Role of Riverine Dissolved Organic and Inorganic Carbon and Nutrients in Global-ocean Air-sea CO_2 Fluxes

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Supporting Information

Text S1: Amazon River Runoff Set-up

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

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

River	**Freshwater Discharge (km^3 yr^{-1})**	t_{DIC} **(Tg C yr^{-1})**	t_{DOC} **(Tg C yr^{-1})**	t_{DIN} **(Tg N yr^{-1})**	t_{DON} **(Tg N yr^{-1})**	t_{DSi} **(Tg Si 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

Text S2: Suggested Land-to-Ocean Model Improvements

In this section, we elaborate on additional model improvements that are necessary to better quantify the role of riverine exports in air-sea CO_2 fluxes.

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

Furthermore, we only considered surface-ocean freshwater discharge, which represents about 39,000 km^3 yr^{-1} delivered to the ocean. However, a significant part of freshwater discharge to the ocean (10%) comes from groundwater discharge (Taniguchi et al., 2002). While the net impact on the open-ocean carbon cycle is small, this discharge volume and associated biogeochemical elements can substantially impact the coastal ocean through eutrophication (Luijendijk et al., 2020). Groundwater discharge exports the equivalent of 23%, 7.5%, and 8% of riverine DIC, DIN, and DSi, respectively (Luijendijk et al., 2020). In addition to groundwater discharge, subglacial discharge from marine-terminating glaciers, particularly in Greenland, would need to be fluxed at subsurface depths and take plume entrainment into account (Carroll et al., 2016; Slater & Straneo, 2022). In addition to the physical impact of freshwater inputs on the ocean, subglacial upwelling of nutrients (Hopwood et al., 2018) and meltwater from ice sheets and icebergs (Hopwood et al., 2020) is a significant source of reactive iron that can support coastal high-latitude marine ecosystems (Hawkings et al., 2014; Hopwood et al., 2020). While their present contribution to global-ocean carbon cycling remains unknown, groundwater and subglacial discharge are expected to be altered by climate change (changes in storm and cyclone frequency and intensity, rising land and ocean temperatures, increased cryosphere melt, changes in ocean chemistry and coastal erosion) and human activities such as groundwater extraction (Richardson et al., 2024).

Moreover, heat from river discharge is omitted in our simulations. In the Arctic Ocean, where sea-ice cover is negatively correlated with heat from river discharge, the addition of point-source freshwater discharge should be supplemented with realistic water temperature in order to accurately represent sea-ice dynamics in response to riverine heat fluxes (Manak & Mysak, 1989; Park et al., 2020; Dong et al., 2022). Additionally, chromophoric dissolved organic matter (CDOM) absorbs heat and thus can increase thermal stratification near the surface ocean (Morris et al., 1995; Laurion et al., 1997; Caplanne & Laurion, 2008). In the Chukchi Sea, Hill (2008) associated the 40%-increase of energy absorption by the mixed layer in spring to the presence of ice algae. The heat absorption by dissolved organic matter could cause an amplification of Arctic Ocean warming if the delivered amount of terrestrial material and DOC increases in the future.

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

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

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 biogeochemical runoff may be an additional source of drift in the simulations presented in this study. While the use of a Green's Functions-based optimization has been shown to reduce spin-up and drift in previous ECCO-Darwin solutions (Brix et al., 2015; Carroll et al., 2020), it will be necessary to optimize a new ECCO-Darwin solution that includes biogeochemical runoff to select the initial conditions and model parameters that will minimize model-data misfit (i.e., cost) and reduce drift; this is a topic of ongoing work. Assuming that total loads of carbon or nutrients over each watershed are routed to the ocean is also a misrepresentation, as losses and gains occur through the LOAC, especially in estuaries. Sharples et al. (2017) estimated that 25% of the global DIN load was removed on continental shelves through biological uptake and denitrification and anaerobic oxidation. Current global-ocean biogeochemistry and Earth System Models (ESMs) used in IPCC Assessment Reports compute the amount of carbon delivered to coastal grid cells (i.e, the lateral flux) from reference watersheds or land-surface models that do not resolve the transport and transformation of carbon through the LOAC and, especially, 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 are a pivotal filter of carbon and biogeochemical elements, their action on reactive species has yet to be included in most models (Cai, 2011).

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