr<sup>-1</sup>).



**Figure 6.** Pathways of change in climatological (January 2000 to December 2019) air-sea CO<sub>2</sub> flux driven by riverine exports. Colors represent the dominant flux shown in Figure 4. The black line delineates the coastal ocean from the open ocean.

## 4 Discussion

### 4.1 Fate of Riverine Dissolved Carbon and Nutrients

Once in the ocean, terrestrial dissolved carbon ( $t_{DOC}$  and  $t_{DIC}$ ) result in a source of CO<sub>2</sub> to the atmosphere through a reduction of the solubility pump (Figure 7). Terrestrial nutrients, such as nitrogen and silica ( $t_{DIN}$ , and  $t_{DSi}$ ), fertilize phytoplankton and elevate CO<sub>2</sub> uptake via increased NPP.

The resultant export of marine organic carbon ( $m_{OC}$ ) from the surface ocean drives additional CO<sub>2</sub> uptake via the solubility pump; at depth, the exported  $m_{OC}$  is remineralized to inorganic carbon ( $m_{IC}$ ) (Figures 4b and 7). Thus, terrestrial nutrients have the

potential to shift riverine carbon-driven  $\text{CO}_2$  outgassing to uptake, due to assimilation of carbon by primary producers. Despite a stronger increase of NPP in the coastal ocean ( $+5.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ ,  $+7\%$ ) compared to the open ocean ( $+1 \text{ g C m}^{-2} \text{ yr}^{-1}$ ,  $+1\%$ ), the outgassing of  $\text{CO}_2$  driven by riverine carbon through the solubility pump dominates changes in air-sea  $\text{CO}_2$  flux close to river mouths. In contrast, the riverine nitrogen and silica signal spreads further offshore and enhances NPP and  $\text{CO}_2$  uptake — this mechanism dominates the change in air-sea  $\text{CO}_2$  flux in open-ocean regions.

In carbon-dominated terrestrial margins, such as TROP-ATL and ARCT, rivers drive a large source of  $\text{CO}_2$  from the ocean to the atmosphere. However, in nitrogen-dominated margins, such as SE-ASIA, the addition of lateral fluxes drives a substantial ocean carbon sink. Globally, these two processes tend to compensate each other and our simulations suggest that the addition of riverine dissolved carbon, nitrogen, and silica result in a small net source of atmospheric  $\text{CO}_2$  in the global ocean.

**Table 4.** Riverine exports loads.

Domain	Export (Tg $\text{yr}^{-1}$ )	$\text{ALL}_{\text{run}}$	Literature Value
<b>Global</b>	$t_{\text{DOC}}$	170.1	130–262 <sup>1</sup>
	$t_{\text{DIC}}$	381.8	320–453 <sup>1</sup>
	$t_{\text{DON}}$	11.7	11.8 <sup>1</sup>
	$t_{\text{DIN}}$	23.3	17–22.8 <sup>1</sup>
	$t_{\text{DSi}}$	139.7	158–171 <sup>1</sup>
<b>ARCT</b>	$t_{\text{DOC}}$	22.6	34–37.7 <sup>2</sup>
	$t_{\text{DIC}}$	56.8	57 <sup>2</sup>
	$t_{\text{DON}}$	1.4	0.05–0.84 <sup>2</sup>
	$t_{\text{DIN}}$	1.1	0.04–0.43 <sup>2</sup>
	$t_{\text{DSi}}$	12.6	11.4 <sup>2</sup>
<b>TROP-ATL</b>	$t_{\text{DOC}}$	67.2	46 <sup>3</sup>
	$t_{\text{DIC}}$	78.1	50 <sup>3</sup>
	$t_{\text{DON}}$	4.2	N/A
	$t_{\text{DIN}}$	4.5	15.3 <sup>3</sup>
	$t_{\text{DSi}}$	44.9	53 <sup>3</sup>
<b>SE-ASIA</b>	$t_{\text{DOC}}$	36.6	N/A
	$t_{\text{DIC}}$	163.8	40 <sup>4</sup>
	$t_{\text{DON}}$	2.6	N/A
	$t_{\text{DIN}}$	10.6	2.1–8.4 <sup>4*</sup>
	$t_{\text{DSi}}$	41.5	N/A

<sup>1</sup> (Drake et al., 2018; Mayorga et al., 2010; Frings et al., 2016; Sharples et al., 2017; Lacroix et al., 2020; Tivig et al., 2021; Tian et al., 2023; M. Li et al., 2017; Lacroix et al., 2020; Battin et al., 2023; Tian et al., 2023)

<sup>2</sup> (Manizza et al., 2011; Tank et al., 2012; Holmes et al., 2012; Le Fouest et al., 2013)

<sup>3</sup> (Cotrim da Cunha et al., 2007; Araujo et al., 2014)

<sup>4</sup> (Singh & Ramesh, 2011; H.-M. Li et al., 2014; J. Wang et al., 2020; Nishina et al., 2021; Piao et al., 2012; Patra et al., 2013)

\* Computed from the sum of regional estimates

**Table 5.** Change in air-sea CO<sub>2</sub> flux and NPP driven by riverine exports.

Domain	$\Delta\text{CO}_2/\text{NPP}$	$\text{ALL}_{run}$ (Pg C yr <sup>-1</sup> )	Literature Value (Pg C yr <sup>-1</sup> )
<b>Global</b>	$\Delta\text{CO}_2$	+0.03	+0.11 <sup>1</sup>
	$\Delta\text{NPP}$	+0.6	+0.6–3.9 <sup>1</sup>
<b>ARCT</b>	$\Delta\text{CO}_2$	+22.8	+0.6–20 <sup>2*</sup>
	$\Delta\text{NPP}$	+7.4	+58 <sup>2</sup>
<b>TROP-ATL</b>	$\Delta\text{CO}_2$	+20	+5–20 <sup>3**</sup>
	$\Delta\text{NPP}$	+170	+80–400 <sup>3</sup>
<b>SE-ASIA</b>	$\Delta\text{CO}_2$	-24.7	N/A
	$\Delta\text{NPP}$	+296	+100 <sup>4</sup>

<sup>1</sup> (Tivig et al., 2021; Cotrim da Cunha et al., 2007)<sup>2</sup> (Manizza et al., 2011; Terhaar et al., 2021)<sup>3</sup> (da Cunha & Buitenhuis, 2013; Louchard et al., 2021)<sup>4</sup> (Tivig et al., 2021)\* Effect of  $t_{DOC}$  only

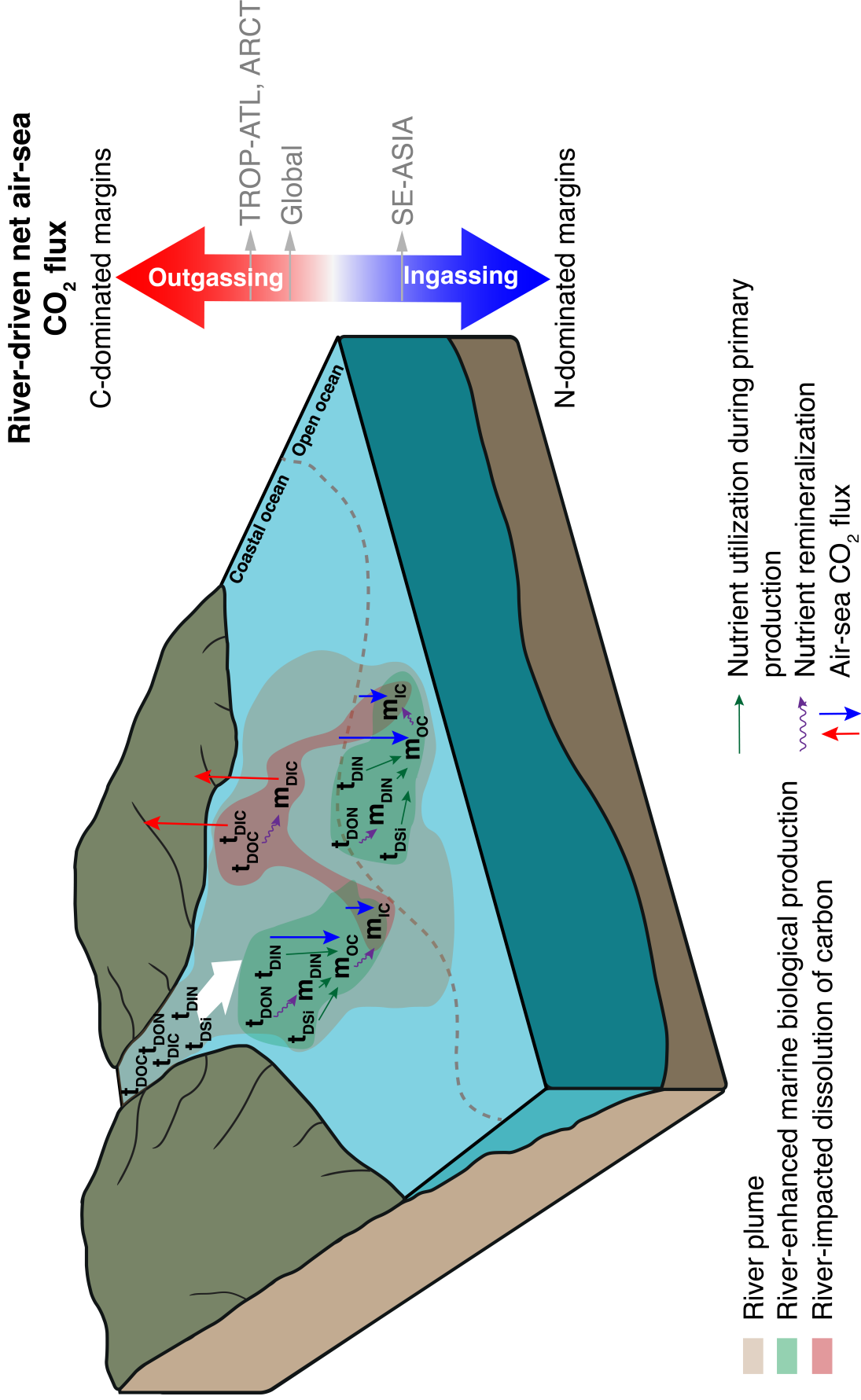
\*\* Lower bound is for smaller domain in western TROP-ATL

For both Baseline and  $\text{ALL}_{run}$ , the ocean CO<sub>2</sub> sink (2.55–2.58 Pg C yr<sup>-1</sup>) lies within the range of recent estimates (Resplandy et al., 2018; Regnier et al., 2022; Friedlingstein et al., 2023). This present-day ocean CO<sub>2</sub> sink reflects the contribution of climate and anthropogenic perturbations on top of preindustrial levels. In this study, a net riverine carbon export of 0.55 Pg C yr<sup>-1</sup> (Table 1,  $t_{DOC} + t_{DIC}$ ) drives a CO<sub>2</sub> outgassing of 0.22 Pg C yr<sup>-1</sup>, while 35 Tg N yr<sup>-1</sup> (Table 1,  $t_{DON} + t_{DIN}$ ) drives a CO<sub>2</sub> uptake of 0.17 Pg C yr<sup>-1</sup> from enhanced ocean fertilization. We note that our multi-decadal estimates are not in steady state and do have a realistic representation of estuarine, blue carbon, and bottom sediment processes. Therefore, they are not directly comparable to steady-state, pre-industrial estimates of the river loop (Resplandy et al., 2018).

The introduction of terrestrial nutrients, such as inorganic nitrogen and silica, increased global-ocean marine NPP by 0.6 Pg C yr<sup>-1</sup> compared to Baseline. The addition of  $t_{DIN}$  and  $t_{DON}$  also increased ocean NPP by 0.6 Pg C yr<sup>-1</sup> in the model described in Tivig et al. (2021) (Table 5). The modeling study by Lacroix et al. (2020) also depicted a 3% increase of ocean NPP in response to the addition of riverine nutrients. In our study, the increase of NPP driven by riverine exports was stronger in the coastal ocean compared to the open ocean, relative to their respective surface areas. This is consistent with the recent study of Mathis et al. (2024), which demonstrates the role of increased riverine nutrient loads in driving stronger biological carbon fixation and thus an enhanced CO<sub>2</sub> sink in the coastal ocean during the last century.

## 4.2 Spatial Variability

In this section, we analyze the impact of riverine exports on the spatial variability of the ocean carbon cycle for our three regions of interest: ARCT, TROP-ATL, and SE-ASIA.



**Figure 7.** Fate of riverine exports in the coastal and open ocean.  $t_{DOC}$ : terrestrial DOC,  $t_{DIC}$ : terrestrial DIC,  $t_{DON}$ : terrestrial DON,  $t_{DSi}$ : terrestrial DSi,  $m_{DIC}$ : marine DIC,  $m_{DIN}$ : marine DIN,  $m_{DOC}$ : marine DOC, and  $m_{OC}$ : marine organic carbon. The dashed grey line delineates the coastal ocean from the open ocean.

#### 4.2.1 Arctic Ocean (ARCT)

In the present study, the amount of freshwater,  $t_{DIC}$ ,  $t_{DOC}$ ,  $t_{DON}$ ,  $t_{DIN}$ , and  $t_{DSi}$  delivered to the ARCT by individual rivers (Yenisey, Lena, Ob, and Mackenzie) falls within the range of observations from Tank et al. (2012), Le Fouest et al. (2013), and Holmes et al. (2012) (Supporting Information Table S1); suggesting that our estimates are reliable at the pan-Arctic scale (Table 4). In Baseline, ARCT uptakes 213.9 Tg C yr<sup>-1</sup> of atmospheric CO<sub>2</sub>. The addition of riverine exports reduces this CO<sub>2</sub> sink by 20 Tg C yr<sup>-1</sup> and results in ECCO-Darwin having a more-consistent Arctic Ocean sink compared to previous studies (Manizza et al., 2011; Mortenson et al., 2020). In this region, riverine carbon dominates the response of air-sea CO<sub>2</sub> flux, with riverine  $t_{DOC}$  being responsible of 80% of CO<sub>2</sub> outgassing in ARCT. In Bertin et al. (2023), riverine exports from the Mackenzie River drove a CO<sub>2</sub> outgassing of roughly 0.5 Tg C yr<sup>-1</sup> in the river plume. Our model depicts a CO<sub>2</sub> outgassing of similar magnitude in the river plume region ( $\sim 0.1$  Tg C yr<sup>-1</sup>).

Due to anthropogenic climate change, thawing of carbon-rich permafrost is supplementing the load of  $t_{DOC}$  into Arctic rivers (Spencer et al., 2015). Permafrost-derived DOC has a relatively fast remineralization rate ( $\sim 2$  weeks) that could lead to strong CO<sub>2</sub> outgassing along coastal Arctic margins, which are dominated by permafrost-covered watersheds (Bertin et al., 2023). Furthermore, the degradation of organic carbon by microbial activity may be enhanced by changes in environmental conditions, such as increasing sea-surface temperature in ARCT (Carvalho & Wang, 2020). This would likely increase ocean CO<sub>2</sub> outgassing in response to the riverine carbon depicted in our study. Additionally, riverine nutrients also contribute to the Arctic Ocean carbon sink as they fertilize coastal waters. NPP in the Arctic Ocean increased by 3% (+7.4 Tg C yr<sup>-1</sup>) in  $ALL_{run}$  compared to Baseline. However, recent estimates by Terhaar et al. (2021) suggests that riverine nutrients support up to 9–11% (+58 Tg C yr<sup>-1</sup>) of marine NPP in the ARCT, in agreement with estimates by (Le Fouest et al., 2013, 2015) (Table 5). Therefore, CO<sub>2</sub> uptake driven by ocean fertilization from riverine nitrogen, and its capacity to compensate CO<sub>2</sub> outgassing in ARCT, might be underestimated in our study.

#### 4.2.2 Tropical Atlantic (TROP-ATL)

Four of the top-15 global largest rivers (Amazon, Congo, Mississippi, and Niger) discharge into TROP-ATL. In total, rivers carry 67.2 Tg C yr<sup>-1</sup> as  $t_{DOC}$ , 78.1 Tg C yr<sup>-1</sup> as  $t_{DIC}$ , 4.2 Tg N yr<sup>-1</sup> as  $t_{DON}$ , 4.5 Tg N yr<sup>-1</sup> as  $t_{DIN}$ , and 44.9 Tg Si yr<sup>-1</sup> as  $t_{DSi}$  into TROP-ATL. Riverine  $t_{DOC}$ ,  $t_{DIC}$ , and silica loads in our study are consistent with estimates from Cotrim da Cunha et al. (2007) and Araujo et al. (2014) (46 and  $\sim 50$  Tg C yr<sup>-1</sup> and 53 Tg Si yr<sup>-1</sup>, respectively; Table 4). Our estimate of  $t_{DIN}$  delivered to this region is 3-fold lower than the value of 15.3 Tg N yr<sup>-1</sup> reported by Cotrim da Cunha et al. (2007) (Table 4). However,  $t_{DIN}$  export from the Amazon river (1 Tg N yr<sup>-1</sup>) agrees well with Louchard et al. (2021) (0.9 Tg N yr<sup>-1</sup>). A dynamic land ecosystem model that explicitly resolves fluxes over the entire watershed estimated that 0.9 Tg N yr<sup>-1</sup> is exported as  $t_{DIN}$  from the Mississippi River (Tian et al., 2020), which is in general agreement with the 0.7 Tg N yr<sup>-1</sup> that we use as input for our model. The load of  $t_{DIN}$  from the Congo River (0.2 Tg N yr<sup>-1</sup>) is also the same order of magnitude compared to data from Jouanno et al. (2021). However, our Global-NEWS-2-based estimate of 0.1 Tg N yr<sup>-1</sup> remains lower than previous estimates for the Niger River (Robertson & Rosswall, 1986) (0.5 Tg N yr<sup>-1</sup>). We stress that in Africa river systems, nutrient loads are poorly constrained due to sparse data.

In Baseline, TROP-ATL is a source of CO<sub>2</sub> to the atmosphere (0.10 Pg C yr<sup>-1</sup>), which agrees with both interpolation-based products (Landschützer et al., 2016; Jersild et al., 2023; Rödenbeck, 2005) (0.04–0.08 Pg C yr<sup>-1</sup>) and model results (da Cunha & Buitenhuis, 2013; Louchard et al., 2021) (0.03–0.04 Pg C yr<sup>-1</sup>). We note that previous

studies show a river-driven increase in  $\text{CO}_2$  uptake of 0.005 and 0.02  $\text{Pg C yr}^{-1}$  when adding biogeochemical runoff in TROP-ATL and western TROP-ATL, respectively (da Cunha & Buitenhuis, 2013; Louchard et al., 2021). However, in our simulations, the addition of riverine exports in  $\text{ALL}_{run}$  enhanced the source of  $\text{CO}_2$  (+0.02  $\text{Pg C yr}^{-1}$ ) (Table 5).

Contrary to the estimates of Louchard et al. (2021), which include physical effects associated with freshwater, such as enhanced upper-ocean stratification and gas solubility, our baseline simulation already includes these processes. Therefore, our suite of experiments cannot isolate and quantify the impact of freshwater discharge on ocean biogeochemistry. Freshwater in river plumes facilitates the uptake of atmospheric  $\text{CO}_2$  through the solubility pump, which in turn overlaps with the sink of  $\text{CO}_2$  associated with biogeochemical runoff. In addition to nitrogen, Louchard et al. (2021) also included inorganic phosphorus loads and a regionally-adjusted plankton ecosystem, e.g., by including a nitrogen-fixing phytoplankton functional type, which increased the model’s capability to better resolve the biological pump and hence  $\text{CO}_2$  uptake. For our simulations, we find that the increase of NPP associated with rivers in TROP-ATL (0.17  $\text{Pg C yr}^{-1}$ ) lies within the value of 0.08  $\text{Pg C yr}^{-1}$  reported in Louchard et al. (2021) (Table 5) and the value of 0.4  $\text{Pg C yr}^{-1}$  reported in Cotrim da Cunha et al. (2007). We note that horizontal resolution is also important for realistic representation of coastal processes. In their higher-resolution study, Louchard et al. (2021) were able to separately resolve the estuarine and plume/shelf waters of the Amazon River as a  $\text{CO}_2$  source and sink, respectively, whereas our model intrinsically lacks such fine delineation.

The Amazon River clearly dominates the  $\text{CO}_2$  outgassing signal in TROP-ATL, which is driven by the large load of  $t_{DOC}$ . Along with other rivers such as the Congo, Niger, and Orinoco Rivers, the Amazon River delivers a large amount of  $t_{DOC}$ , which originates from tropical forests. These forests contribute roughly one third of terrestrial NPP and their soil contains large amount of organic carbon, globally (Cleveland et al., 2010). As these watersheds are being drained by runoff from high precipitation, the subsequent high discharge, combined with carbon-rich soil and vegetation, leads to routing of  $t_{DOC}$ -rich waters to the coastal ocean (M. Li et al., 2019). At present time, it is critical to better constrain export of carbon from watersheds to coastal waters and characterize their fate in the ocean, as current efforts may be overestimating the land sink of carbon associated with tropical forests (Lauerwald et al., 2020). Additionally, the composition (refractory black carbon from combustion) and the quantity ( $\text{CO}_2$  fertilization from NPP and soil erosion with deforestation) of carbon exports from the Amazon River remains uncertain due to ongoing changes in regional climate and fire regimes (Fleischer et al., 2019; Jones et al., 2020; Riquetti et al., 2023).

#### 4.2.3 Southeast Asia (SE-ASIA)

Riverine biogeochemical runoff in SE-ASIA is dominated by high loads of  $t_{DIN}$  (10.6  $\text{Tg N yr}^{-1}$ ) and  $t_{DIC}$  (163.8  $\text{Tg C yr}^{-1}$ ), especially from the Ganges and Yangtze Rivers. The magnitude of the riverine  $t_{DIN}$  load for SE-ASIA compares with individual estimates for the Bay of Bengal (0.4  $\text{Tg N yr}^{-1}$ ), the Arabian Sea (0.06  $\text{Tg N yr}^{-1}$ ), and the East China Sea (1.6–7.9  $\text{Tg N yr}^{-1}$ ) (Singh & Ramesh, 2011; H.-M. Li et al., 2014; J. Wang et al., 2020; Nishina et al., 2021) (Table 4). Our estimate of the  $t_{DIC}$  load in SE-ASIA remains higher than values reported in the literature ( $\sim 40 \text{ Tg C yr}^{-1}$ ) (Piao et al., 2012; Patra et al., 2013) and thus would require a regional adjustment as we did for the Amazon River (Table 4 and Supporting Information Text S1). This is explained by overestimated  $t_{DIC}$  loads from the Yangtze (45.9  $\text{Tg yr}^{-1}$ ) and the Ganges (18  $\text{Tg yr}^{-1}$ ) Rivers compared to reported values (20 and 3–4  $\text{Tg C yr}^{-1}$ , respectively) (F. Wang et al., 2007; Guo et al., 2015; Y. Gao et al., 2017; Samanta et al., 2015). This overestimation is related to the relationship based on river discharge and the dominant lithology (Amiotte Suchet et al., 2003; M. Li et al., 2017). Both rivers exhibit high discharge combined with weathering-



prone lithologies (carbonate rocks and shales for the Yangtze and Ganges rivers, respectively), which consume atmospheric CO<sub>2</sub> due to high rates of rock weathering (Amiotte Suchet et al., 2003). The Yangtze River is also known for its high river CO<sub>2</sub> emission flux due to the large permafrost area in the Qinghai-Tibet Plateau that releases large DIC loads during warm and rainy summer conditions (Song et al., 2020). As for ARCT, the  $t_{DIC}$  load from the Yangtze watershed remains uncertain, as its permafrost region is degrading quickly under the effect of climate warming (Cheng & Wu, 2007; Yang et al., 2010).

Similar to ARCT, SE-ASIA is a sink of atmospheric CO<sub>2</sub> in Baseline (0.3 Pg C yr<sup>-1</sup>). Combining air-sea CO<sub>2</sub> budgets for the different regions composing SE-ASIA from literature (East-Pacific, Indonesian seas, and North Indian Ocean without including Oman and Somalian upwelling regions), we estimate a carbon sink of  $\sim 0.2$  Pg C yr<sup>-1</sup> for the entire SE-ASIA domain (Kartadikaria et al., 2015; De Verneil et al., 2021; Zhong et al., 2022; Hood et al., 2023). Our study provides the first estimate of the contribution of present-day riverine exports to the carbon sink in SE-ASIA. The net air-sea CO<sub>2</sub> exchange balance driven by riverine exports in SE-ASIA results in a carbon sink of 0.02 Pg C yr<sup>-1</sup> in  $ALL_{run}$ . Compared to ARCT and TROP-ATL, carbon uptake in SE-ASIA is enhanced by a strong increase in marine NPP (+0.30 Pg C yr<sup>-1</sup>, +9%) driven by riverine  $t_{DIN}$ . In Tivig et al. (2021), the simulated increase of NPP in response to riverine nitrogen was roughly 0.1 Pg C yr<sup>-1</sup> in Asia, with the strongest increase in the Yellow Sea, similar to our results (Table 5). Riverine nitrogen loads in this domain, and especially in the China seas, have been supplemented by increased nitrogen deposition, nitrogen fertilizer, manure, and human sewage over the last 50 years (Nishina et al., 2021). Even if nitrogen runoff is declining, agricultural-driven nitrogen loads will remain at significant levels and continue to fertilize phytoplankton blooms in this nitrogen-depleted marine region due to high denitrification (Michael Beman et al., 2005; Nishina et al., 2021). Locally, the addition of riverine biogeochemical runoff also drives a source of CO<sub>2</sub> to the atmosphere, which is primarily limited to near river mouth locations in SE-ASIA. In the Yellow Sea and the Northern Bay of Bengal, close to the Yangtze and Ganges Rivers, the addition of riverine exports at preindustrial levels in an ocean model also drove a CO<sub>2</sub> outgassing in Lacroix et al. (2020). Noticeably, in our simulations, riverine carbon turns the northern Bay of Bengal into a carbon source as suggested by Hood et al. (2023).

### 4.3 Model Improvements

Our study is a first attempt to add global, time-varying biogeochemical discharge in the ECCO-Darwin ocean carbon estimation framework. Here, we elaborate on some necessary, and potentially consequential, simplifications made in this study. In light of these simplifications, some next-step model improvements are described in Supporting Information Text S2.

Rivers are a significant source of phosphorus and iron that is pivotal for ocean biogeochemistry (Krachler et al., 2005; Tagliabue et al., 2017; Duhamel et al., 2021; Savenko & Savenko, 2021). Consequently, our results may underestimate the global-ocean air-sea CO<sub>2</sub> uptake due to the absence of riverine phosphorus or iron in the model, as they might be limiting for ocean NPP relative to the excess of terrestrial inorganic nitrogen. Additionally, riverine  $t_{ALK}$  flux was computed based on a constant ALK:DIC ratio, globally (0.98). We note that the GLORICH database used to compute the mean ALK:DIC ratio has relatively good coverage over the American continent but Eurasia and Africa are underrepresented (Hartmann et al., 2014). As such, the ALK:DIC ratio can vary substantially over regional scales. The lack of this spatially-granular information in our simulated exports may misrepresent riverine  $t_{ALK}$  fluxes and the alkalinity-driven buffering capacity of simulated river plumes (Dubois et al., 2010; Tank et al., 2012; Mol et al., 2018; Ghosh et al., 2021; Gomez et al., 2023). While in estuaries the absence of ALK relative to DIC leads to higher partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in upper-ocean waters and enhanced CO<sub>2</sub> outgassing, rivers also bring an excess of ALK relative to DIC on con-

575 timental shelves, which can reduce ocean  $p\text{CO}_2$  through buffering and thus facilitate  $\text{CO}_2$   
 576 uptake (W.-J. Cai et al., 2010; Louchard et al., 2021). Furthermore, the fate of riverine  
 577  $t_{ALK}$  in the ocean is associated with the biological activity of calcifying organisms and  
 578 exchange at the sediment-water interface (Middelburg et al., 2020) — an undergoing de-  
 579 velopment in our modeling system.

580 In our model, the global-ocean net  $\text{CO}_2$  outgassing driven by riverine exports re-  
 581 flects the stronger effect of riverine carbon on the solubility pump ( $\text{CO}_2$  source) com-  
 582 pared to the change in the  $\text{CO}_2$  uptake associated with the increase in NPP. This im-  
 583 balance can result from an overestimation of  $\text{CO}_2$  outgassing driven by riverine carbon,  
 584 and especially  $t_{DOC}$ . First, assuming that total loads of carbon or nutrients over each  
 585 watershed are routed to the ocean is a misrepresentation, as losses and gains occur through  
 586 the LOAC (W.-J. Cai, 2011). Second,  $t_{DOC}$  is degraded in coastal waters at different  
 587 rates depending on its origin and subsequent labile fraction (Lønborg et al., 2020). In  
 588 the present study, in addition to not accounting for refractory and labile fractions of  $t_{DOC}$ ,  
 589 marine and terrestrial DOC are both being remineralized at the same rate (3 months).  
 590 Overall, this could lead to an overestimation of  $t_{DOC}$  remineralization and thus ocean  
 591  $\text{CO}_2$  outgassing due to the subsequent excess of DIC. For instance, the Amazon River  
 592 — the main source of riverine  $t_{DOC}$  into the ocean — contributes to almost 50% (+0.014  
 593  $\text{Pg C yr}^{-1}$ ) of the global-ocean  $\text{CO}_2$  outgassing in response to riverine exports in our study.  
 594 However,  $t_{DOC}$  from the Amazon River shows stronger stability in the coastal ocean and  
 595 is exported from the continental margin to the open ocean (Medeiros et al., 2015; Louchard  
 596 et al., 2021). Increasing the refractory pool of Amazon  $t_{DOC}$  could therefore decrease  
 597  $\text{CO}_2$  outgassing in our simulations. While recent modeling studies include separate pools  
 598 of refractory and labile  $t_{DOC}$  with different remineralization rates at regional scales (Louchard  
 599 et al., 2021; Gibson et al., 2022; Bertin et al., 2023), the nature of  $t_{DOC}$  needs to be bet-  
 600 ter accounted for in global-ocean biogeochemistry models.

## 601 5 Perspectives

602 Biogeochemical inputs from rivers into the ocean are subject to variability from cli-  
 603 mate change and/or human activities. Over the last century, loads of riverine exports  
 604 such as nitrogen and phosphorus increased dramatically — mostly due to anthropogenic  
 605 perturbations (+349% and +233%, respectively) (Lacroix et al., 2021). In the coastal  
 606 ocean, this has strongly increased NPP associated with the regions in which our model  
 607 depicts the strongest impact of riverine nutrients on NPP (TROP-ATL and SE-ASIA)  
 608 (Lacroix et al., 2021). Over the past 20 years, fertilizers and aquaculture have been iden-  
 609 tified as global drivers of phytoplankton blooms in coastal waters (Dai et al., 2023). The  
 610 load of riverine  $t_{DOC}$  also increased globally over the period 1860–2010 (+17%), due to  
 611  $\text{CO}_2$  fertilization of terrestrial vegetation and climate change (Nakhavali et al., 2024).  
 612 In the near future (2050), the global contribution of natural sources of nitrogen and phos-  
 613 phorus in riverine inputs is expected to continue to decrease due to land-use change, while  
 614 anthropogenic sources from human waste, agriculture, and aquaculture are projected to  
 615 increase for every potential Shared Socioeconomic Pathways (SSP) scenario (Beusen et  
 616 al., 2022). However, the export of nutrients from anthropogenic sources to the ocean will  
 617 decrease in industrialized regions such as North America, Europe (including the Russian  
 618 Federation), Japan, and Oceania in most SSPs (Beusen & Bouwman, 2022). For instance,  
 619 in the contiguous United States, the riverine load of nitrogen from human waste and at-  
 620 mospheric pollution decreased over 1930–2017 (Byrnes et al., 2020). Nonetheless, the load  
 621 of nitrogen from agricultural sources kept increasing over the same period (Byrnes et al.,  
 622 2020). Consequently, only the long-term adoption of the Paris Agreement and sustain-  
 623 able development scenarios, such as SSP1 where the use of resources and the dependency  
 624 on fossil fuels are significantly reduced, would lead to better stream water quality (Beusen  
 625 & Bouwman, 2022; Beusen et al., 2022). Over the 21<sup>st</sup> century, the increase of ocean NPP  
 626 and the associated carbon sink driven by the historical increase of nutrients loads is ex-

pected to be dampened by the increase of CO<sub>2</sub> outgassing from elevated terrestrial organic matter loads (S. Gao et al., 2023).

Depicting the role of riverine exports in the ocean carbon cycle remains limited by the spatial and temporal coverage/resolution of models, forcing products, and observations. As river discharge is associated with suspended particulate loads, ocean color retrievals from spaceborne instruments can be an effective tool for monitoring river plumes systems. However, the complexity of optical properties and their large space-time variability requires high-resolution sensors to capture the actual constituents of ocean biogeochemistry. The recently launched Plankton, Aerosol, Cloud, ocean Ecosystem (PACE) satellite mission (<https://pace.oceansciences.org/>) and its onboard high-resolution spectrometer will bring new insights into the water quality of coastal regions near river mouths. Combined, with river discharge retrievals from the Surface Water and Ocean Topography (SWOT, <https://swot.jpl.nasa.gov/>), combined spaceborne observations of ocean color and terrestrial fluxes of freshwater into the ocean will pave the way for an integrated Earth Observation System, where the connection between the land and the ocean will be better understood. While effective, these satellite missions are expensive and should not replace critical in-situ and ground-truthed observations. We highlight that ambitious spaceborne missions can indeed be complemented by more modest initiatives, such as citizen science or stakeholder engagement to monitor water quality in river systems (Abbott et al., 2018).

## 6 Conclusion

Our simulations suggest that the role of present-day riverine exports is moderate, with an outgassing of 0.03 Pg C yr<sup>-1</sup> to the atmosphere, globally. We find that riverine inputs drive contrasting regional patterns in air-sea CO<sub>2</sub> flux. Terrestrial dissolved carbon, and especially t<sub>DOC</sub>, contributes to an outgassing of CO<sub>2</sub> through a reduction of the ocean’s solubility pump. Terrestrial nutrients, and in particular t<sub>DIN</sub>, fertilizes phytoplankton and increases marine NPP and the associated carbon biomass. Thus, terrestrial nutrients such as inorganic nitrogen and silica enhance the uptake of atmospheric CO<sub>2</sub> into the ocean. While outgassing of CO<sub>2</sub> is primarily located near river mouths, the fertilization by riverine nitrogen and silica spreads further offshore and into the open ocean. In carbon-dominated margins such as ARCT or TROP-ATL, rivers contribute a large source of CO<sub>2</sub> from the ocean to the atmosphere. However, in nitrogen-dominated margins such as SE-ASIA, rivers drive a large sink of atmospheric CO<sub>2</sub> into the ocean. This work highlights that a better quantification of lateral riverine exports and the incorporation of these fluxes in global models is pivotal for regional and global carbon budgets. Conducting sensitivity experiments could support national policy decisions and inform climate resilience strategies for land and marine practices.

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## Open Research

ECCO-Darwin model output is available at the ECCO Data Portal: <http://data.nas.nasa.gov/ecco/>. Model code and platform-independent instructions for running the ECCO-Darwin sim-

ulations used in this paper and generating runoff forcing are available at: 10.5281/zenodo.10562713.

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