Role of Riverine Dissolved Organic and Inorganic Carbon and Nutrients in Global-ocean Air-sea CO2 Fluxes

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April 16, 2024

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 CO2 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 CO2 outgassing by 0.22 Pg C yr-1 via the solubility pump, while nitrogen exports increase the ocean sink by 0.17 Pg C yr-1 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 CO2 outgassing (+10 and +20%, respectively). In contrast, Southeast Asia is dominated by nitrogen from anthropogenic sources, such as agriculture and pollution, leading to increased CO2 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.

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Key Points:

ton fertilization

17	•	We assess how global lateral exports impact air-sea CO ₂ flux and carbon cycling
18		in ECCO-Darwin ocean biogeochemistry simulations
19	•	Near river mouths, changes in CO_2 flux are dominated by the solubility pump and
20		lead to outgassing
21	•	Further offshore, riverine nitrogen leads to increased CO ₂ uptake via phytoplank-

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23 Abstract

While the preindustrial ocean was assumed to be in equilibrium with the atmosphere, 24 the modern ocean is a carbon sink, resulting from natural variability and anthropogenic 25 perturbations, such as fossil fuel emissions and changes in riverine exports over the past 26 two centuries. Here we use a suite of sensitivity experiments based on the ECCO-Darwin 27 global-ocean biogeochemistry model to evaluate the response of air-sea CO_2 flux and car-28 bon cycling to present-day lateral fluxes of carbon, nitrogen, and silica. We generate a 29 daily export product by combining point-source freshwater discharge from JRA55-do with 30 31 the Global NEWS 2 watershed model, accounting for lateral fluxes from 5171 watersheds worldwide. From 2000 to 2019, carbon exports increase CO₂ outgassing by 0.22 Pg C 32 yr^{-1} via the solubility pump, while nitrogen exports increase the ocean sink by 0.17 Pg 33 $C \text{ yr}^{-1}$ due to phytoplankton fertilization. On regional scales, exports to the Tropical 34 Atlantic and Arctic Ocean are dominated by organic carbon, which originates from ter-35 restrial vegetation and peats and increases CO_2 outgassing (+10 and +20\%, respectively). 36 In contrast, Southeast Asia is dominated by nitrogen from anthropogenic sources, such 37 as agriculture and pollution, leading to increased CO_2 uptake (+7%). Our results demon-38 strate that the magnitude and composition of riverine exports, which are determined in 39 part from upstream watersheds and anthropogenic perturbations, substantially impact 40 present-day regional-to-global-ocean carbon cycling. Ultimately, this work stresses that 41 lateral fluxes must be included in ocean biogeochemistry and Earth System Models to 42 better constrain the transport of carbon, nutrients, and metals across the land-ocean-43 aquatic-continuum. 44

45 Plain Language Summary

Due to ongoing climate change and human activities, the transport of carbon and 46 nutrients from rivers to the ocean has changed, with rivers now contributing to the mod-47 ern ocean's sequestration of atmospheric carbon dioxide (CO_2) . In this study, we add 48 the effect of present-day rivers to a numerical model of the ocean carbon cycle (ECCO-49 Darwin) and then estimate their impact on air-sea CO_2 exchange and ocean biogeochem-50 istry. Over a 20-year period, riverine carbon saturates the surface ocean and increases 51 the amount of CO₂ released to the atmosphere, while nitrogen fertilizes phytoplankton 52 and increases the capture of atmospheric CO₂ via photosynthesis. In the Tropical At-53 lantic and Arctic Oceans, organic carbon drained from vegetation and peats causes out-54 gassing of ocean carbon. In Southeast Asia, the large amount of riverine nitrogen orig-55 inating from human activities, such as agriculture or waste water, increases ocean CO_2 56 sequestration. Our work highlights how rivers, which are affected by present-day human 57 actions and climate change, impacts the ocean's carbon cycle across regional-to-global 58 scales. 59

60 1 Introduction

Globally, shelf and marginal seas are typically sinks of CO_2 , where uptake driven 61 by strong biological productivity exceeds outgassing from organic matter degradation 62 and carbon enrichment by river runoff and coastal upwelling (Ianson et al., 2009; W.-63 J. Cai, 2011; W. Cai et al., 2013; Laruelle et al., 2017; Bertin et al., 2023). Rivers trans-64 port roughly $0.8-0.9 \text{ Pg C yr}^{-1}$ from land to coastal regions as dissolved organic carbon 65 (DOC), dissolved inorganic carbon (DIC), particulate organic carbon (POC), and par-66 ticulate inorganic carbon (PIC); a third of the aforementioned total riverine export of 67 carbon is buried in coastal sediments (Regnier et al., 2022; Battin et al., 2023). Nutri-68 ents such as phosphorus, nitrogen, and silica are also conveyed by rivers along with car-69 bon. Terrestrial inorganic carbon and nutrients in streams originate from weathering of 70 the lithosphere and the associated sink of atmospheric CO_2 , along with the remineral-71 ization of organic matter in streams and/or on land (Suchet & Probst, 1995; Battin et 72

al., 2023). Riverine organic carbon and nutrients are further supplemented by primary
production from land vegetation and organic matter mobilized through direct literfall,
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 77 to the atmosphere in the form of CO_2 , due to the saturation of surface-ocean waters by 78 terrestrial DIC and remineralization of terrestrial organic matter (Hartmann et al., 2009; 79 Lacroix et al., 2020; Bertin et al., 2023) in shallow, well-mixed water columns. The nat-80 81 ural transport of carbon from terrestrial ecosystems to ocean outgassing, the so-called "river loop", is estimated to be 0.65 ± 0.3 Pg C yr⁻¹ (Regnier et al., 2022; Friedlingstein 82 et al., 2023). With respect to inorganic nutrients, their injection into the surface ocean 83 can fertilize growth of photosynthetic organisms in nutrient-limited regions. Globally, 84 this lateral flux increases ocean primary productivity and contributes to a coastal-ocean 85 sink of ~ 0.25 Pg C yr⁻¹, which is roughly 17% of the global-ocean sink (W.-J. Cai, 2011; 86 Lacroix et al., 2021; S. Gao et al., 2023). 87

Over the past two centuries, terrestrial anthropogenic perturbations have led to a 88 substantial increase in the load of nitrogen and phosphorus through agricultural fertil-89 ization, leaked sewage, and land-use change (Smith et al., 2003; Lee et al., 2016; Lacroix 90 et al., 2021). Projections of the historical riverine dissolved nitrogen and phosphorus load 91 depict a three- to four-fold increase over the period 1900–2019 (Lacroix et al., 2021). When 92 delivered in excessive amounts, these nutrients can alter aquatic and ocean ecosystems, 93 resulting in eutrophication, hypoxia, and acidification in coastal waters (Laurent et al., 94 2017; Fennel & Testa, 2019). Dissolved and particulate carbon are also affected region-95 ally by agricultural liming, the addition of sulfuric acid to watersheds, changes in ero-96 sion patterns, and river management (Monteith et al., 2007; Raymond et al., 2008; Calmels 97 et al., 2007; Regnier et al., 2013; Maavara et al., 2017). Projected trends for river bio-98 geochemical loads remain uncertain and exhibit disparate regional responses over the 21^{st} qq century depending on the chosen shared socioeconomic pathway (Beusen et al., 2022; Beusen 100 & Bouwman, 2022; Vishwakarma et al., 2022; Zhang et al., 2022). 101

While present estimates of riverine freshwater and biogeochemical fluxes are poorly 102 sampled in space and time, land surface and watershed models can provide spatiotemporally-103 resolved lateral exports at global scales (Mayorga et al., 2010; Krinner et al., 2005; Hage-104 mann & Dümenil, 1997; Hagemann & Gates, 2003; M. Li et al., 2017; Bloom et al., 2020). 105 Coupled with ocean biogeochemical models, it is thus possible to quantify the response 106 of the coastal and open-ocean carbon cycle to lateral fluxes (Lacroix et al., 2020, 2021; 107 Mathis et al., 2022; Louchard et al., 2021; da Cunha & Buitenhuis, 2013; Le Fouest et 108 al., 2013; S. Gao et al., 2023; Bertin et al., 2023). Regarding the importance of lateral 109 exports in ocean carbon cycling, it is critical that ocean biogeochemical models better 110 account for coastal mechanisms occurring across the land-ocean-aquatic-continuum (LOAC) 111 (Ward et al., 2020; Mathis et al., 2022). Such improvements will come from 1) finer hor-112 izontal and vertical grid resolution to resolve small-scale ocean physics (vertical mixing, 113 submesoscale processes) and associated biology (hypoxia, phytoplankton blooms) and 114 2) improved representation of LOAC components (river and groundwater discharge, bot-115 tom sediment diagenesis, and estuarine biogeochemical filtering) (Ward et al., 2020; Sharples 116 et al., 2017). While recent modeling efforts have made improvements in this regard (Volta 117 et al., 2016; Laruelle et al., 2017; Mathis et al., 2022, 2024), the respective contribution 118 of riverine exports to air-sea CO_2 fluxes across the global ocean remains to be assessed. 119

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 CO₂ flux and ocean biogeochemistry to daily point-source river forcing from 2000–2019. We compute daily riverine biogeochemical export by combining pointsource 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 CO₂ 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.

132 2 Methods

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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 140 in detail in (Forget et al., 2015). The nominal horizontal grid resolution in ECCO v4 LLC90 141 is $1^{\circ}(\sim 55 \text{ km at high latitudes})$. The vertical discretization consists of 50 z-levels, rang-142 ing from 10-m thickness in the top 7 levels to 450 m at depth. ECCO v4 uses a third-143 order, direct-space-time tracer advection scheme in the horizontal and an implicit third-144 order upwind scheme in the vertical; a time step of 3600 s is used. Vertical mixing is pa-145 rameterized using the Gaspar–Grégoris–Lefevre (GGL) mixing-layer turbulence closure 146 and convective adjustment scheme (Gaspar et al., 1990). ECCO v4 assimilates physi-147 cal observations via the 4-D adjoint method (Wunsch et al., 2009; Wunsch & Heimbach, 148 2013).149

Daily river runoff in the present configuration is based on the Japanese 55-year at-150 mospheric reanalysis (JRA55-do) river forcing dataset, which uses the CaMa-Flood global 151 river routing model and adjusted runoff from the land component of JRA-55 (Suzuki et 152 al., 2018; Tsujino et al., 2018; Feng et al., 2021). Point source JRA55-do freshwater runoff 153 $(m s^{-1})$ was added to ECCO v4 as a real freshwater flux in the surface ocean (first ver-154 tical level) at the closest ECCO v4 LLC90 grid cell along the coastal periphery. The fresh-155 water flux was adjusted according to the difference in grid cell area between JRA55-do 156 (0.25°x 0.25°) and ECCO v4 LLC90. A full evaluation of ocean physics from ECCO v4 157 LLC90 compared to observations can be found in the Supporting Information and Feng 158 et al. (2021). 159

ECCO v4 LLC90 ocean physics was coupled online with the Massachusetts Insti-160 tute of Technology Darwin Project ecosystem model described in Brix et al. (2015). The 161 ecosystem model solves 39 prognostic variables such as carbon, nitrogen, phosphorus, 162 iron, silica, oxygen, and alkalinity. The model simulates their respective cycle from in-163 organic pools to living/dead matter of plankton organisms and the subsequent reminer-164 alization, all driven by the ocean physics. The carbonate chemistry is solved by the method 165 in Follows et al. (2006). Plankton species consist of five large-to-small functional phy-166 toplankton types (diatoms, other large eukaryotes, Synechococcus, and low- and high-167 light adapted *Prochlorococcus*), and two zooplankton types. Atmospheric CO_2 partial 168 pressure at sea level $(apCO_2)$ from the National Oceanic and Atmospheric Administra-169 tion Marine Boundary Layer Reference product (Andrews et al., 2014) was used to drive 170 air-sea CO_2 fluxes computed by the model according to Wanninkhof (1992). Atmospheric 171 iron dust is deposited at the ocean surface based on the monthly climatology of Mahowald 172 et al. (2009). Once at the ocean bottom, particulate inorganic and organic matter is re-173 moved at the sinking rate to limit the accumulation of particulates on the seafloor. Bio-174 geochemical observations were used to optimize the biogeochemical model using a Green's 175

Functions approach (Menemenlis et al., 2005); the optimization methodology and asso-176 ciated data are fully described in Carroll et al. (2020). The ECCO-Darwin solution was 177 previously published using monthly climatological freshwater runoff forcing from Fekete 178 et al. (2002). Here, the Baseline simulation consists of the same ocean biogeochemistry 179 simulation as Carroll et al. (2020), but with daily point-source freshwater runoff from 180 January 1992 to December 2019. To allow partial adjustment to these new boundary con-181 ditions, the analysis period hereinbelow spans the last 20 years of the simulation, Jan-182 uary 2000 to December 2019. Figure 1 shows the general match-up between time-mean 183 ECCO-Darwin air-sea CO₂ fluxes and the MPI SOM FFN v2022 (Landschützer et al., 184 2016; Jersild et al., 2023) and Jena CarboScope v2023 (Rödenbeck et al., 2013) prod-185 ucts for the 2000–2019 study period. 186



Figure 1. Climatological global-ocean air-sea CO_2 flux for (a) ECCO-Darwin Baseline, (b) MPI SOM FFN, and (c) Jena CarboScope. Positive values represent CO_2 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.

187 2.2 Biogeochemical River Runoff

In addition to the Baseline simulation, we conducted a suite of sensitivity exper-188 iments where we added terrestrial DOC (t_{DOC}), DIC (t_{DIC}), total alkalinity (t_{ALK}), 189 dissolved inorganic nitrogen (t_{DIN}) , dissolved organic nitrogen (t_{DON}) , and dissolved 190 silica (t_{DSi}) , henceforth referred to as riverine exports in this study. We excluded phos-191 phorus and iron due to the complexity of their reactions when entering the marine en-192 vironment (i.e., absorption, bio-availability). Except for t_{DIC} and t_{ALK} , riverine exports 193 are provided by the Global NEWS 2 (Global Nutrient Export from WaterSheds) model 194 (Mayorga et al., 2010). 195

Global NEWS 2 uses statistical and mechanistic relations at the watershed scale 196 to compute annual-mean freshwater discharge and riverine loads based on natural and 197 anthropogenic sources, with 6292 individual watersheds delineated according to the global 198 river systems dataset from Vörösmarty et al. (2000). t_{DIN} was partitioned into nitrite 199 (NO_2^-) , nitrate (NO_3^-) , and ammonium (NH_4^+) , according to the mean fraction of each 200 species concentration relative to the total DIN concentration from the GLObal RIver CHem-201 istry Database (GLORICH) (Hartmann et al., 2014). The NO₂⁻:DIN, NO₃⁻:DIN, and NH₄⁺:DIN 202 ratios were estimated to be 0.02, 0.65, and 0.33, respectively. Riverine t_{DIC} loads were 203 computed using an empirical relation between freshwater discharge and gross CO_2 con-204 sumption from rock weathering as described in M. Li et al. (2017, equation 9). CO_2 con-205 sumption by rock weathering over each Global NEWS 2 watershed was estimated based 206 on the freshwater discharge and the basin-dominant lithology (Amiotte Suchet et al., 2003). 207 t_{ALK} loads were computed using an ALK:DIC ratio (0.98) based on the mean total ALK 208 compared to DIC from GLORICH. t_{DOC} was not considered to be more refractory than 209 marine DOC; the DOC remineralization rate is set to 1 over 100 days. We used Global 210 NEWS 2 outputs for year 2000 as representative of present-day carbon and nutrient loads 211 (Mayorga et al., 2010). 212

Global NEWS 2 river mouth locations were associated with JRA55-do grid points 213 exhibiting the closest annual-mean freshwater discharge in 2000 within a euclidean dis-214 tance of 5° . The top-100 largest rivers (by watershed extent) from Global NEWS 2 were 215 imposed on JRA55-do grid points as a function of distance only. In total, 5171 river mouths 216 were associated with JRA55-do grid points. For each discharge point, export concentra-217 tions from the associated river were estimated by dividing the load by the annual vol-218 ume of freshwater from Global NEWS 2; the concentration was then converted to a daily 219 flux using the corresponding daily-mean freshwater flux from JRA55-do. Exports were 220 adjusted according to the grid cell area difference between JRA55-do and ECCO v4 LLC90. 221 These biogeochemical exports were then added as point-source discharge along riverine 222 freshwater flux (Figure 2). Due to extreme values in our automated Global-NEWS-2-223 derived computation for the Amazon River, the DIC load for this system was set to a 224 more-realistic, literature-mean of 2.54 Tmol yr^{-1} (da Cunha & Buitenhuis, 2013; Probst 225 et al., 1994; M. Li et al., 2017) (for more details see Supporting Information Text S1). 226



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 km³ yr⁻¹ are shown.

As riverine t_{DOC} , t_{DIN} , t_{DON} , and t_{DSi} were computed from Global NEWS 2 con-227 centration and modulated with JRA55-do freshwater runoff, our fluxes agree well with 228 existing estimates based on the NEWS 2 database (Mayorga et al., 2010; Frings et al., 229 2016; Sharples et al., 2017; Lacroix et al., 2020; Tivig et al., 2021; Tian et al., 2023). t_{DIC} 230 lateral export from rivers was estimated according to Amiotte Suchet et al. (2003); May-231 orga et al. (2010); M. Li et al. (2017), resulting in a t_{DIC} load of 381.81 Tg C yr⁻¹ to 232 the ocean, which is in general agreement with recent studies (Drake et al., 2018; M. Li 233 et al., 2017; Lacroix et al., 2020; Battin et al., 2023; Tian et al., 2023). 234

2.3 Sensitivity Experiments and Analysis

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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.

Experiment Name	${f t}_{DOC} \ ({f Tg} \ {f C} \ {f yr}^{-1})$	${f t}_{DIC} \ ({f Tg} \ {f C} \ {f yr}^{-1})$	${f t}_{DON} \ ({f Tg} \ {f N} \ {f yr}^{-1})$	${f t}_{DIN} \ ({f Tg} \ {f N} \ {f yr}^{-1})$	${f t}_{DSi} \ ({f Tg}\ {f Si}\ {f yr}^{-1})$
Baseline	0	0	0	0	0
DC_{run}	170.1	381.8	0	0	0
$\mathrm{DIC}_{\mathrm{run}}$	0	381.8	0	0	0
$\mathbf{DN}_{\mathbf{run}}$	0	0	11.7	23.3	0
$\mathrm{DIN}_{\mathrm{run}}$	0	0	0	23.3	0
$\mathrm{DSi}_{\mathrm{run}}$	0	0	0	0	139.7
$\overline{\mathrm{ALL}}_{\mathrm{run}}$	170.1	381.8	11.7	23.3	139.7

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

We analyzed monthly-mean model fields along the coastal ocean (limits set by the 243 furthest point from the coastline, either the 1000-m isobath or a distance of 300 km; 58 244 $\times 10^6$ km²) and the open ocean (300 $\times 10^6$ km²) during 2000–2019. In addition to the 245 global ocean, we also evaluated the sensitivity of ocean carbon cycling in three specific 246 regions that receive large volumes of freshwater from major river systems: the Arctic Ocean 247 (ARCT, 22 x 10⁶ km²), Tropical Atlantic (TROP-ATL, 77 x 10⁶ km²), and Southeast 248 Asia (SE-ASIA, $62 \ge 10^6 \text{ km}^2$). Coastal and open ocean boundaries are delineated by 249 the black line in Figure 1. Monthly-mean net primary production (NPP) was integrated 250 over the upper 100 m. 251

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_2 flux (ΔCO_2) in the ALL_{run} as:

$$\Delta \text{CO}_{2ALL_{run}} = \Delta \text{CO}_2^{\text{solub}^C} + \Delta \text{CO}_2^{\text{solub}^{N,Si}} + \Delta \text{CO}_2^{\text{NPP}^{N,Si}}, \quad (1)$$

where $\Delta CO_2^{solub^C}$ and $\Delta CO_2^{solub^{N,Si}}$ are the changes in air-sea CO_2 flux associated with the solubility pump due to the addition of terrestrial carbon and nitrogen/silica, respectively. $\Delta CO_2^{NPP^{N,Si}}$ is the change in air-sea CO_2 flux driven by NPP in response to terrestrial nitrogen and silica.

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In DC_{run} , changes in air-sea CO_2 flux are only associated with the solubility pump:

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

We then associated the change in surface-ocean DIC concentration with ΔCO_2 driven by the solubility pump in DC_{run} to isolate ΔCO_2 due to the solubility pump relative to changes in surface-ocean DIC concentration in DN and DSi_{runs}:

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

The change in ΔCO_2 due to changes in NPP in DN and DSi_{runs} was then estimated by subtracting ΔCO_2 due to the solubility pump from the total ΔCO_2 :

$$\Delta \text{CO}_2^{\text{NPP}^{N,Si}} = \Delta \text{CO}_{2DN,DSi_{runs}} - \Delta \text{CO}_2^{\text{solub}^{N,Si}}.$$
(4)

265 **3 Results**

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3.1 Climatological Global Analysis

Along with 39,687 km³ yr⁻¹ of riverine freshwater, total loads of 551.9 Tg C yr⁻¹, 35 Tg N yr⁻¹, and 139.7 Tg Si yr⁻¹ were exported into the global ocean in ALL_{run} (Table 1). The addition of dissolved carbon, nitrogen, and silica in ALL_{run} led to an increase in CO₂ outgassing of 0.03 Pg C yr⁻¹ compared to the Baseline, globally (Figure 3a and Figure 4a, Table 2). The majority of CO₂ outgassing (0.04 Pg C yr⁻¹) occurs in the coastal ocean (Figure 3a and Table 2). In the open ocean, riverine exports slightly increased CO₂ uptake by 0.01 Pg C yr⁻¹ (Figure 3a and Table 2).

In ALL_{run} , changes in air-sea CO_2 flux resulted from compensation between the 274 effects of riverine carbon and nitrogen, as DC_{run} and DN_{run} experiments result in el-275 evated CO_2 outgassing and uptake, respectively (Table 2). In DC_{run} , the increase in ocean 276 carbon due to riverine exports diminished the ocean's capacity to take up atmospheric 277 CO_2 , resulting in a net CO_2 outgassing of 0.22 Pg C yr⁻¹ (Table 2). In DN_{run} , the in-278 crease in nutrients to the euphotic zone led to increased phytoplankton productivity. The 279 additional uptake of carbon by phytoplankton decreased surface-ocean DIC, resulting 280 in an additional CO₂ sink of 0.17 Pg C yr⁻¹ (Table 2). 281

²⁸² CO₂ outgassing driven by riverine carbon (DC_{run}) was dominated by t_{DOC} (70%), ²⁸³ with a smaller contribution from t_{DIC} (30%) (Figure 4a). While outgassing driven by ²⁸⁴ riverine carbon was compensated by uptake due to nitrogen in the open ocean, CO₂ up-²⁸⁵ take due to nitrogen was 36% lower than riverine-carbon-driven coastal outgassing, lead-²⁸⁶ ing to global-ocean net CO₂ outgassing in ALL_{run} (Table 2).

Riverine dissolved carbon, nitrogen, and silica also resulted in a NPP increase of 287 0.6 Pg C yr⁻¹ (+2%) compared to Baseline (Figure 3b and Figure 4b, Table 2). River-288 ine t_{DIN} (DIN_{run}) contributed to 70% and 86% of the CO₂ uptake and NPP increase 289 simulated in DN_{run} , respectively (Figure 4b). The total increase of NPP in ALL_{run} from 290 riverine exports was equally distributed between the coastal and open ocean (0.3 Pg C)291 yr^{-1} for each) (Figure 4b). However, the increase of NPP was stronger in the coastal ocean 292 $(+5.2 \text{ g C m}^{-2} \text{ yr}^{-1}, +7\%)$ compared to the open ocean $(+1 \text{ g C m}^{-2} \text{ yr}^{-1}, +1\%)$ rel-293 ative to their surface area. 294

		\mathbf{CO}_2 Flux	NPP
Domain	Experiment	$(Pg \ C \ yr^{-1})$	$(Pg \ C \ yr^{-1})$
Coastal			
Ocean	Baseline	-0.68	3.8
	$ALL_{run} - Baseline$	+0.04	+0.3
	$DC_{run} - Baseline$	+0.1	0.0
	$DN_{run} - Baseline$	-0.07	+0.3
	$DSi_{run} - Baseline$	-0.01	+0.01
Open			
Ocean	Baseline	-1.90	20.6
	$ALL_{run} - Baseline$	-0.01	+0.3
	$DC_{run} - Baseline$	+0.1	0.0
	$DN_{run} - Baseline$	-0.1	+0.3
	$DSi_{run} - Baseline$	-0.01	+0.01
Global			
Ocean	Baseline	-2.58	24.4
	$ALL_{run} - Baseline$	+0.03	+0.6
	$DC_{run} - Baseline$	+0.22	0.0
	$DN_{run} - Baseline$	-0.17	+0.6
	$DSi_{run} - Baseline$	-0.01	+0.01

Table 2. Air-sea CO_2 flux and NPP for each experiment in the coastal ocean, open ocean, and global ocean. Positive values represent CO_2 outgassing; negative values are uptake.

3.2 Climatological Regional Analysis

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The Arctic Ocean region (Figure 1, ARCT) received 5,138 km³ yr⁻¹ of freshwater 296 from rivers in Baseline, which is roughly 13% of global freshwater discharge. In ALL_{run}, 297 freshwater discharge was supplemented with 22.6 and 56.8 Tg C yr⁻¹ of t_{DOC} and t_{DIC} , 298 respectively (Figure 2). The river load of carbon and t_{DOC} into ARCT represented 15% 299 and 12% of their associated global loads, respectively. ARCT also received 2.5 Tg N yr⁻¹ 300 as t_{DON} (56%) and t_{DIN} (44%) in ALL_{run}. The t_{DSi} river load was 12.6 Tg Si yr⁻¹ (Fig-301 ure 2) in this region. Riverine export loads were primarily from the Ob, Yenisei, Lena, 302 and Mackenzie Rivers (Figure 2 and Supporting Information Table S1). 303

In Baseline, ARCT produced a CO_2 uptake of roughly 0.21 Pg C yr⁻¹. When river-304 ine carbon, nitrogen, and silica were added in ALL_{run} , ARCT CO₂ uptake was reduced 305 by 0.02 Pg C yr⁻¹, with the majority of the response (80%) in the coastal ocean (Fig-306 ure 3a and Figure 4a). Riverine-induced CO_2 outgassing was dominated by the input 307 of t_{DOC} in ARCT (Figure 4a). 50% of the riverine-induced CO₂ outgassing was due to 308 the Ob, Yenisei, Lena, and Mackenzie Rivers (Table 3). In the Baseline experiment, NPP 309 was $0.22 \text{ Pg C yr}^{-1}$, with a similar magnitude in the coastal and open ocean. The ad-310 dition of riverine nitrogen into ARCT increased coastal NPP by 40% (Figure 3b and Fig-311 ure 4b). 312

The Tropical Atlantic (Figure 1, TROP-ATL) received 36% of global freshwater discharge (14,228 km³ yr⁻¹) and 35% of the global t_{DOC} load from rivers (67.2 Tg C yr⁻¹). Combined with t_{DIC} , the net carbon load was 145.3 Tg C yr⁻¹ (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 CO₂ outgassing of 319 $0.02 \text{ Pg C yr}^{-1}$ compared to Baseline (0.10 Pg C yr}^{-1}). This imbalance resulted from 320 CO_2 outgassing driven by carbon, which was 30% larger than uptake due to increased 321 phytoplankton productivity from riverine nitrogen (Figure 4a). 85% of CO₂ outgassing 322 in DC_{run} was driven by riverine t_{DOC} (Figure 4a). Riverine t_{DOC} indirectly drives CO_2 323 outgassing by first being remineralized to DIC, which increases DIC concentration in the 324 ocean and thus limits the ocean's capacity to take up atmospheric CO_2 . Most of the CO_2 325 outgassing driven by t_{DOC} occurs in the open ocean (Figure 3a and Figure 4a). The Ama-326 zon River drove 70% of riverine-induced CO_2 outgassing in TROP-ATL (Table 3). In 327 Baseline, NPP in TROP-ATL was 3.18 Pg C yr⁻¹. The increase in NPP driven by river-328 ine t_{DIN} occurred predominantly in the open ocean (~60%) compared to the coastal (~40%) 329 zone (Figure 4b). The Amazon River was responsible for 65% of the NPP increase driven 330 by riverine exports (Figure 4b). 331

In Baseline, the freshwater discharge into SE-ASIA was 7,841 km³ yr⁻¹, roughly 332 20% of global discharge. In ALL_{run}, SE-ASIA received 38% of dissolved carbon from rivers, 333 globally (207.39 Tg C yr^{-1}). 81% of dissolved carbon delivered into SE-ASIA was in-334 organic, representing 42% of the global t_{DIC} river load (Figure 2). SE-ASIA also received 335 45% (10.6 Tg N yr⁻¹) of the global t_{DIN} load from rivers (Figure 2). 41.5 Tg Si yr⁻¹ 336 was discharged into SE-ASIA (Figure 2). Nutrient loads into SE-ASIA were dominated 337 by high riverine t_{DIC} and t_{DIN} from the Ganges and Yangtze Rivers (Figure 2 and Sup-338 porting Information Table S1). The Yangtze river contributed 12% of t_{DIC} river loads, 339 globally (Figure 2 and Supporting Information Table S1). Taken together, the Yangtze 340 and Ganges Rivers delivered 20% of the global t_{DIN} river load (Figure 2 and Support-341 ing Information Table S1). 342

SE-ASIA had a CO₂ sink of 0.30 Pg C yr⁻¹ in Baseline, while CO₂ uptake increased by 0.02 Pg C yr⁻¹ in ALL_{run} (Figure 4a). Riverine carbon- and nitrogen-driven air-sea CO₂ flux was compensated in the coastal ocean (± 0.03 Pg C yr⁻¹). However, in the open ocean, the riverine nitrogen-driven increase in NPP and associated CO₂ uptake was two times higher than carbon-driven outgassing — leading to an overall imbalance and resulting in net CO₂ uptake in the domain (Figure 4a).

t_{DIN} was responsible for 85% of biological CO₂ uptake (Figure 4a). The Ganges River (58%), combined with the Indus and Yangtze Rivers, were responsible for 77% of CO₂ uptake in SE-ASIA (Table 3). NPP in SE-ASIA without the addition of riverine exports was 3.3 Pg C yr⁻¹. In ALL_{run}, NPP increased by 0.30 Pg C yr⁻¹ 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_2 flux and (b) NPP driven by riverine exports in ALL_{run} . 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 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_2 flux and NPP. Positive values represent CO_2 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_{run} , where only the corresponding river was included. Locations of river mouths are shown in Figure 1.

Rank	River	$egin{array}{lll} \Delta \ {f CO}_2 \ {f Flux} \ ({f Tg} \ {f C} \ {f yr}^{-1}) \end{array}$	$egin{array}{c} \Delta {f NPP} \ ({f Tg} {f C} {f yr}^{-1}) \end{array}$
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

355

3.3 Mechanisms of River-driven Air-sea CO₂ Flux

From January 2000 to December 2019, the time-mean surface-ocean DIC mass in 356 DC_{run} increased by 370.7 Tg C. This triggered a solubility-pump-driven outgassing of 357 222.4 Tg C yr^{-1} (Figure 4a). Over the same period, the addition of terrestrial nitrogen 358 and silica, the sum of DN_{run} and DSi_{run} , drove a reduction of 21.5 Tg C in the surface-359 ocean DIC mass. Assuming the same ratio of surface-ocean DIC and air-sea $\rm CO_2$ flux 360 as in DC_{run} , the input of terrestrial nitrogen and silica will cause a CO_2 uptake of 12.9 361 Tg C yr⁻¹ (Figure 4b). Since the net ocean CO_2 uptake increased by 186.2 Tg C yr⁻¹ 362 in response to terrestrial nitrogen and silica fertilization of NPP, the net increase in global 363 CO_2 uptake is 173.3 Tg C yr⁻¹ (Figure 4c). 364



Figure 5. Climatological (January 2000 to December 2019) air-sea CO₂ flux CO₂associated 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_2 flux driven by riverine exports was dominated 365 1) by the solubility pump near river mouths in response to terrestrial carbon and 2) by 366 NPP in the open ocean where CO₂ uptake from nitrogen- and silica-driven phytoplank-367 ton blooms exceeded riverine carbon-driven outgassing (Figure 4 and Figure 6). TROP-368 ATL and ARCT were dominated by riverine-driven CO_2 outgassing (71.9 and 24 Tg C 369 yr^{-1} , respectively) and CO₂ uptake due to NPP fertilization in TROP-ATL and ARCT 370 was minor (44.4 and 3.3 Tg C yr⁻¹, respectively). In SE-ASIA, the increase of CO_2 up-371 take due to enhanced NPP (69.6 Tg C yr⁻¹) exceeded CO_2 outgassing driven by river-372 ine carbon (53.9 Tg C yr^{-1}). 373



Figure 6. Pathways of change in climatological (January 2000 to December 2019) air-sea CO_2 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.

374 4 Discussion

375

4.1 Fate of Riverine Dissolved Carbon and Nutrients

Once in the ocean, terrestrial dissolved carbon $(t_{DOC} \text{ and } t_{DIC})$ result in a source of CO₂ to the atmosphere through a reduction of the solubility pump (Figure 7). Terrestrial nutrients, such as nitrogen and silica $(t_{DIN}, \text{ and } t_{DSi})$, fertilize phytoplankton and elevate CO₂ uptake via increased NPP.

The resultant export of marine organic carbon (m_{OC}) from the surface ocean drives additional CO₂ 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 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 g C m⁻² yr⁻¹, +7%) compared to the open ocean (+1 g C m⁻² yr⁻¹, +1%), the outgassing of CO_2 driven by riverine carbon through the solubility pump dominates changes in air-sea CO_2 flux close to river mouths. In contrast, the riverine nitrogen and silica signal spreads further offshore and enhances NPP and CO_2 uptake — this mechanism dominates the change in air-sea CO_2 flux in open-ocean regions.

In carbon-dominated terrestrial margins, such as TROP-ATL and ARCT, rivers drive a large source of CO₂ 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 CO₂ in the global ocean.

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

 Table 4.
 Riverine exports loads.

 ¹ (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)

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

- 3 (Cotrim da Cunha et al., 2007; Araujo et al., 2014)
- ⁴ (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

Domain	$\Delta \mathrm{CO}_2/\mathrm{NPP}$	$egin{array}{l} \mathbf{ALL}_{run} \ (\mathbf{Pg} \ \mathbf{C} \ \mathbf{yr}^{-1}) \end{array}$	$\begin{array}{c} {\rm Literature~Value}\\ {\rm (Pg~C~yr^{-1})} \end{array}$
Global	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	+0.03 +0.6	+0.11 ¹ +0.6-3.9 ¹
ARCT	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	+22.8 +7.4	+0.6-20 ^{2*} +58 ²
TROP-ATL	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	+20 +170	$+5-20^{3^{**}}$ +80-400 ³
SE-ASIA	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	-24.7 + 296	$^{ m N/A}_{ m +100}$ 4

Table 5. Change in air-sea CO_2 flux and NPP driven by riverine exports.

¹ (Tivig et al., 2021; Cotrim da Cunha et al., 2007)

 2 (Manizza et al., 2011; Terhaar et al., 2021)

³ (da Cunha & Buitenhuis, 2013; Louchard et al., 2021)

 4 (Tivig et al., 2021)

* Effect of t_{DOC} only

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

For both Baseline and ALL_{run}, the ocean CO₂ sink (2.55–2.58 Pg C yr⁻¹) lies within 396 the range of recent estimates (Resplandy et al., 2018; Regnier et al., 2022; Friedlingstein 397 et al., 2023). This present-day ocean CO_2 sink reflects the contribution of climate and 398 anthropogenic perturbations on top of preindustrial levels. In this study, a net riverine 399 carbon export of 0.55 Pg C yr⁻¹ (Table 1, $t_{DOC} + t_{DIC}$) drives a CO₂ outgassing of 0.22 Pg C yr⁻¹, while 35 Tg N yr⁻¹ (Table 1, $t_{DON} + t_{DIN}$) drives a CO₂ uptake of 0.17 Pg 400 401 $C \text{ yr}^{-1}$ from enhanced ocean fertilization. We note that our multi-decadal estimates are 402 not in steady state and do have a realistic representation of estuarine, blue carbon, and 403 bottom sediment processes. Therefore, they are not directly comparable to steady-state, 404 pre-industrial estimates of the river loop (Resplandy et al., 2018). 405

The introduction of terrestrial nutrients, such as inorganic nitrogen and silica, in-406 creased global-ocean marine NPP by 0.6 Pg C yr^{-1} compared to Baseline. The addition 407 of t_{DIN} and t_{DON} also increased ocean NPP by 0.6 Pg C yr⁻¹ in the model described 408 in Tivig et al. (2021) (Table 5). The modeling study by Lacroix et al. (2020) also depicted 409 a 3% increase of ocean NPP in response to the addition of riverine nutrients. In our study, 410 the increase of NPP driven by riverine exports was stronger in the coastal ocean com-411 pared to the open ocean, relative to their respective surface areas. This is consistent with 412 the recent study of Mathis et al. (2024), which demonstrates the role of increased river-413 ine nutrient loads in driving stronger biological carbon fixation and thus an enhanced 414 CO_2 sink in the coastal ocean during the last century. 415

416 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.



-20-

420 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} 421 delivered to the ARCT by individual rivers (Yenisey, Lena, Ob, and Mackenzie) falls within 422 the range of observations from Tank et al. (2012), Le Fouest et al. (2013), and Holmes 423 et al. (2012) (Supporting Information Table S1); suggesting that our estimates are re-424 liable at the pan-Arctic scale (Table 4). In Baseline, ARCT uptakes 213.9 Tg C yr⁻¹ of 425 atmospheric CO_2 The addition of riverine exports reduces this CO_2 sink by 20 Tg C yr⁻¹ 426 and results in ECCO-Darwin having a more-consistent Arctic Ocean sink compared to 427 previous studies (Manizza et al., 2011; Mortenson et al., 2020). In this region, riverine 428 carbon dominates the response of air-sea CO_2 flux, with riverine t_{DOC} being responsi-429 ble of 80% of CO₂ outgassing in ARCT. In Bertin et al. (2023), riverine exports from 430 the Mackenzie River drove a CO_2 outgassing of roughly 0.5 Tg C yr⁻¹ in the river plume. 431 Our model depicts a CO_2 outgassing of similar magnitude in the river plume region (~0.1 432 Tg C yr^{-1}). 433

Due to anthropogenic climate change, thawing of carbon-rich permafrost is supple-434 menting the load of t_{DOC} into Arctic rivers (Spencer et al., 2015). Permafrost-derived 435 DOC has a relatively fast remineralization rate (~ 2 weeks) that could lead to strong 436 CO_2 outgassing along coastal Arctic margins, which are dominated by permafrost-covered 437 watersheds (Bertin et al., 2023). Furthermore, the degradation of organic carbon by mi-438 crobial activity may be enhanced by changes in environmental conditions, such as increas-439 ing sea-surface temperature in ARCT (Carvalho & Wang, 2020). This would likely in-440 crease ocean CO_2 outgassing in response to the riverine carbon depicted in our study. 441 Additionally, riverine nutrients also contribute to the Arctic Ocean carbon sink as they 442 fertilize coastal waters. NPP in the Arctic Ocean increased by 3% (+7.4 Tg C yr⁻¹) in 443 ALL_{run} compared to Baseline. However, recent estimates by Terhaar et al. (2021) sug-444 gests that riverine nutrients support up to 9-11% (+58 Tg C yr⁻¹) of marine NPP in 445 the ARCT, in agreement with estimates by (Le Fouest et al., 2013, 2015) (Table 5). There-446 fore, CO_2 uptake driven by ocean fertilization from riverine nitrogen, and its capacity 447 to compensate CO_2 outgassing in ARCT, might be underestimated in our study. 448

4.2.2 Tropical Atlantic (TROP-ATL)

449

Four of the top-15 global largest rivers (Amazon, Congo, Mississippi, and Niger) 450 discharge into TROP-ATL. In total, rivers carry 67.2 Tg C yr⁻¹ as t_{DOC} , 78.1 Tg C yr⁻¹ 451 as t_{DIC} , 4.2 Tg N yr⁻¹ as t_{DON} , 4.5 Tg N yr⁻¹ as t_{DIN} , and 44.9 Tg Si yr⁻¹ as t_{DSi} 452 into TROP-ATL. Riverine t_{DOC} , t_{DIC} , and silica loads in our study are consistent with 453 estimates from Cotrim da Cunha et al. (2007) and Araujo et al. (2014) (46 and \sim 50 Tg 454 C yr⁻¹ and 53 Tg Si yr⁻¹, respectively; Table 4). Our estimate of t_{DIN} delivered to this 455 region is 3-fold lower than the value of 15.3 Tg N yr^{-1} reported by Cotrim da Cunha et 456 al. (2007) (Table 4). However, t_{DIN} export from the Amazon river (1 Tg N yr⁻¹) agrees 457 well with Louchard et al. (2021) (0.9 Tg N yr⁻¹). A dynamic land ecosystem model that 458 explicitly resolves fluxes over the entire watershed estimated that 0.9 Tg N yr⁻¹ is ex-459 ported as t_{DIN} from the Mississippi River (Tian et al., 2020), which is in general agree-460 ment with the 0.7 Tg N yr⁻¹ that we use as input for our model. The load of t_{DIN} from the Congo River (0.2 Tg N yr⁻¹) is also the same order of magnitude compared to data 461 462 from Jouanno et al. (2021). However, our Global-NEWS-2-based estimate of 0.1 Tg N 463 yr^{-1} remains lower than previous estimates for the Niger River (Robertson & Rosswall, 464 1986) (0.5 Tg N yr⁻¹). We stress that in Africa river systems, nutrient loads are poorly 465 constrained due to sparse data. 466

⁴⁶⁷ In Baseline, TROP-ATL is a source of CO_2 to the atmosphere (0.10 Pg C yr⁻¹), ⁴⁶⁸ which agrees with both interpolation-based products (Landschützer et al., 2016; Jersild ⁴⁶⁹ et al., 2023; Rödenbeck, 2005) (0.04–0.08 Pg C yr⁻¹) and model results (da Cunha & ⁴⁷⁰ Buitenhuis, 2013; Louchard et al., 2021) (0.03–0.04 Pg C yr⁻¹). We note that previous studies show a river-driven increase in CO₂ uptake of 0.005 and 0.02 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 ALL_{run} enhanced the source of CO₂ (+0.02 Pg C yr⁻¹) (Table 5).

Contrary to the estimates of Louchard et al. (2021), which include physical effects 476 associated with freshwater, such as enhanced upper-ocean stratification and gas solubil-477 ity, our baseline simulation already includes these processes. Therefore, our suite of ex-478 periments cannot isolate and quantify the impact of freshwater discharge on ocean bio-479 geochemistry. Freshwater in river plumes facilitates the uptake of atmospheric CO_2 through 480 the solubility pump, which in turn overlaps with the sink of CO_2 associated with bio-481 geochemical runoff. In addition to nitrogen, Louchard et al. (2021) also included inor-482 ganic phosphorus loads and a regionally-adjusted plankton ecosystem, e.g., by includ-483 ing a nitrogen-fixing phytoplankton functional type, which increased the model's capa-484 bility to better resolve the biological pump and hence CO₂ uptake. For our simulations, 485 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 Pg C yr⁻¹ reported in Louchard et al. (2021) (Table 5) and 487 the value of 0.4 Pg C yr⁻¹ reported in Cotrim da Cunha et al. (2007). We note that hor-488 izontal resolution is also important for realistic representation of coastal processes. In 489 their higher-resolution study, Louchard et al. (2021) were able to separately resolve the 490 estuarine and plume/shelf waters of the Amazon River as a CO_2 source and sink, respec-491 tively, whereas our model intrinsically lacks such fine delineation. 492

The Amazon River clearly dominates the CO₂ outgassing signal in TROP-ATL, which 493 is driven by the large load of t_{DOC} . Along with other rivers such as the Congo, Niger, 494 and Orinoco Rivers, the Amazon River delivers a large amount of t_{DOC} , which originates 495 from tropical forests. These forests contribute roughly one third of terrestrial NPP and 496 their soil contains large amount of organic carbon, globally (Cleveland et al., 2010). As 497 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 499 waters to the coastal ocean (M. Li et al., 2019). At present time, it is critical to better 500 constrain export of carbon from watersheds to coastal waters and characterize their fate 501 in the ocean, as current efforts may be overestimating the land sink of carbon associated 502 with tropical forests (Lauerwald et al., 2020). Additionally, the composition (refractory 503 black carbon from combustion) and the quantity $(CO_2$ fertilization from NPP and soil 504 erosion with deforestation) of carbon exports from the Amazon River remains uncertain 505 due to ongoing changes in regional climate and fire regimes (Fleischer et al., 2019; Jones 506 et al., 2020; Riquetti et al., 2023). 507

508

4.2.3 Southeast Asia (SE-ASIA)

Riverine biogeochemical runoff in SE-ASIA is dominated by high loads of t_{DIN} (10.6) 509 Tg N yr⁻¹) and t_{DIC} (163.8 Tg C yr⁻¹), especially from the Ganges and Yangtze Rivers. 510 The magnitude of the riverine t_{DIN} load for SE-ASIA compares with individual estimates 511 for the Bay of Bengal (0.4 Tg N yr⁻¹), the Arabian Sea (0.06 Tg N yr⁻¹), and the East China Sea (1.6–7.9 Tg N yr⁻¹) (Singh & Ramesh, 2011; H.-M. Li et al., 2014; J. Wang 512 513 et al., 2020; Nishina et al., 2021) (Table 4). Our estimate of the t_{DIC} load in SE-ASIA 514 remains higher than values reported in the literature ($\sim 40 \text{ Tg C yr}^{-1}$) (Piao et al., 2012; 515 Patra et al., 2013) and thus would require a regional adjustment as we did for the Ama-516 zon River (Table 4 and Supporting Information Text S1). This is explained by overes-517 timated t_{DIC} loads from the Yangtze (45.9 Tg yr⁻¹) and the Ganges (18 Tg yr⁻¹) Rivers 518 compared to reported values (20 and 3–4 Tg C yr⁻¹, respectively) (F. Wang et al., 2007; 519 Guo et al., 2015; Y. Gao et al., 2017; Samanta et al., 2015). This overestimation is re-520 lated to the relationship based on river discharge and the dominant lithology (Amiotte Suchet 521 et al., 2003; M. Li et al., 2017). Both rivers exhibit high discharge combined with weathering-522

prone lithologies (carbonate rocks and shales for the Yangtze and Ganges rivers, respectively), which consume atmospheric CO_2 due to high rates of rock weathering (Amiotte Suchet et al., 2003). The Yangtze River is also known for its high river CO_2 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_2 in Baseline (0.3 Pg C yr⁻¹). 530 Combining air-sea CO_2 budgets for the different regions composing SE-ASIA from lit-531 erature (East-Pacific, Indonesian seas, and North Indian Ocean without including Oman 532 and Somalian upwelling regions), we estimate a carbon sink of $\sim 0.2 \text{ Pg C yr}^{-1}$ for the 533 entire SE-ASIA domain (Kartadikaria et al., 2015; De Verneil et al., 2021; Zhong et al., 534 2022; Hood et al., 2023). Our study provides the first estimate of the contribution of present-535 day riverine exports to the carbon sink in SE-ASIA. The net air-sea CO_2 exchange bal-536 ance driven by riverine exports in SE-ASIA results in a carbon sink of 0.02 Pg C yr⁻¹ 537 in ALL_{run} . Compared to ARCT and TROP-ATL, carbon uptake in SE-ASIA is enhanced 538 by a strong increase in marine NPP (+0.30 Pg C yr⁻¹, +9%) driven by riverine t_{DIN} . 539 In Tivig et al. (2021), the simulated increase of NPP in response to riverine nitrogen was 540 roughly 0.1 Pg C yr^{-1} in Asia, with the strongest increase in the Yellow Sea, similar to 541 our results (Table 5). Riverine nitrogen loads in this domain, and especially in the China 542 seas, have been supplemented by increased nitrogen deposition, nitrogen fertilizer, ma-543 nure, and human sewage over the last 50 years (Nishina et al., 2021). Even if nitrogen 544 runoff is declining, agricultural-driven nitrogen loads will remain at significant levels and 545 continue to fertilize phytoplankton blooms in this nitrogen-depleted marine region due 546 to high denitrification (Michael Beman et al., 2005; Nishina et al., 2021). Locally, the 547 addition of riverine biogeochemical runoff also drives a source of CO_2 to the atmosphere, 548 which is primarily limited to near river mouth locations in SE-ASIA. In the Yellow Sea 549 and the Northern Bay of Bengal, close to the Yangtze and Ganges Rivers, the addition 550 of riverine exports at preindustrial levels in an ocean model also drove a CO_2 outgassing 551 in Lacroix et al. (2020). Noticeably, in our simulations, riverine carbon turns the north-552 ern Bay of Bengal into a carbon source as suggested by Hood et al. (2023). 553

4.3 Model Improvements

554

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 bio-560 geochemistry (Krachler et al., 2005; Tagliabue et al., 2017; Duhamel et al., 2021; Savenko 561 & Savenko, 2021). Consequently, our results may underestimate the global-ocean air-562 sea CO_2 uptake due to the absence of riverine phosphorus or iron in the model, as they 563 might be limiting for ocean NPP relative to the excess of terrestrial inorganic nitrogen. 564 Additionally, riverine t_{ALK} flux was computed based on a constant ALK:DIC ratio, glob-565 ally (0.98). We note that the GLORICH database used to compute the mean ALK:DIC 566 ratio has relatively good coverage over the American continent but Eurasia and Africa 567 are underrepresented (Hartmann et al., 2014). As such, the ALK:DIC ratio can vary sub-568 stantially over regional scales. The lack of this spatially-granular information in our sim-569 ulated exports may misrepresent riverine t_{ALK} fluxes and the alkalinity-driven buffer-570 ing capacity of simulated river plumes (Dubois et al., 2010; Tank et al., 2012; Mol et al., 571 2018; Ghosh et al., 2021; Gomez et al., 2023). While in estuaries the absence of ALK 572 relative to DIC leads to higher partial pressure of CO_2 (p CO_2) in upper-ocean waters 573 and enhanced CO₂ outgassing, rivers also bring an excess of ALK relative to DIC on con-574

tinental shelves, which can reduce ocean pCO₂ through buffering and thus facilitate CO₂ uptake (W.-J. Cai et al., 2010; Louchard et al., 2021). Furthermore, the fate of riverine t_{ALK} in the ocean is associated with the biological activity of calcifying organisms and exchange at the sediment-water interface (Middelburg et al., 2020) — an undergoing development in our modeling system.

In our model, the global-ocean net CO₂ outgassing driven by riverine exports re-580 flects the stronger effect of riverine carbon on the solubility pump (CO_2 source) com-581 pared to the change in the CO_2 uptake associated with the increase in NPP. This im-582 balance can result from an overestimation of CO_2 outgassing driven by riverine carbon, 583 and especially t_{DOC} . First, assuming that total loads of carbon or nutrients over each 584 watershed are routed to the ocean is a misrepresentation, as losses and gains occur through 585 the LOAC (W.-J. Cai, 2011). Second, t_{DOC} is degraded in coastal waters at different 586 rates depending on its origin and subsequent labile fraction (Lønborg et al., 2020). In 587 the present study, in addition to not accounting for refractory and labile fractions of t_{DOC} , 588 marine and terrestrial DOC are both being remineralized at the same rate (3 months). 589 Overall, this could lead to an overestimation of t_{DOC} remineralization and thus ocean 590 CO_2 outgassing due to the subsequent excess of DIC. For instance, the Amazon River 591 — the main source of riverine t_{DOC} into the ocean — contributes to almost 50% (+0.014 592 Pg C yr⁻¹) of the global-ocean CO_2 outgassing in response to riverine exports in our study. 593 However, t_{DOC} from the Amazon River shows stronger stability in the coastal ocean and 594 is exported from the continental margin to the open ocean (Medeiros et al., 2015; Louchard 595 et al., 2021). Increasing the refractory pool of Amazon t_{DOC} could therefore decrease 596 CO_2 outgassing in our simulations. While recent modeling studies include separate pools 597 of refractory and labile t_{DOC} with different remineralization rates at regional scales (Louchard 598 et al., 2021; Gibson et al., 2022; Bertin et al., 2023), the nature of t_{DOC} needs to be bet-599 ter accounted for in global-ocean biogeochemistry models. 600

5 Perspectives

Biogeochemical inputs from rivers into the ocean are subject to variability from cli-602 mate change and/or human activities. Over the last century, loads of riverine exports 603 such as nitrogen and phosphorus increased dramatically — mostly due to anthropogenic 604 perturbations (+349% and +233%, respectively) (Lacroix et al., 2021). In the coastal 605 ocean, this has strongly increased NPP associated with the regions in which our model 606 depicts the strongest impact of riverine nutrients on NPP (TROP-ATL and SE-ASIA) 607 (Lacroix et al., 2021). Over the past 20 years, fertilizers and aquaculture have been iden-608 tified as global drivers of phytoplankton blooms in coastal waters (Dai et al., 2023). The 609 load of riverine t_{DOC} also increased globally over the period 1860–2010 (+17%), due to 610 CO_2 fertilization of terrestrial vegetation and climate change (Nakhavali et al., 2024). 611 In the near future (2050), the global contribution of natural sources of nitrogen and phos-612 phorus in riverine inputs is expected to continue to decrease due to land-use change, while 613 anthropogenic sources from human waste, agriculture, and aquaculture are projected to 614 increase for every potential Shared Socioeconomic Pathways (SSP) scenario (Beusen et 615 al., 2022). However, the export of nutrients from anthropogenic sources to the ocean will 616 decrease in industrialized regions such as North America, Europe (including the Russian 617 Federation), Japan, and Oceania in most SSPs (Beusen & Bouwman, 2022). For instance, 618 in the contiguous United States, the riverine load of nitrogen from human waste and at-619 mospheric pollution decreased over 1930–2017 (Byrnes et al., 2020). Nonetheless, the load 620 of nitrogen from agricultural sources kept increasing over the same period (Byrnes et al., 621 2020). Consequently, only the long-term adoption of the Paris Agreement and sustain-622 able development scenarios, such as SSP1 where the use of resources and the dependency 623 on fossil fuels are significantly reduced, would lead to better stream water quality (Beusen 624 & Bouwman, 2022; Beusen et al., 2022). Over the 21st century, the increase of ocean NPP 625 and the associated carbon sink driven by the historical increase of nutrients loads is ex-626

pected to be dampened by the increase of CO_2 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 629 the spatial and temporal coverage/resolution of models, forcing products, and observa-630 tions. As river discharge is associated with suspended particulate loads, ocean color re-631 trievals from spaceborne instruments can be an effective tool for monitoring river plumes 632 systems. However, the complexity of optical properties and their large space-time vari-633 ability requires high-resolution sensors to capture the actual constituents of ocean bio-634 geochemistry. The recently launched Plankton, Aerosol, Cloud, ocean Ecosystem (PACE) 635 satellite mission (https://pace.oceansciences.org/) and its onboard high-resolution spec-636 trometer will bring new insights into the water quality of coastal regions near river mouths. 637 Combined, with river discharge retrievals from the Surface Water and Ocean Topogra-638 phy (SWOT, https://swot.jpl.nasa.gov/), combined spaceborne observations of ocean 639 color and terrestrial fluxes of freshwater into the ocean will pave the way for an integrated 640 Earth Observation System, where the connection between the land and the ocean will 641 be better understood. While effective, these satellite missions are expensive and should 642 not replace critical in-situ and ground-truthed observations. We highlight that ambitious 643 spaceborne missions can indeed be complemented by more modest initiatives, such as 644 citizen science or stakeholder engagement to monitor water quality in river systems (Ab-645 bott et al., 2018). 646

647 6 Conclusion

Our simulations suggest that the role of present-day riverine exports is moderate, 648 with an outgassing of $0.03 \text{ Pg C yr}^{-1}$ to the atmosphere, globally. We find that river-649 ine inputs drive contrasting regional patterns in air-sea CO_2 flux. Terrestrial dissolved 650 carbon, and especially t_{DOC} , contributes to an outgassing of CO₂ through a reduction 651 of the ocean's solubility pump. Terrestrial nutrients, and in particular t_{DIN} , fertilizes 652 phytoplankton and increases marine NPP and the associated carbon biomass. Thus, ter-653 restrial nutrients such as inorganic nitrogen and silica enhance the uptake of atmospheric CO_2 into the ocean. While outgassing of CO_2 is primarily located near river mouths, 655 the fertilization by riverine nitrogen and silica spreads further offshore and into the open 656 ocean. In carbon-dominated margins such as ARCT or TROP-ATL, rivers contribute 657 a large source of CO_2 from the ocean to the atmosphere. However, in nitrogen-dominated 658 margins such as SE-ASIA, rivers drive a large sink of atmospheric CO_2 into the ocean. 659 This work highlights that a better quantification of lateral riverine exports and the in-660 corporation of these fluxes in global models is pivotal for regional and global carbon bud-661 gets. Conducting sensitivity experiments could support national policy decisions and in-662 form climate resilience strategies for land and marine practices. 663

664 Acknowledgments

A portion of this research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (80NM0018D0004). Support from the Carbon Cycle Science (CCS) and Carbon Monitoring Systems (CMS) programs are acknowledged. High-end computing resources were provided by the NASA Advanced Supercomputing (NAS) Division of the Ames Research Center. Government sponsorship acknowledged. © 2024. All rights reserved

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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 sim⁶⁷⁵ ulations used in this paper and generating runoff forcing are available at: 10.5281/zen-⁶⁷⁶ odo.10562713.

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Role of Riverine Dissolved Organic and Inorganic Carbon and Nutrients in Global-ocean Air-sea CO₂ Fluxes

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Key Points:

ton fertilization

17	•	We assess how global lateral exports impact air-sea CO ₂ flux and carbon cycling
18		in ECCO-Darwin ocean biogeochemistry simulations
19	•	Near river mouths, changes in CO_2 flux are dominated by the solubility pump and
20		lead to outgassing
21	•	Further offshore, riverine nitrogen leads to increased CO ₂ uptake via phytoplank-

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23 Abstract

While the preindustrial ocean was assumed to be in equilibrium with the atmosphere, 24 the modern ocean is a carbon sink, resulting from natural variability and anthropogenic 25 perturbations, such as fossil fuel emissions and changes in riverine exports over the past 26 two centuries. Here we use a suite of sensitivity experiments based on the ECCO-Darwin 27 global-ocean biogeochemistry model to evaluate the response of air-sea CO_2 flux and car-28 bon cycling to present-day lateral fluxes of carbon, nitrogen, and silica. We generate a 29 daily export product by combining point-source freshwater discharge from JRA55-do with 30 31 the Global NEWS 2 watershed model, accounting for lateral fluxes from 5171 watersheds worldwide. From 2000 to 2019, carbon exports increase CO₂ outgassing by 0.22 Pg C 32 yr^{-1} via the solubility pump, while nitrogen exports increase the ocean sink by 0.17 Pg 33 $C \text{ yr}^{-1}$ due to phytoplankton fertilization. On regional scales, exports to the Tropical 34 Atlantic and Arctic Ocean are dominated by organic carbon, which originates from ter-35 restrial vegetation and peats and increases CO_2 outgassing (+10 and +20\%, respectively). 36 In contrast, Southeast Asia is dominated by nitrogen from anthropogenic sources, such 37 as agriculture and pollution, leading to increased CO_2 uptake (+7%). Our results demon-38 strate that the magnitude and composition of riverine exports, which are determined in 39 part from upstream watersheds and anthropogenic perturbations, substantially impact 40 present-day regional-to-global-ocean carbon cycling. Ultimately, this work stresses that 41 lateral fluxes must be included in ocean biogeochemistry and Earth System Models to 42 better constrain the transport of carbon, nutrients, and metals across the land-ocean-43 aquatic-continuum. 44

45 Plain Language Summary

Due to ongoing climate change and human activities, the transport of carbon and 46 nutrients from rivers to the ocean has changed, with rivers now contributing to the mod-47 ern ocean's sequestration of atmospheric carbon dioxide (CO_2) . In this study, we add 48 the effect of present-day rivers to a numerical model of the ocean carbon cycle (ECCO-49 Darwin) and then estimate their impact on air-sea CO_2 exchange and ocean biogeochem-50 istry. Over a 20-year period, riverine carbon saturates the surface ocean and increases 51 the amount of CO₂ released to the atmosphere, while nitrogen fertilizes phytoplankton 52 and increases the capture of atmospheric CO₂ via photosynthesis. In the Tropical At-53 lantic and Arctic Oceans, organic carbon drained from vegetation and peats causes out-54 gassing of ocean carbon. In Southeast Asia, the large amount of riverine nitrogen orig-55 inating from human activities, such as agriculture or waste water, increases ocean CO_2 56 sequestration. Our work highlights how rivers, which are affected by present-day human 57 actions and climate change, impacts the ocean's carbon cycle across regional-to-global 58 scales. 59

60 1 Introduction

Globally, shelf and marginal seas are typically sinks of CO_2 , where uptake driven 61 by strong biological productivity exceeds outgassing from organic matter degradation 62 and carbon enrichment by river runoff and coastal upwelling (Ianson et al., 2009; W.-63 J. Cai, 2011; W. Cai et al., 2013; Laruelle et al., 2017; Bertin et al., 2023). Rivers trans-64 port roughly $0.8-0.9 \text{ Pg C yr}^{-1}$ from land to coastal regions as dissolved organic carbon 65 (DOC), dissolved inorganic carbon (DIC), particulate organic carbon (POC), and par-66 ticulate inorganic carbon (PIC); a third of the aforementioned total riverine export of 67 carbon is buried in coastal sediments (Regnier et al., 2022; Battin et al., 2023). Nutri-68 ents such as phosphorus, nitrogen, and silica are also conveyed by rivers along with car-69 bon. Terrestrial inorganic carbon and nutrients in streams originate from weathering of 70 the lithosphere and the associated sink of atmospheric CO_2 , along with the remineral-71 ization of organic matter in streams and/or on land (Suchet & Probst, 1995; Battin et 72

al., 2023). Riverine organic carbon and nutrients are further supplemented by primary
production from land vegetation and organic matter mobilized through direct literfall,
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 77 to the atmosphere in the form of CO_2 , due to the saturation of surface-ocean waters by 78 terrestrial DIC and remineralization of terrestrial organic matter (Hartmann et al., 2009; 79 Lacroix et al., 2020; Bertin et al., 2023) in shallow, well-mixed water columns. The nat-80 81 ural transport of carbon from terrestrial ecosystems to ocean outgassing, the so-called "river loop", is estimated to be 0.65 ± 0.3 Pg C yr⁻¹ (Regnier et al., 2022; Friedlingstein 82 et al., 2023). With respect to inorganic nutrients, their injection into the surface ocean 83 can fertilize growth of photosynthetic organisms in nutrient-limited regions. Globally, 84 this lateral flux increases ocean primary productivity and contributes to a coastal-ocean 85 sink of ~ 0.25 Pg C yr⁻¹, which is roughly 17% of the global-ocean sink (W.-J. Cai, 2011; 86 Lacroix et al., 2021; S. Gao et al., 2023). 87

Over the past two centuries, terrestrial anthropogenic perturbations have led to a 88 substantial increase in the load of nitrogen and phosphorus through agricultural fertil-89 ization, leaked sewage, and land-use change (Smith et al., 2003; Lee et al., 2016; Lacroix 90 et al., 2021). Projections of the historical riverine dissolved nitrogen and phosphorus load 91 depict a three- to four-fold increase over the period 1900–2019 (Lacroix et al., 2021). When 92 delivered in excessive amounts, these nutrients can alter aquatic and ocean ecosystems, 93 resulting in eutrophication, hypoxia, and acidification in coastal waters (Laurent et al., 94 2017; Fennel & Testa, 2019). Dissolved and particulate carbon are also affected region-95 ally by agricultural liming, the addition of sulfuric acid to watersheds, changes in ero-96 sion patterns, and river management (Monteith et al., 2007; Raymond et al., 2008; Calmels 97 et al., 2007; Regnier et al., 2013; Maavara et al., 2017). Projected trends for river bio-98 geochemical loads remain uncertain and exhibit disparate regional responses over the 21^{st} qq century depending on the chosen shared socioeconomic pathway (Beusen et al., 2022; Beusen 100 & Bouwman, 2022; Vishwakarma et al., 2022; Zhang et al., 2022). 101

While present estimates of riverine freshwater and biogeochemical fluxes are poorly 102 sampled in space and time, land surface and watershed models can provide spatiotemporally-103 resolved lateral exports at global scales (Mayorga et al., 2010; Krinner et al., 2005; Hage-104 mann & Dümenil, 1997; Hagemann & Gates, 2003; M. Li et al., 2017; Bloom et al., 2020). 105 Coupled with ocean biogeochemical models, it is thus possible to quantify the response 106 of the coastal and open-ocean carbon cycle to lateral fluxes (Lacroix et al., 2020, 2021; 107 Mathis et al., 2022; Louchard et al., 2021; da Cunha & Buitenhuis, 2013; Le Fouest et 108 al., 2013; S. Gao et al., 2023; Bertin et al., 2023). Regarding the importance of lateral 109 exports in ocean carbon cycling, it is critical that ocean biogeochemical models better 110 account for coastal mechanisms occurring across the land-ocean-aquatic-continuum (LOAC) 111 (Ward et al., 2020; Mathis et al., 2022). Such improvements will come from 1) finer hor-112 izontal and vertical grid resolution to resolve small-scale ocean physics (vertical mixing, 113 submesoscale processes) and associated biology (hypoxia, phytoplankton blooms) and 114 2) improved representation of LOAC components (river and groundwater discharge, bot-115 tom sediment diagenesis, and estuarine biogeochemical filtering) (Ward et al., 2020; Sharples 116 et al., 2017). While recent modeling efforts have made improvements in this regard (Volta 117 et al., 2016; Laruelle et al., 2017; Mathis et al., 2022, 2024), the respective contribution 118 of riverine exports to air-sea CO_2 fluxes across the global ocean remains to be assessed. 119

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 CO₂ flux and ocean biogeochemistry to daily point-source river forcing from 2000–2019. We compute daily riverine biogeochemical export by combining pointsource 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 CO₂ 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.

132 2 Methods

133

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 140 in detail in (Forget et al., 2015). The nominal horizontal grid resolution in ECCO v4 LLC90 141 is $1^{\circ}(\sim 55 \text{ km at high latitudes})$. The vertical discretization consists of 50 z-levels, rang-142 ing from 10-m thickness in the top 7 levels to 450 m at depth. ECCO v4 uses a third-143 order, direct-space-time tracer advection scheme in the horizontal and an implicit third-144 order upwind scheme in the vertical; a time step of 3600 s is used. Vertical mixing is pa-145 rameterized using the Gaspar–Grégoris–Lefevre (GGL) mixing-layer turbulence closure 146 and convective adjustment scheme (Gaspar et al., 1990). ECCO v4 assimilates physi-147 cal observations via the 4-D adjoint method (Wunsch et al., 2009; Wunsch & Heimbach, 148 2013).149

Daily river runoff in the present configuration is based on the Japanese 55-year at-150 mospheric reanalysis (JRA55-do) river forcing dataset, which uses the CaMa-Flood global 151 river routing model and adjusted runoff from the land component of JRA-55 (Suzuki et 152 al., 2018; Tsujino et al., 2018; Feng et al., 2021). Point source JRA55-do freshwater runoff 153 $(m s^{-1})$ was added to ECCO v4 as a real freshwater flux in the surface ocean (first ver-154 tical level) at the closest ECCO v4 LLC90 grid cell along the coastal periphery. The fresh-155 water flux was adjusted according to the difference in grid cell area between JRA55-do 156 (0.25°x 0.25°) and ECCO v4 LLC90. A full evaluation of ocean physics from ECCO v4 157 LLC90 compared to observations can be found in the Supporting Information and Feng 158 et al. (2021). 159

ECCO v4 LLC90 ocean physics was coupled online with the Massachusetts Insti-160 tute of Technology Darwin Project ecosystem model described in Brix et al. (2015). The 161 ecosystem model solves 39 prognostic variables such as carbon, nitrogen, phosphorus, 162 iron, silica, oxygen, and alkalinity. The model simulates their respective cycle from in-163 organic pools to living/dead matter of plankton organisms and the subsequent reminer-164 alization, all driven by the ocean physics. The carbonate chemistry is solved by the method 165 in Follows et al. (2006). Plankton species consist of five large-to-small functional phy-166 toplankton types (diatoms, other large eukaryotes, Synechococcus, and low- and high-167 light adapted *Prochlorococcus*), and two zooplankton types. Atmospheric CO_2 partial 168 pressure at sea level $(apCO_2)$ from the National Oceanic and Atmospheric Administra-169 tion Marine Boundary Layer Reference product (Andrews et al., 2014) was used to drive 170 air-sea CO_2 fluxes computed by the model according to Wanninkhof (1992). Atmospheric 171 iron dust is deposited at the ocean surface based on the monthly climatology of Mahowald 172 et al. (2009). Once at the ocean bottom, particulate inorganic and organic matter is re-173 moved at the sinking rate to limit the accumulation of particulates on the seafloor. Bio-174 geochemical observations were used to optimize the biogeochemical model using a Green's 175

Functions approach (Menemenlis et al., 2005); the optimization methodology and asso-176 ciated data are fully described in Carroll et al. (2020). The ECCO-Darwin solution was 177 previously published using monthly climatological freshwater runoff forcing from Fekete 178 et al. (2002). Here, the Baseline simulation consists of the same ocean biogeochemistry 179 simulation as Carroll et al. (2020), but with daily point-source freshwater runoff from 180 January 1992 to December 2019. To allow partial adjustment to these new boundary con-181 ditions, the analysis period hereinbelow spans the last 20 years of the simulation, Jan-182 uary 2000 to December 2019. Figure 1 shows the general match-up between time-mean 183 ECCO-Darwin air-sea CO₂ fluxes and the MPI SOM FFN v2022 (Landschützer et al., 184 2016; Jersild et al., 2023) and Jena CarboScope v2023 (Rödenbeck et al., 2013) prod-185 ucts for the 2000–2019 study period. 186



Figure 1. Climatological global-ocean air-sea CO_2 flux for (a) ECCO-Darwin Baseline, (b) MPI SOM FFN, and (c) Jena CarboScope. Positive values represent CO_2 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.

187 2.2 Biogeochemical River Runoff

In addition to the Baseline simulation, we conducted a suite of sensitivity exper-188 iments where we added terrestrial DOC (t_{DOC}), DIC (t_{DIC}), total alkalinity (t_{ALK}), 189 dissolved inorganic nitrogen (t_{DIN}) , dissolved organic nitrogen (t_{DON}) , and dissolved 190 silica (t_{DSi}) , henceforth referred to as riverine exports in this study. We excluded phos-191 phorus and iron due to the complexity of their reactions when entering the marine en-192 vironment (i.e., absorption, bio-availability). Except for t_{DIC} and t_{ALK} , riverine exports 193 are provided by the Global NEWS 2 (Global Nutrient Export from WaterSheds) model 194 (Mayorga et al., 2010). 195

Global NEWS 2 uses statistical and mechanistic relations at the watershed scale 196 to compute annual-mean freshwater discharge and riverine loads based on natural and 197 anthropogenic sources, with 6292 individual watersheds delineated according to the global 198 river systems dataset from Vörösmarty et al. (2000). t_{DIN} was partitioned into nitrite 199 (NO_2^-) , nitrate (NO_3^-) , and ammonium (NH_4^+) , according to the mean fraction of each 200 species concentration relative to the total DIN concentration from the GLObal RIver CHem-201 istry Database (GLORICH) (Hartmann et al., 2014). The NO₂⁻:DIN, NO₃⁻:DIN, and NH₄⁺:DIN 202 ratios were estimated to be 0.02, 0.65, and 0.33, respectively. Riverine t_{DIC} loads were 203 computed using an empirical relation between freshwater discharge and gross CO_2 con-204 sumption from rock weathering as described in M. Li et al. (2017, equation 9). CO_2 con-205 sumption by rock weathering over each Global NEWS 2 watershed was estimated based 206 on the freshwater discharge and the basin-dominant lithology (Amiotte Suchet et al., 2003). 207 t_{ALK} loads were computed using an ALK:DIC ratio (0.98) based on the mean total ALK 208 compared to DIC from GLORICH. t_{DOC} was not considered to be more refractory than 209 marine DOC; the DOC remineralization rate is set to 1 over 100 days. We used Global 210 NEWS 2 outputs for year 2000 as representative of present-day carbon and nutrient loads 211 (Mayorga et al., 2010). 212

Global NEWS 2 river mouth locations were associated with JRA55-do grid points 213 exhibiting the closest annual-mean freshwater discharge in 2000 within a euclidean dis-214 tance of 5° . The top-100 largest rivers (by watershed extent) from Global NEWS 2 were 215 imposed on JRA55-do grid points as a function of distance only. In total, 5171 river mouths 216 were associated with JRA55-do grid points. For each discharge point, export concentra-217 tions from the associated river were estimated by dividing the load by the annual vol-218 ume of freshwater from Global NEWS 2; the concentration was then converted to a daily 219 flux using the corresponding daily-mean freshwater flux from JRA55-do. Exports were 220 adjusted according to the grid cell area difference between JRA55-do and ECCO v4 LLC90. 221 These biogeochemical exports were then added as point-source discharge along riverine 222 freshwater flux (Figure 2). Due to extreme values in our automated Global-NEWS-2-223 derived computation for the Amazon River, the DIC load for this system was set to a 224 more-realistic, literature-mean of 2.54 Tmol yr^{-1} (da Cunha & Buitenhuis, 2013; Probst 225 et al., 1994; M. Li et al., 2017) (for more details see Supporting Information Text S1). 226



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 km³ yr⁻¹ are shown.

As riverine t_{DOC} , t_{DIN} , t_{DON} , and t_{DSi} were computed from Global NEWS 2 con-227 centration and modulated with JRA55-do freshwater runoff, our fluxes agree well with 228 existing estimates based on the NEWS 2 database (Mayorga et al., 2010; Frings et al., 229 2016; Sharples et al., 2017; Lacroix et al., 2020; Tivig et al., 2021; Tian et al., 2023). t_{DIC} 230 lateral export from rivers was estimated according to Amiotte Suchet et al. (2003); May-231 orga et al. (2010); M. Li et al. (2017), resulting in a t_{DIC} load of 381.81 Tg C yr⁻¹ to 232 the ocean, which is in general agreement with recent studies (Drake et al., 2018; M. Li 233 et al., 2017; Lacroix et al., 2020; Battin et al., 2023; Tian et al., 2023). 234

2.3 Sensitivity Experiments and Analysis

235

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.

Experiment Name	${f t}_{DOC} \ ({f Tg} \ {f C} \ {f yr}^{-1})$	${f t}_{DIC} \ ({f Tg} \ {f C} \ {f yr}^{-1})$	${f t}_{DON} \ ({f Tg} \ {f N} \ {f yr}^{-1})$	${f t}_{DIN} \ ({f Tg} \ {f N} \ {f yr}^{-1})$	${f t}_{DSi} \ ({f Tg}\ {f Si}\ {f yr}^{-1})$
Baseline	0	0	0	0	0
DC_{run}	170.1	381.8	0	0	0
$\mathrm{DIC}_{\mathrm{run}}$	0	381.8	0	0	0
$\mathbf{DN}_{\mathbf{run}}$	0	0	11.7	23.3	0
$\mathrm{DIN}_{\mathrm{run}}$	0	0	0	23.3	0
$\mathrm{DSi}_{\mathrm{run}}$	0	0	0	0	139.7
$\overline{\mathrm{ALL}}_{\mathrm{run}}$	170.1	381.8	11.7	23.3	139.7

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

We analyzed monthly-mean model fields along the coastal ocean (limits set by the 243 furthest point from the coastline, either the 1000-m isobath or a distance of 300 km; 58 244 $\times 10^6$ km²) and the open ocean (300 $\times 10^6$ km²) during 2000–2019. In addition to the 245 global ocean, we also evaluated the sensitivity of ocean carbon cycling in three specific 246 regions that receive large volumes of freshwater from major river systems: the Arctic Ocean 247 (ARCT, 22 x 10⁶ km²), Tropical Atlantic (TROP-ATL, 77 x 10⁶ km²), and Southeast 248 Asia (SE-ASIA, $62 \ge 10^6 \text{ km}^2$). Coastal and open ocean boundaries are delineated by 249 the black line in Figure 1. Monthly-mean net primary production (NPP) was integrated 250 over the upper 100 m. 251

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_2 flux (ΔCO_2) in the ALL_{run} as:

$$\Delta \text{CO}_{2ALL_{run}} = \Delta \text{CO}_2^{\text{solub}^C} + \Delta \text{CO}_2^{\text{solub}^{N,Si}} + \Delta \text{CO}_2^{\text{NPP}^{N,Si}}, \quad (1)$$

where $\Delta CO_2^{solub^C}$ and $\Delta CO_2^{solub^{N,Si}}$ are the changes in air-sea CO_2 flux associated with the solubility pump due to the addition of terrestrial carbon and nitrogen/silica, respectively. $\Delta CO_2^{NPP^{N,Si}}$ is the change in air-sea CO_2 flux driven by NPP in response to terrestrial nitrogen and silica.

259

In DC_{run} , changes in air-sea CO_2 flux are only associated with the solubility pump:

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

We then associated the change in surface-ocean DIC concentration with ΔCO_2 driven by the solubility pump in DC_{run} to isolate ΔCO_2 due to the solubility pump relative to changes in surface-ocean DIC concentration in DN and DSi_{runs}:

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

The change in ΔCO_2 due to changes in NPP in DN and DSi_{runs} was then estimated by subtracting ΔCO_2 due to the solubility pump from the total ΔCO_2 :

$$\Delta \text{CO}_2^{\text{NPP}^{N,Si}} = \Delta \text{CO}_{2DN,DSi_{runs}} - \Delta \text{CO}_2^{\text{solub}^{N,Si}}.$$
(4)

265 **3 Results**

266

3.1 Climatological Global Analysis

Along with 39,687 km³ yr⁻¹ of riverine freshwater, total loads of 551.9 Tg C yr⁻¹, 35 Tg N yr⁻¹, and 139.7 Tg Si yr⁻¹ were exported into the global ocean in ALL_{run} (Table 1). The addition of dissolved carbon, nitrogen, and silica in ALL_{run} led to an increase in CO₂ outgassing of 0.03 Pg C yr⁻¹ compared to the Baseline, globally (Figure 3a and Figure 4a, Table 2). The majority of CO₂ outgassing (0.04 Pg C yr⁻¹) occurs in the coastal ocean (Figure 3a and Table 2). In the open ocean, riverine exports slightly increased CO₂ uptake by 0.01 Pg C yr⁻¹ (Figure 3a and Table 2).

In ALL_{run} , changes in air-sea CO_2 flux resulted from compensation between the 274 effects of riverine carbon and nitrogen, as DC_{run} and DN_{run} experiments result in el-275 evated CO_2 outgassing and uptake, respectively (Table 2). In DC_{run} , the increase in ocean 276 carbon due to riverine exports diminished the ocean's capacity to take up atmospheric 277 CO_2 , resulting in a net CO_2 outgassing of 0.22 Pg C yr⁻¹ (Table 2). In DN_{run} , the in-278 crease in nutrients to the euphotic zone led to increased phytoplankton productivity. The 279 additional uptake of carbon by phytoplankton decreased surface-ocean DIC, resulting 280 in an additional CO₂ sink of 0.17 Pg C yr⁻¹ (Table 2). 281

²⁸² CO₂ outgassing driven by riverine carbon (DC_{run}) was dominated by t_{DOC} (70%), ²⁸³ with a smaller contribution from t_{DIC} (30%) (Figure 4a). While outgassing driven by ²⁸⁴ riverine carbon was compensated by uptake due to nitrogen in the open ocean, CO₂ up-²⁸⁵ take due to nitrogen was 36% lower than riverine-carbon-driven coastal outgassing, lead-²⁸⁶ ing to global-ocean net CO₂ outgassing in ALL_{run} (Table 2).

Riverine dissolved carbon, nitrogen, and silica also resulted in a NPP increase of 287 0.6 Pg C yr⁻¹ (+2%) compared to Baseline (Figure 3b and Figure 4b, Table 2). River-288 ine t_{DIN} (DIN_{run}) contributed to 70% and 86% of the CO₂ uptake and NPP increase 289 simulated in DN_{run} , respectively (Figure 4b). The total increase of NPP in ALL_{run} from 290 riverine exports was equally distributed between the coastal and open ocean (0.3 Pg C)291 yr^{-1} for each) (Figure 4b). However, the increase of NPP was stronger in the coastal ocean 292 $(+5.2 \text{ g C m}^{-2} \text{ yr}^{-1}, +7\%)$ compared to the open ocean $(+1 \text{ g C m}^{-2} \text{ yr}^{-1}, +1\%)$ rel-293 ative to their surface area. 294

		\mathbf{CO}_2 Flux	NPP
Domain	Experiment	$(Pg \ C \ yr^{-1})$	$(Pg \ C \ yr^{-1})$
Coastal			
Ocean	Baseline	-0.68	3.8
	$ALL_{run} - Baseline$	+0.04	+0.3
	$DC_{run} - Baseline$	+0.1	0.0
	$DN_{run} - Baseline$	-0.07	+0.3
	$DSi_{run} - Baseline$	-0.01	+0.01
Open			
Ocean	Baseline	-1.90	20.6
	$ALL_{run} - Baseline$	-0.01	+0.3
	$DC_{run} - Baseline$	+0.1	0.0
	$DN_{run} - Baseline$	-0.1	+0.3
	$DSi_{run} - Baseline$	-0.01	+0.01
Global			
Ocean	Baseline	-2.58	24.4
	$ALL_{run} - Baseline$	+0.03	+0.6
	$DC_{run} - Baseline$	+0.22	0.0
	$DN_{run} - Baseline$	-0.17	+0.6
	$DSi_{run} - Baseline$	-0.01	+0.01

Table 2. Air-sea CO_2 flux and NPP for each experiment in the coastal ocean, open ocean, and global ocean. Positive values represent CO_2 outgassing; negative values are uptake.

3.2 Climatological Regional Analysis

295

The Arctic Ocean region (Figure 1, ARCT) received 5,138 km³ yr⁻¹ of freshwater 296 from rivers in Baseline, which is roughly 13% of global freshwater discharge. In ALL_{run}, 297 freshwater discharge was supplemented with 22.6 and 56.8 Tg C yr⁻¹ of t_{DOC} and t_{DIC} , 298 respectively (Figure 2). The river load of carbon and t_{DOC} into ARCT represented 15% 299 and 12% of their associated global loads, respectively. ARCT also received 2.5 Tg N yr⁻¹ 300 as t_{DON} (56%) and t_{DIN} (44%) in ALL_{run}. The t_{DSi} river load was 12.6 Tg Si yr⁻¹ (Fig-301 ure 2) in this region. Riverine export loads were primarily from the Ob, Yenisei, Lena, 302 and Mackenzie Rivers (Figure 2 and Supporting Information Table S1). 303

In Baseline, ARCT produced a CO_2 uptake of roughly 0.21 Pg C yr⁻¹. When river-304 ine carbon, nitrogen, and silica were added in ALL_{run} , ARCT CO₂ uptake was reduced 305 by 0.02 Pg C yr⁻¹, with the majority of the response (80%) in the coastal ocean (Fig-306 ure 3a and Figure 4a). Riverine-induced CO_2 outgassing was dominated by the input 307 of t_{DOC} in ARCT (Figure 4a). 50% of the riverine-induced CO₂ outgassing was due to 308 the Ob, Yenisei, Lena, and Mackenzie Rivers (Table 3). In the Baseline experiment, NPP 309 was $0.22 \text{ Pg C yr}^{-1}$, with a similar magnitude in the coastal and open ocean. The ad-310 dition of riverine nitrogen into ARCT increased coastal NPP by 40% (Figure 3b and Fig-311 ure 4b). 312

The Tropical Atlantic (Figure 1, TROP-ATL) received 36% of global freshwater discharge (14,228 km³ yr⁻¹) and 35% of the global t_{DOC} load from rivers (67.2 Tg C yr⁻¹). Combined with t_{DIC} , the net carbon load was 145.3 Tg C yr⁻¹ (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 CO₂ outgassing of 319 $0.02 \text{ Pg C yr}^{-1}$ compared to Baseline (0.10 Pg C yr}^{-1}). This imbalance resulted from 320 CO_2 outgassing driven by carbon, which was 30% larger than uptake due to increased 321 phytoplankton productivity from riverine nitrogen (Figure 4a). 85% of CO₂ outgassing 322 in DC_{run} was driven by riverine t_{DOC} (Figure 4a). Riverine t_{DOC} indirectly drives CO_2 323 outgassing by first being remineralized to DIC, which increases DIC concentration in the 324 ocean and thus limits the ocean's capacity to take up atmospheric CO_2 . Most of the CO_2 325 outgassing driven by t_{DOC} occurs in the open ocean (Figure 3a and Figure 4a). The Ama-326 zon River drove 70% of riverine-induced CO_2 outgassing in TROP-ATL (Table 3). In 327 Baseline, NPP in TROP-ATL was 3.18 Pg C yr⁻¹. The increase in NPP driven by river-328 ine t_{DIN} occurred predominantly in the open ocean (~60%) compared to the coastal (~40%) 329 zone (Figure 4b). The Amazon River was responsible for 65% of the NPP increase driven 330 by riverine exports (Figure 4b). 331

In Baseline, the freshwater discharge into SE-ASIA was 7,841 km³ yr⁻¹, roughly 332 20% of global discharge. In ALL_{run}, SE-ASIA received 38% of dissolved carbon from rivers, 333 globally (207.39 Tg C yr^{-1}). 81% of dissolved carbon delivered into SE-ASIA was in-334 organic, representing 42% of the global t_{DIC} river load (Figure 2). SE-ASIA also received 335 45% (10.6 Tg N yr⁻¹) of the global t_{DIN} load from rivers (Figure 2). 41.5 Tg Si yr⁻¹ 336 was discharged into SE-ASIA (Figure 2). Nutrient loads into SE-ASIA were dominated 337 by high riverine t_{DIC} and t_{DIN} from the Ganges and Yangtze Rivers (Figure 2 and Sup-338 porting Information Table S1). The Yangtze river contributed 12% of t_{DIC} river loads, 339 globally (Figure 2 and Supporting Information Table S1). Taken together, the Yangtze 340 and Ganges Rivers delivered 20% of the global t_{DIN} river load (Figure 2 and Support-341 ing Information Table S1). 342

SE-ASIA had a CO₂ sink of 0.30 Pg C yr⁻¹ in Baseline, while CO₂ uptake increased by 0.02 Pg C yr⁻¹ in ALL_{run} (Figure 4a). Riverine carbon- and nitrogen-driven air-sea CO₂ flux was compensated in the coastal ocean (± 0.03 Pg C yr⁻¹). However, in the open ocean, the riverine nitrogen-driven increase in NPP and associated CO₂ uptake was two times higher than carbon-driven outgassing — leading to an overall imbalance and resulting in net CO₂ uptake in the domain (Figure 4a).

t_{DIN} was responsible for 85% of biological CO₂ uptake (Figure 4a). The Ganges River (58%), combined with the Indus and Yangtze Rivers, were responsible for 77% of CO₂ uptake in SE-ASIA (Table 3). NPP in SE-ASIA without the addition of riverine exports was 3.3 Pg C yr⁻¹. In ALL_{run}, NPP increased by 0.30 Pg C yr⁻¹ 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_2 flux and (b) NPP driven by riverine exports in ALL_{run} . 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 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_2 flux and NPP. Positive values represent CO_2 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_{run} , where only the corresponding river was included. Locations of river mouths are shown in Figure 1.

Rank	River	$egin{array}{lll} \Delta \ {f CO}_2 \ {f Flux} \ ({f Tg} \ {f C} \ {f yr}^{-1}) \end{array}$	$egin{array}{c} \Delta \ {f NPP} \ ({f Tg} \ {f C} \ {f yr}^{-1}) \end{array}$
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

355

3.3 Mechanisms of River-driven Air-sea CO₂ Flux

From January 2000 to December 2019, the time-mean surface-ocean DIC mass in 356 DC_{run} increased by 370.7 Tg C. This triggered a solubility-pump-driven outgassing of 357 222.4 Tg C yr^{-1} (Figure 4a). Over the same period, the addition of terrestrial nitrogen 358 and silica, the sum of DN_{run} and DSi_{run} , drove a reduction of 21.5 Tg C in the surface-359 ocean DIC mass. Assuming the same ratio of surface-ocean DIC and air-sea $\rm CO_2$ flux 360 as in DC_{run} , the input of terrestrial nitrogen and silica will cause a CO_2 uptake of 12.9 361 Tg C yr⁻¹ (Figure 4b). Since the net ocean CO_2 uptake increased by 186.2 Tg C yr⁻¹ 362 in response to terrestrial nitrogen and silica fertilization of NPP, the net increase in global 363 CO_2 uptake is 173.3 Tg C yr⁻¹ (Figure 4c). 364



Figure 5. Climatological (January 2000 to December 2019) air-sea CO₂ flux CO₂associated 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_2 flux driven by riverine exports was dominated 365 1) by the solubility pump near river mouths in response to terrestrial carbon and 2) by 366 NPP in the open ocean where CO₂ uptake from nitrogen- and silica-driven phytoplank-367 ton blooms exceeded riverine carbon-driven outgassing (Figure 4 and Figure 6). TROP-368 ATL and ARCT were dominated by riverine-driven CO_2 outgassing (71.9 and 24 Tg C 369 yr^{-1} , respectively) and CO₂ uptake due to NPP fertilization in TROP-ATL and ARCT 370 was minor (44.4 and 3.3 Tg C yr⁻¹, respectively). In SE-ASIA, the increase of CO_2 up-371 take due to enhanced NPP (69.6 Tg C yr⁻¹) exceeded CO_2 outgassing driven by river-372 ine carbon (53.9 Tg C yr^{-1}). 373



Figure 6. Pathways of change in climatological (January 2000 to December 2019) air-sea CO_2 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.

374 4 Discussion

375

4.1 Fate of Riverine Dissolved Carbon and Nutrients

Once in the ocean, terrestrial dissolved carbon $(t_{DOC} \text{ and } t_{DIC})$ result in a source of CO₂ to the atmosphere through a reduction of the solubility pump (Figure 7). Terrestrial nutrients, such as nitrogen and silica $(t_{DIN}, \text{ and } t_{DSi})$, fertilize phytoplankton and elevate CO₂ uptake via increased NPP.

The resultant export of marine organic carbon (m_{OC}) from the surface ocean drives additional CO₂ 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 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 g C m⁻² yr⁻¹, +7%) compared to the open ocean (+1 g C m⁻² yr⁻¹, +1%), the outgassing of CO_2 driven by riverine carbon through the solubility pump dominates changes in air-sea CO_2 flux close to river mouths. In contrast, the riverine nitrogen and silica signal spreads further offshore and enhances NPP and CO_2 uptake — this mechanism dominates the change in air-sea CO_2 flux in open-ocean regions.

In carbon-dominated terrestrial margins, such as TROP-ATL and ARCT, rivers drive a large source of CO₂ 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 CO₂ in the global ocean.

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

 Table 4.
 Riverine exports loads.

 ¹ (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)

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

- 3 (Cotrim da Cunha et al., 2007; Araujo et al., 2014)
- ⁴ (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

Domain	$\Delta \mathbf{CO}_2 / \mathbf{NPP}$	$egin{array}{l} \mathbf{ALL}_{run} \ (\mathbf{Pg} \ \mathbf{C} \ \mathbf{yr}^{-1}) \end{array}$	$\begin{array}{c} {\rm Literature~Value}\\ {\rm (Pg~C~yr^{-1})} \end{array}$
Global	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	+0.03 +0.6	+0.11 ¹ +0.6-3.9 ¹
ARCT	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	+22.8 +7.4	+0.6-20 ^{2*} +58 ²
TROP-ATL	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	+20 +170	$+5-20^{3^{**}}$ +80-400 ³
SE-ASIA	$\begin{array}{c} \Delta \ \mathrm{CO}_2 \\ \Delta \ \mathrm{NPP} \end{array}$	-24.7 + 296	$^{ m N/A}_{ m +100}$ 4

Table 5. Change in air-sea CO_2 flux and NPP driven by riverine exports.

¹ (Tivig et al., 2021; Cotrim da Cunha et al., 2007)

 2 (Manizza et al., 2011; Terhaar et al., 2021)

³ (da Cunha & Buitenhuis, 2013; Louchard et al., 2021)

 4 (Tivig et al., 2021)

* Effect of t_{DOC} only

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

For both Baseline and ALL_{run}, the ocean CO₂ sink (2.55–2.58 Pg C yr⁻¹) lies within 396 the range of recent estimates (Resplandy et al., 2018; Regnier et al., 2022; Friedlingstein 397 et al., 2023). This present-day ocean CO_2 sink reflects the contribution of climate and 398 anthropogenic perturbations on top of preindustrial levels. In this study, a net riverine 399 carbon export of 0.55 Pg C yr⁻¹ (Table 1, $t_{DOC} + t_{DIC}$) drives a CO₂ outgassing of 0.22 Pg C yr⁻¹, while 35 Tg N yr⁻¹ (Table 1, $t_{DON} + t_{DIN}$) drives a CO₂ uptake of 0.17 Pg 400 401 $C \text{ yr}^{-1}$ from enhanced ocean fertilization. We note that our multi-decadal estimates are 402 not in steady state and do have a realistic representation of estuarine, blue carbon, and 403 bottom sediment processes. Therefore, they are not directly comparable to steady-state, 404 pre-industrial estimates of the river loop (Resplandy et al., 2018). 405

The introduction of terrestrial nutrients, such as inorganic nitrogen and silica, in-406 creased global-ocean marine NPP by 0.6 Pg C yr^{-1} compared to Baseline. The addition 407 of t_{DIN} and t_{DON} also increased ocean NPP by 0.6 Pg C yr⁻¹ in the model described 408 in Tivig et al. (2021) (Table 5). The modeling study by Lacroix et al. (2020) also depicted 409 a 3% increase of ocean NPP in response to the addition of riverine nutrients. In our study, 410 the increase of NPP driven by riverine exports was stronger in the coastal ocean com-411 pared to the open ocean, relative to their respective surface areas. This is consistent with 412 the recent study of Mathis et al. (2024), which demonstrates the role of increased river-413 ine nutrient loads in driving stronger biological carbon fixation and thus an enhanced 414 CO_2 sink in the coastal ocean during the last century. 415

416 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.



-20-

420 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} 421 delivered to the ARCT by individual rivers (Yenisey, Lena, Ob, and Mackenzie) falls within 422 the range of observations from Tank et al. (2012), Le Fouest et al. (2013), and Holmes 423 et al. (2012) (Supporting Information Table S1); suggesting that our estimates are re-424 liable at the pan-Arctic scale (Table 4). In Baseline, ARCT uptakes 213.9 Tg C yr⁻¹ of 425 atmospheric CO_2 The addition of riverine exports reduces this CO_2 sink by 20 Tg C yr⁻¹ 426 and results in ECCO-Darwin having a more-consistent Arctic Ocean sink compared to 427 previous studies (Manizza et al., 2011; Mortenson et al., 2020). In this region, riverine 428 carbon dominates the response of air-sea CO_2 flux, with riverine t_{DOC} being responsi-429 ble of 80% of CO₂ outgassing in ARCT. In Bertin et al. (2023), riverine exports from 430 the Mackenzie River drove a CO_2 outgassing of roughly 0.5 Tg C yr⁻¹ in the river plume. 431 Our model depicts a CO_2 outgassing of similar magnitude in the river plume region (~0.1 432 Tg C yr^{-1}). 433

Due to anthropogenic climate change, thawing of carbon-rich permafrost is supple-434 menting the load of t_{DOC} into Arctic rivers (Spencer et al., 2015). Permafrost-derived 435 DOC has a relatively fast remineralization rate (~ 2 weeks) that could lead to strong 436 CO_2 outgassing along coastal Arctic margins, which are dominated by permafrost-covered 437 watersheds (Bertin et al., 2023). Furthermore, the degradation of organic carbon by mi-438 crobial activity may be enhanced by changes in environmental conditions, such as increas-439 ing sea-surface temperature in ARCT (Carvalho & Wang, 2020). This would likely in-440 crease ocean CO_2 outgassing in response to the riverine carbon depicted in our study. 441 Additionally, riverine nutrients also contribute to the Arctic Ocean carbon sink as they 442 fertilize coastal waters. NPP in the Arctic Ocean increased by 3% (+7.4 Tg C yr⁻¹) in 443 ALL_{run} compared to Baseline. However, recent estimates by Terhaar et al. (2021) sug-444 gests that riverine nutrients support up to 9-11% (+58 Tg C yr⁻¹) of marine NPP in 445 the ARCT, in agreement with estimates by (Le Fouest et al., 2013, 2015) (Table 5). There-446 fore, CO_2 uptake driven by ocean fertilization from riverine nitrogen, and its capacity 447 to compensate CO_2 outgassing in ARCT, might be underestimated in our study. 448

4.2.2 Tropical Atlantic (TROP-ATL)

449

Four of the top-15 global largest rivers (Amazon, Congo, Mississippi, and Niger) 450 discharge into TROP-ATL. In total, rivers carry 67.2 Tg C yr⁻¹ as t_{DOC} , 78.1 Tg C yr⁻¹ 451 as t_{DIC} , 4.2 Tg N yr⁻¹ as t_{DON} , 4.5 Tg N yr⁻¹ as t_{DIN} , and 44.9 Tg Si yr⁻¹ as t_{DSi} 452 into TROP-ATL. Riverine t_{DOC} , t_{DIC} , and silica loads in our study are consistent with 453 estimates from Cotrim da Cunha et al. (2007) and Araujo et al. (2014) (46 and \sim 50 Tg 454 C yr⁻¹ and 53 Tg Si yr⁻¹, respectively; Table 4). Our estimate of t_{DIN} delivered to this 455 region is 3-fold lower than the value of 15.3 Tg N yr^{-1} reported by Cotrim da Cunha et 456 al. (2007) (Table 4). However, t_{DIN} export from the Amazon river (1 Tg N yr⁻¹) agrees 457 well with Louchard et al. (2021) (0.9 Tg N yr⁻¹). A dynamic land ecosystem model that 458 explicitly resolves fluxes over the entire watershed estimated that 0.9 Tg N yr⁻¹ is ex-459 ported as t_{DIN} from the Mississippi River (Tian et al., 2020), which is in general agree-460 ment with the 0.7 Tg N yr⁻¹ that we use as input for our model. The load of t_{DIN} from the Congo River (0.2 Tg N yr⁻¹) is also the same order of magnitude compared to data 461 462 from Jouanno et al. (2021). However, our Global-NEWS-2-based estimate of 0.1 Tg N 463 yr^{-1} remains lower than previous estimates for the Niger River (Robertson & Rosswall, 464 1986) (0.5 Tg N yr⁻¹). We stress that in Africa river systems, nutrient loads are poorly 465 constrained due to sparse data. 466

⁴⁶⁷ In Baseline, TROP-ATL is a source of CO_2 to the atmosphere (0.10 Pg C yr⁻¹), ⁴⁶⁸ which agrees with both interpolation-based products (Landschützer et al., 2016; Jersild ⁴⁶⁹ et al., 2023; Rödenbeck, 2005) (0.04–0.08 Pg C yr⁻¹) and model results (da Cunha & ⁴⁷⁰ Buitenhuis, 2013; Louchard et al., 2021) (0.03–0.04 Pg C yr⁻¹). We note that previous studies show a river-driven increase in CO₂ uptake of 0.005 and 0.02 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 ALL_{run} enhanced the source of CO₂ (+0.02 Pg C yr⁻¹) (Table 5).

Contrary to the estimates of Louchard et al. (2021), which include physical effects 476 associated with freshwater, such as enhanced upper-ocean stratification and gas solubil-477 ity, our baseline simulation already includes these processes. Therefore, our suite of ex-478 periments cannot isolate and quantify the impact of freshwater discharge on ocean bio-479 geochemistry. Freshwater in river plumes facilitates the uptake of atmospheric CO_2 through 480 the solubility pump, which in turn overlaps with the sink of CO_2 associated with bio-481 geochemical runoff. In addition to nitrogen, Louchard et al. (2021) also included inor-482 ganic phosphorus loads and a regionally-adjusted plankton ecosystem, e.g., by includ-483 ing a nitrogen-fixing phytoplankton functional type, which increased the model's capa-484 bility to better resolve the biological pump and hence CO₂ uptake. For our simulations, 485 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 Pg C yr⁻¹ reported in Louchard et al. (2021) (Table 5) and 487 the value of 0.4 Pg C yr⁻¹ reported in Cotrim da Cunha et al. (2007). We note that hor-488 izontal resolution is also important for realistic representation of coastal processes. In 489 their higher-resolution study, Louchard et al. (2021) were able to separately resolve the 490 estuarine and plume/shelf waters of the Amazon River as a CO_2 source and sink, respec-491 tively, whereas our model intrinsically lacks such fine delineation. 492

The Amazon River clearly dominates the CO₂ outgassing signal in TROP-ATL, which 493 is driven by the large load of t_{DOC} . Along with other rivers such as the Congo, Niger, 494 and Orinoco Rivers, the Amazon River delivers a large amount of t_{DOC} , which originates 495 from tropical forests. These forests contribute roughly one third of terrestrial NPP and 496 their soil contains large amount of organic carbon, globally (Cleveland et al., 2010). As 497 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 499 waters to the coastal ocean (M. Li et al., 2019). At present time, it is critical to better 500 constrain export of carbon from watersheds to coastal waters and characterize their fate 501 in the ocean, as current efforts may be overestimating the land sink of carbon associated 502 with tropical forests (Lauerwald et al., 2020). Additionally, the composition (refractory 503 black carbon from combustion) and the quantity $(CO_2$ fertilization from NPP and soil 504 erosion with deforestation) of carbon exports from the Amazon River remains uncertain 505 due to ongoing changes in regional climate and fire regimes (Fleischer et al., 2019; Jones 506 et al., 2020; Riquetti et al., 2023). 507

508

4.2.3 Southeast Asia (SE-ASIA)

Riverine biogeochemical runoff in SE-ASIA is dominated by high loads of t_{DIN} (10.6) 509 Tg N yr⁻¹) and t_{DIC} (163.8 Tg C yr⁻¹), especially from the Ganges and Yangtze Rivers. 510 The magnitude of the riverine t_{DIN} load for SE-ASIA compares with individual estimates 511 for the Bay of Bengal (0.4 Tg N yr⁻¹), the Arabian Sea (0.06 Tg N yr⁻¹), and the East China Sea (1.6–7.9 Tg N yr⁻¹) (Singh & Ramesh, 2011; H.-M. Li et al., 2014; J. Wang 512 513 et al., 2020; Nishina et al., 2021) (Table 4). Our estimate of the t_{DIC} load in SE-ASIA 514 remains higher than values reported in the literature ($\sim 40 \text{ Tg C yr}^{-1}$) (Piao et al., 2012; 515 Patra et al., 2013) and thus would require a regional adjustment as we did for the Ama-516 zon River (Table 4 and Supporting Information Text S1). This is explained by overes-517 timated t_{DIC} loads from the Yangtze (45.9 Tg yr⁻¹) and the Ganges (18 Tg yr⁻¹) Rivers 518 compared to reported values (20 and 3–4 Tg C yr⁻¹, respectively) (F. Wang et al., 2007; 519 Guo et al., 2015; Y. Gao et al., 2017; Samanta et al., 2015). This overestimation is re-520 lated to the relationship based on river discharge and the dominant lithology (Amiotte Suchet 521 et al., 2003; M. Li et al., 2017). Both rivers exhibit high discharge combined with weathering-522

prone lithologies (carbonate rocks and shales for the Yangtze and Ganges rivers, respectively), which consume atmospheric CO_2 due to high rates of rock weathering (Amiotte Suchet et al., 2003). The Yangtze River is also known for its high river CO_2 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_2 in Baseline (0.3 Pg C yr⁻¹). 530 Combining air-sea CO_2 budgets for the different regions composing SE-ASIA from lit-531 erature (East-Pacific, Indonesian seas, and North Indian Ocean without including Oman 532 and Somalian upwelling regions), we estimate a carbon sink of $\sim 0.2 \text{ Pg C yr}^{-1}$ for the 533 entire SE-ASIA domain (Kartadikaria et al., 2015; De Verneil et al., 2021; Zhong et al., 534 2022; Hood et al., 2023). Our study provides the first estimate of the contribution of present-535 day riverine exports to the carbon sink in SE-ASIA. The net air-sea CO_2 exchange bal-536 ance driven by riverine exports in SE-ASIA results in a carbon sink of 0.02 Pg C yr⁻¹ 537 in ALL_{run} . Compared to ARCT and TROP-ATL, carbon uptake in SE-ASIA is enhanced 538 by a strong increase in marine NPP (+0.30 Pg C yr⁻¹, +9%) driven by riverine t_{DIN} . 539 In Tivig et al. (2021), the simulated increase of NPP in response to riverine nitrogen was 540 roughly 0.1 Pg C yr^{-1} in Asia, with the strongest increase in the Yellow Sea, similar to 541 our results (Table 5). Riverine nitrogen loads in this domain, and especially in the China 542 seas, have been supplemented by increased nitrogen deposition, nitrogen fertilizer, ma-543 nure, and human sewage over the last 50 years (Nishina et al., 2021). Even if nitrogen 544 runoff is declining, agricultural-driven nitrogen loads will remain at significant levels and 545 continue to fertilize phytoplankton blooms in this nitrogen-depleted marine region due 546 to high denitrification (Michael Beman et al., 2005; Nishina et al., 2021). Locally, the 547 addition of riverine biogeochemical runoff also drives a source of CO_2 to the atmosphere, 548 which is primarily limited to near river mouth locations in SE-ASIA. In the Yellow Sea 549 and the Northern Bay of Bengal, close to the Yangtze and Ganges Rivers, the addition 550 of riverine exports at preindustrial levels in an ocean model also drove a CO_2 outgassing 551 in Lacroix et al. (2020). Noticeably, in our simulations, riverine carbon turns the north-552 ern Bay of Bengal into a carbon source as suggested by Hood et al. (2023). 553

4.3 Model Improvements

554

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 bio-560 geochemistry (Krachler et al., 2005; Tagliabue et al., 2017; Duhamel et al., 2021; Savenko 561 & Savenko, 2021). Consequently, our results may underestimate the global-ocean air-562 sea CO_2 uptake due to the absence of riverine phosphorus or iron in the model, as they 563 might be limiting for ocean NPP relative to the excess of terrestrial inorganic nitrogen. 564 Additionally, riverine t_{ALK} flux was computed based on a constant ALK:DIC ratio, glob-565 ally (0.98). We note that the GLORICH database used to compute the mean ALK:DIC 566 ratio has relatively good coverage over the American continent but Eurasia and Africa 567 are underrepresented (Hartmann et al., 2014). As such, the ALK:DIC ratio can vary sub-568 stantially over regional scales. The lack of this spatially-granular information in our sim-569 ulated exports may misrepresent riverine t_{ALK} fluxes and the alkalinity-driven buffer-570 ing capacity of simulated river plumes (Dubois et al., 2010; Tank et al., 2012; Mol et al., 571 2018; Ghosh et al., 2021; Gomez et al., 2023). While in estuaries the absence of ALK 572 relative to DIC leads to higher partial pressure of CO_2 (p CO_2) in upper-ocean waters 573 and enhanced CO₂ outgassing, rivers also bring an excess of ALK relative to DIC on con-574

tinental shelves, which can reduce ocean pCO₂ through buffering and thus facilitate CO₂ uptake (W.-J. Cai et al., 2010; Louchard et al., 2021). Furthermore, the fate of riverine t_{ALK} in the ocean is associated with the biological activity of calcifying organisms and exchange at the sediment-water interface (Middelburg et al., 2020) — an undergoing development in our modeling system.

In our model, the global-ocean net CO₂ outgassing driven by riverine exports re-580 flects the stronger effect of riverine carbon on the solubility pump (CO_2 source) com-581 pared to the change in the CO_2 uptake associated with the increase in NPP. This im-582 balance can result from an overestimation of CO_2 outgassing driven by riverine carbon, 583 and especially t_{DOC} . First, assuming that total loads of carbon or nutrients over each 584 watershed are routed to the ocean is a misrepresentation, as losses and gains occur through 585 the LOAC (W.-J. Cai, 2011). Second, t_{DOC} is degraded in coastal waters at different 586 rates depending on its origin and subsequent labile fraction (Lønborg et al., 2020). In 587 the present study, in addition to not accounting for refractory and labile fractions of t_{DOC} , 588 marine and terrestrial DOC are both being remineralized at the same rate (3 months). 589 Overall, this could lead to an overestimation of t_{DOC} remineralization and thus ocean 590 CO_2 outgassing due to the subsequent excess of DIC. For instance, the Amazon River 591 — the main source of riverine t_{DOC} into the ocean — contributes to almost 50% (+0.014 592 $Pg C yr^{-1}$) of the global-ocean CO_2 outgassing in response to riverine exports in our study. 593 However, t_{DOC} from the Amazon River shows stronger stability in the coastal ocean and 594 is exported from the continental margin to the open ocean (Medeiros et al., 2015; Louchard 595 et al., 2021). Increasing the refractory pool of Amazon t_{DOC} could therefore decrease 596 CO_2 outgassing in our simulations. While recent modeling studies include separate pools 597 of refractory and labile t_{DOC} with different remineralization rates at regional scales (Louchard 598 et al., 2021; Gibson et al., 2022; Bertin et al., 2023), the nature of t_{DOC} needs to be bet-599 ter accounted for in global-ocean biogeochemistry models. 600

5 Perspectives

Biogeochemical inputs from rivers into the ocean are subject to variability from cli-602 mate change and/or human activities. Over the last century, loads of riverine exports 603 such as nitrogen and phosphorus increased dramatically — mostly due to anthropogenic 604 perturbations (+349% and +233%, respectively) (Lacroix et al., 2021). In the coastal 605 ocean, this has strongly increased NPP associated with the regions in which our model 606 depicts the strongest impact of riverine nutrients on NPP (TROP-ATL and SE-ASIA) 607 (Lacroix et al., 2021). Over the past 20 years, fertilizers and aquaculture have been iden-608 tified as global drivers of phytoplankton blooms in coastal waters (Dai et al., 2023). The 609 load of riverine t_{DOC} also increased globally over the period 1860–2010 (+17%), due to 610 CO_2 fertilization of terrestrial vegetation and climate change (Nakhavali et al., 2024). 611 In the near future (2050), the global contribution of natural sources of nitrogen and phos-612 phorus in riverine inputs is expected to continue to decrease due to land-use change, while 613 anthropogenic sources from human waste, agriculture, and aquaculture are projected to 614 increase for every potential Shared Socioeconomic Pathways (SSP) scenario (Beusen et 615 al., 2022). However, the export of nutrients from anthropogenic sources to the ocean will 616 decrease in industrialized regions such as North America, Europe (including the Russian 617 Federation), Japan, and Oceania in most SSPs (Beusen & Bouwman, 2022). For instance, 618 in the contiguous United States, the riverine load of nitrogen from human waste and at-619 mospheric pollution decreased over 1930–2017 (Byrnes et al., 2020). Nonetheless, the load 620 of nitrogen from agricultural sources kept increasing over the same period (Byrnes et al., 621 2020). Consequently, only the long-term adoption of the Paris Agreement and sustain-622 able development scenarios, such as SSP1 where the use of resources and the dependency 623 on fossil fuels are significantly reduced, would lead to better stream water quality (Beusen 624 & Bouwman, 2022; Beusen et al., 2022). Over the 21st century, the increase of ocean NPP 625 and the associated carbon sink driven by the historical increase of nutrients loads is ex-626

pected to be dampened by the increase of CO_2 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 629 the spatial and temporal coverage/resolution of models, forcing products, and observa-630 tions. As river discharge is associated with suspended particulate loads, ocean color re-631 trievals from spaceborne instruments can be an effective tool for monitoring river plumes 632 systems. However, the complexity of optical properties and their large space-time vari-633 ability requires high-resolution sensors to capture the actual constituents of ocean bio-634 geochemistry. The recently launched Plankton, Aerosol, Cloud, ocean Ecosystem (PACE) 635 satellite mission (https://pace.oceansciences.org/) and its onboard high-resolution spec-636 trometer will bring new insights into the water quality of coastal regions near river mouths. 637 Combined, with river discharge retrievals from the Surface Water and Ocean Topogra-638 phy (SWOT, https://swot.jpl.nasa.gov/), combined spaceborne observations of ocean 639 color and terrestrial fluxes of freshwater into the ocean will pave the way for an integrated 640 Earth Observation System, where the connection between the land and the ocean will 641 be better understood. While effective, these satellite missions are expensive and should 642 not replace critical in-situ and ground-truthed observations. We highlight that ambitious 643 spaceborne missions can indeed be complemented by more modest initiatives, such as 644 citizen science or stakeholder engagement to monitor water quality in river systems (Ab-645 bott et al., 2018). 646

647 6 Conclusion

Our simulations suggest that the role of present-day riverine exports is moderate, 648 with an outgassing of $0.03 \text{ Pg C yr}^{-1}$ to the atmosphere, globally. We find that river-649 ine inputs drive contrasting regional patterns in air-sea CO_2 flux. Terrestrial dissolved 650 carbon, and especially t_{DOC} , contributes to an outgassing of CO₂ through a reduction 651 of the ocean's solubility pump. Terrestrial nutrients, and in particular t_{DIN} , fertilizes 652 phytoplankton and increases marine NPP and the associated carbon biomass. Thus, ter-653 restrial nutrients such as inorganic nitrogen and silica enhance the uptake of atmospheric CO_2 into the ocean. While outgassing of CO_2 is primarily located near river mouths, 655 the fertilization by riverine nitrogen and silica spreads further offshore and into the open 656 ocean. In carbon-dominated margins such as ARCT or TROP-ATL, rivers contribute 657 a large source of CO_2 from the ocean to the atmosphere. However, in nitrogen-dominated 658 margins such as SE-ASIA, rivers drive a large sink of atmospheric CO_2 into the ocean. 659 This work highlights that a better quantification of lateral riverine exports and the in-660 corporation of these fluxes in global models is pivotal for regional and global carbon bud-661 gets. Conducting sensitivity experiments could support national policy decisions and in-662 form climate resilience strategies for land and marine practices. 663

664 Acknowledgments

A portion of this research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (80NM0018D0004). Support from the Carbon Cycle Science (CCS) and Carbon Monitoring Systems (CMS) programs are acknowledged. High-end computing resources were provided by the NASA Advanced Supercomputing (NAS) Division of the Ames Research Center. Government sponsorship acknowledged. © 2024. All rights reserved

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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 sim⁶⁷⁵ ulations used in this paper and generating runoff forcing are available at: 10.5281/zen-⁶⁷⁶ odo.10562713.

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gcmfaces analysis of the solution for JRA55-DO daily runoff

August 1, 2023

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barotropic streamfunction



Figure : 1992-2019 mean – barotropic streamfunction (Sv)

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barotropic streamfunction



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meridional streamfunction (time series)



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meridional heat transport



Figure : 1992-2019 mean - meridional heat transport (PW)

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meridional heat transport



Figure : 1992-2019 standard deviation – meridional heat transport (PW)

meridional seawater transport



Figure : 1992-2019 mean – meridional seawater transport (Sv)

meridional seawater transport

Meridional seawater transport (in Sv)



 $\label{eq:Figure: 1992-2019 standard deviation - meridional seawater transport (Sv)$

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meridional salt transport



Figure : 1992-2019 mean – meridional salt transport (psu.Sv)

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meridional salt transport





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meridional transports (time series)



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Figure : 1992-2019 mean – sea surface height (EXCLUDING ice, in m)



Figure : 1992-2019 mean – sea surface height (INCLUDING ice, in m)

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Figure : 1992-2019 standard deviation – sea surface height (EXCLUDING ice, in m)



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Figure : 1992-2019 mean - temperature (in degC) at 5m

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Figure : 1992-2019 standard deviation – temperature (in degC) at 300m



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Figure : 1992-2019 standard deviation – temperature (in degC) at 1914m



Figure : 1992-2019 mean – temperature (in degC) at 3581m

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Figure : 1992-2019 standard deviation – temperature (in degC) at 3581m



Figure : 1992-2019 mean - salinity (in psu) at 5m

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Figure : 1992-2019 standard deviation - salinity (in psu) at 5m

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Figure : 1992-2019 mean – vertical velocity (in mm/year) at 15m

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Figure : 1992-2019 standard deviation – vertical velocity (in mm/year) at 15m



Figure : 1992-2019 mean - vertical velocity (in mm/year) at 105m

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Figure : 1992-2019 standard deviation – vertical velocity (in mm/year) at 105m



Figure : 1992-2019 mean - vertical velocity (in mm/year) at 300m



Figure : 1992-2019 standard deviation – vertical velocity (in mm/year) at 300m



Figure : 1992-2019 mean - vertical velocity (in mm/year) at 910m

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Figure : 1992-2019 standard deviation – vertical velocity (in mm/year) at 910m



Figure : 1992-2019 mean – vertical velocity (in mm/year) at 1914m



Figure : 1992-2019 standard deviation – vertical velocity (in mm/year) at 1914m



Figure : 1992-2019 mean – vertical velocity (in mm/year) at 3581m



Figure : 1992-2019 standard deviation – vertical velocity (in mm/year) at 3581m



Figure : 1992-2019 mean – QNET to ocean+ice (W/m^2)

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Figure : 1992-2019 mean – QNET to ocean (W/m^2)

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Figure : 1992-2019 standard deviation – QNET to ocean+ice (W/m^2)



Figure : 1992-2019 standard deviation – QNET to ocean (W/m^2)

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Figure : 1992-2019 mean – E-P-R from ocean+ice (mm/day)

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Figure : 1992-2019 mean – E-P-R from ocean (mm/day)

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Figure : 1992-2019 standard deviation – E-P-R to ocean+ice $\left(W/m^2\right)$



Figure : 1992-2019 standard deviation – E-P-R to ocean (W/m^2)

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surface wind stress



Figure : 1992-2019 mean - zonal wind stress (N/m²)

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surface wind stress



Figure : 1992-2019 mean – meridional wind stress (N/m^2)

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surface wind stress



Figure : 1992-2019 standard deviation – tauZ (W/m^2)

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surface wind stress



Figure : 1992-2019 standard deviation – tauM (W/m²)

zonal mean tendencies



Figure : 1992-2019 , last year minus first year – zonal mean temperature (degC; top) and salinity (psu; bottom)

equatorial sections



Figure : 1992-2019 mean – equator temperature (degC;top) and zonal velocity (m/s;bottom)

global mean properties



Figure : global mean T (degC; top) and S (psu; bottom)

global mean properties



Figure : global mean temperature (K; top) and salinity (psu; bottom) minus first year



















zonal mean properties (surface)



Figure : zonal mean temperature (degC; top) and salinity (psu; bottom) minus first year (psu) at 5m depth

zonal mean properties (surface)



Figure : zonal mean SSH (m, uncorrected free surface) minus first year, including ice (top) and below ice (bottom)

zonal mean properties (surface)



Figure : zonal mean ice concentration (no units) and mixed layer depth (m) $% \left(m\right) =0$



Figure : sea ice cover (in $10^{12}m^2$) in northern (top) and southern (bottom) hemisphere



Figure : sea ice volume (in $10^{12}m^3$) in northern (top) and southern (bottom) hemisphere



Figure : snow volume (in $10^{12}m^3$) in northern (top) and southern (bottom) hemisphere

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Figure : sea ice thickness (in m) in northern (top) and southern (bottom) hemisphere



Figure : snow thickness (in m) in northern (top) and southern (bottom) hemisphere



Figure : 1992-2019 March mean – mixed layer depth per Kara formula (m)



Figure : 1992-2019 March mean – mixed layer depth per Suga formula (m)



Figure : 1992-2019 March mean – mixed layer depth per Boyer M. formula (m)



Figure : 1992-2019 September mean – mixed layer depth per Kara formula (m)



Figure : 1992-2019 September mean – mixed layer depth per Suga formula (m)



Figure : 1992-2019 September mean – mixed layer depth per Boyer M. formula (m)

Monthly Thickness Distribution



Figure : 1992-2019 Northern Hemisphere : monthly mean ice (top) and snow (bottom) thickness distribution (in $log(m^2)$)

Monthly Thickness Distribution



Figure : 1992-2019 Southern Hemisphere : monthly mean ice (top) and snow (bottom) thickness distribution (in $log(m^2)$)



Figure : 1992-2019 March mean – ice concentration (unitless)



Figure : 1992-2019 March mean – ice thickness (m)



Figure : 1992-2019 March mean – snow thickness (m)



Figure : 1992-2019 March mean – ice+snow streamfunction (megaton/s)


Figure : 1992-2019 March mean – ice+snow convergence (kiloton/s)



Figure : 1992-2019 September mean – ice concentration (unitless)

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Figure : 1992-2019 September mean – ice thickness (m)

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Figure : 1992-2019 September mean - snow thickness (m)

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Figure : 1992-2019 September mean – ice+snow streamfunction (megaton/s)



Figure : 1992-2019 September mean – ice+snow convergence (kiloton/s)



Figure : 1992-2019 March mean – ice concentration (unitless)



Figure : 1992-2019 March mean – ice thickness (m)



Figure : 1992-2019 March mean – snow thickness (m)



Figure : 1992-2019 March mean – ice+snow streamfunction (megaton/s)



Figure : 1992-2019 March mean – ice+snow convergence (kiloton/s)



Figure : 1992-2019 September mean – ice concentration (unitless)



Figure : 1992-2019 September mean – ice thickness (m)

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Figure : 1992-2019 September mean - snow thickness (m)



Figure : 1992-2019 September mean – ice+snow streamfunction (megaton/s)



Figure : 1992-2019 September mean – ice+snow convergence (kiloton/s)

Role of Riverine Dissolved Organic and Inorganic Carbon and Nutrients in Global-ocean Air-sea CO₂ Fluxes

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15 Supporting Information

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¹⁶ Text S1: Amazon River Runoff Set-up

As we computed riverine nutrient fluxes from the combination of Global NEWS 2 17 loads with JRA55-DO runoff, Global NEWS 2 river concentrations must be snapped onto 18 the JRA55-DO grid points exhibiting the closest annual discharge in order to avoid un-19 der or overestimation of nutrient loads when combined with JRA55-DO runoff. In the 20 case of the Amazon river, where freshwater and nutrient loads are extreme, we manu-21 ally assigned the river mouth location from Global NEWS 2 to the corresponding JRA55-22 DO grid point. In addition, when using equation in Li et al. (2017, equation 9), the DIC 23 load from the Amazon river was overestimated and was therefore set to a literature av-24 erage of 2.54 Tmol yr^{-1} (da Cunha & Buitenhuis, 2013; Probst et al., 1994; Li et al., 2017). 25

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River	$\begin{array}{l} {\bf Freshwater}\\ {\bf Discharge}\\ ({\bf km}^3 \ {\bf yr}^{-1}) \end{array}$	${f t}_{DIC} \ ({f Tg} \ {f C} \ {f yr}^{-1})$	${f t}_{DOC} \ ({ m Tg} \ {f C} \ { m yr}^{-1})$	${f t}_{DIN} \ ({f Tg} \ {f N} \ {f yr}^{-1})$	${f t}_{DON} \ ({ m Tg~N~yr^{-1}})$	${f t}_{DSi} \ ({f Tg}~{f Si}~{f yr}^{-1})$
Amazon	6834.6	32.2	30.7	1	1.9	20.7
Nile	68	1.1	0.3	0.1	0.02	0.2
Congo	1116.2	0.8	5.4	0.2	0.3	2.1
Mississippi	622.5	9.5	3	0.7	0.2	1.5
Ob	453.5	6.75	2.6	0.1	0.15	1.3
Paraná	942.1	9.8	3.8	0.7	0.3	1.1
Yenisei	652.3	6.8	3	0.1	0.2	1
Lena	554.8	8.2	2.4	0.1	0.2	1
Niger	211.2	>0.01	0.9	0.1	0.1	0.9
Yangtze	990.9	45.9	4.2	2.1	0.4	1.4
Amur	384.4	0.01	1.85	0.2	0.1	1.2
Mackenzie	301.4	4	1.8	0.03	0.1	0.7
Ganges	976.4	18.01	5	2.2	0.3	2.8
Zambezi	103.65	>0.01	0.5	0.02	0.03	0.6
Indus	76.3	0.35	0.4	0.1	0.04	0.02

Table S1. Freshwater discharge and nutrient loads for single-river experiments. Locations of river mouths are shown in Figure 1 in the main text.

Text S2: Suggested Land-to-Ocean Model Improvements

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In this section, we elaborate on additional model improvements that are necessary to better quantify the role of riverine exports in air-sea CO₂ fluxes.

First, we scale the annual carbon or nutrient concentration from Global NEWS 2 29 with daily freshwater fluxes from JRA55-do to obtain time-varying riverine biogeochem-30 ical fluxes. Consequently, the seasonal cycle of biogeochemical fluxes follows the season-31 ality of freshwater discharge in JRA55-do. The JRA55-do seasonal cycle of freshwater 32 discharge can be inaccurate in specific regions (e.g., Arctic regions) and we also assume 33 a direct relationship between carbon/nutrient fluxes and freshwater discharge (Suzuki 34 et al., 2018; Tsujino et al., 2018; Feng et al., 2021). Second, we computed carbon/nutrient 35 concentrations based on annual loads and freshwater discharge from Global NEWS 2 and 36 therefore considered it constant through the year. Measurements around the globe have 37 shown that the relationship between carbon/nutrient fluxes and freshwater discharge is 38 not always valid and that concentration can change on a sub-annual basis (Jordan et al., 39 1991; Le Fouest et al., 2013; Holmes et al., 2012; Bittar et al., 2016; Shogren et al., 2021; 40 Kamjunke et al., 2021). Processes such as changes in land use, human inputs, sewage 41 leaks, enhanced permafrost thaw, decomposition, or changes in basin hydrology can sea-42 sonally alter the concentration of biogeochemical substances without inducing changes 43 in freshwater discharge — a work in progress as a land-surface model accounting for such 44 processes is being coupled with the ECCO-Darwin ocean biogeochemistry model. 45

Furthermore, we only considered surface-ocean freshwater discharge, which repre-46 sents about $39,000 \text{ km}^3 \text{ yr}^{-1}$ delivered to the ocean. However, a significant part of fresh-47 water discharge to the ocean (10%) comes from groundwater discharge (Taniguchi et al., 48 2002). While the net impact on the open-ocean carbon cycle is small, this discharge vol-49 ume and associated biogeochemical elements can substantially impact the coastal ocean 50 through eutrophication (Luijendijk et al., 2020). Groundwater discharge exports the equiv-51 alent of 23%, 7.5%, and 8% of riverine DIC, DIN, and DSi, respectively (Luijendijk et 52 al., 2020). In addition to groundwater discharge, subglacial discharge from marine-terminating 53

glaciers, particularly in Greenland, would need to be fluxed at subsurface depths and take 54 plume entrainment into account (Carroll et al., 2016; Slater & Straneo, 2022). In addi-55 tion to the physical impact of freshwater inputs on the ocean, subglacial upwelling of nu-56 trients (Hopwood et al., 2018) and meltwater from ice sheets and icebergs (Hopwood et 57 al., 2020) is a significant source of reactive iron that can support coastal high-latitude 58 marine ecosystems (Hawkings et al., 2014; Hopwood et al., 2020). While their present 59 contribution to global-ocean carbon cycling remains unknown, groundwater and subglacial 60 discharge are expected to be altered by climate change (changes in storm and cyclone 61 frequency and intensity, rising land and ocean temperatures, increased cryosphere melt, 62 changes in ocean chemistry and coastal erosion) and human activities such as ground-63 water extraction (Richardson et al., 2024). 64

Moreover, heat from river discharge is omitted in our simulations. In the Arctic Ocean, 65 where sea-ice cover is negatively correlated with heat from river discharge, the addition 66 of point-source freshwater discharge should be supplemented with realistic water tem-67 perature in order to accurately represent sea-ice dynamics in response to riverine heat 68 fluxes (Manak & Mysak, 1989; Park et al., 2020; Dong et al., 2022). Additionally, chro-69 mophoric dissolved organic matter (CDOM) absorbs heat and thus can increase ther-70 mal stratification near the surface ocean (Morris et al., 1995; Laurion et al., 1997; Ca-71 planne & Laurion, 2008). In the Chukchi Sea, Hill (2008) associated the 40%-increase 72 of energy absorption by the mixed layer in spring to the presence of ice algae. The heat 73 absorption by dissolved organic matter could cause an amplification of Arctic Ocean warm-74 ing if the delivered amount of terrestrial material and DOC increases in the future. 75

The model also lacks some of the observed regional patterns in the CO_2 sink that 76 are associated with ecosystem complexity. For example, in the Amazon River plume, the 77 diatoms-diazotrophs linkage is mostly responsible for NPP and the CO_2 sink, which is 78 associated with the relative amount of different nutrient supply to this region (Louchard 79 et al., 2021). In the present study, riverine nutrients and carbon drive an increase in CO_2 80 outgassing. The fast remineralization rate of terrestrial DOC may be responsible for this 81 overestimation, as generally terrestrial carbon is more refractory and is thus respired at 82 a slower rate compared to marine carbon (Bertin et al., 2023). 83

In the present study, we restricted our sensitivity experiments to dissolved carbon, 84 nitrogen, and silica because riverine particulate matter 1) rapidly sinks to the seafloor 85 near river mouths, and 2) once at the seafloor, sinking particulates are removed to limit 86 the unrealistic accumulation of particulates at depth. The current model set-up is there-87 fore unsuitable for assessing the impact of riverine particulates on ocean carbon cycling 88 as 1) such fine-scale spatial processes exceed the model's horizontal resolution and 2) the 89 simulation does not include sediment-water interface processes that allow for reminer-90 alization of particulates. Development to add a diagenetic sediment model in ECCO-Darwin 91 is currently underway (Sulpis et al., 2022). Nonetheless, in the scope of the current study, 92 future diagenetic sediment models will need to be adjusted for the coastal ocean, where 93 riverine biogeochemical inputs are dominant. As riverine nutrients such as inorganic ni-94 trogen and silica boost marine production, remineralization of sinking particulates as-95 sociated with enhanced marine biomass could also be additional source of dissolved nu-96 trients and carbon to the upper ocean through vertical mixing or upwelling mechanisms; 97 affecting ultimately the air-sea CO_2 exchange depicted by the model in the coastal zone. 98 In our current set-up, particulates from riverine-boosted production might also be re-99 moved at the sediment-water interface too quickly, considering that most of the river-100 ine impact occurs along the coast in shallow waters; increasing our estimate of carbon 101 sink. 102

Finally, we emphasize that adding lateral fluxes of freshwater, carbon, and nutrients into ocean models can result in additional spin-up and drift in simulations. As Baseline and sensitivity experiments are based on the same physical solution, the drift associated with the addition of freshwater is removed from our analysis. We note that bio-

geochemical runoff may be an additional source of drift in the simulations presented in 107 this study. While the use of a Green's Functions-based optimization has been shown to 108 reduce spin-up and drift in previous ECCO-Darwin solutions (Brix et al., 2015; Carroll 109 et al., 2020), it will be necessary to optimize a new ECCO-Darwin solution that includes 110 biogeochemical runoff to select the initial conditions and model parameters that will min-111 imize model-data misfit (i.e., cost) and reduce drift; this is a topic of ongoing work. As-112 suming that total loads of carbon or nutrients over each watershed are routed to the ocean 113 is also a misrepresentation, as losses and gains occur through the LOAC, especially in 114 estuaries. Sharples et al. (2017) estimated that 25% of the global DIN load was removed 115 on continental shelves through biological uptake and denitrification and anaerobic ox-116 idation. Current global-ocean biogeochemistry and Earth System Models (ESMs) used 117 in IPCC Assessment Reports compute the amount of carbon delivered to coastal grid 118 cells (i.e, the lateral flux) from reference watersheds or land-surface models that do not 119 resolve the transport and transformation of carbon through the LOAC and, especially, 120 121 estuaries and associated blue carbon pools (Mayorga et al., 2010; Ciais et al., 2014; Lacroix et al., 2020; Ward et al., 2020). While coastal wetlands, estuaries, and continental shelves 122 are a pivotal filter of carbon and biogeochemical elements, their action on reactive species 123 has yet to be included in most models (Cai, 2011). 124

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