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Reviews and syntheses: Rivers are major sources of dissolved iron to the ocean

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Abstract. Iron (Fe) is a bio-essential micronutrient for all known life. Due to sparse solubility in seawater under oxic conditions, Fe availability often limits, or co-limits, primary production in the ocean. Extensive research in recent decades has therefore aimed to constrain the key Fe sources and sinks in the global ocean. Accordingly, Fe is now recognised as a key nutrient in ocean biogeochemical models, and determining how Fe availability is changing in response to shifts in source dynamics alongside ocean acidification, deoxygenation, and warming remains a major research challenge. A long-standing hypothesis is that rivers make little direct contribution to Fe availability in the ocean on annual-to-interannual timescales. Strong emphasis has instead conventionally been placed on atmospheric deposition, and to a lesser extent shelf sediments and hydrothermal vents, as the major new Fe sources relevant to offshore marine environments. As widely demonstrated in many estuaries worldwide, dissolved Fe (dFe) rapidly flocculates across salinity gradients which markedly attenuates riverine dFe fluxes to the ocean. However, recent work in both the Congo and the Transpolar Drift has challenged the notion that estuarine removal precludes a significant role for rivers in offshore Fe budgets. Multiple analytical approaches have consistently implied dominant contributions of riverine dFe to basin-scale budgets for both the Arctic and the South Atlantic Oceans. In both cases, plumes enriched in river-derived dFe are found to extend >1000 km off-shelf and exceed atmospheric deposition as the major regional dFe source. Yet these dFe plumes, and the associated Fe fluxes, appear to be consistently absent from ocean biogeochemical models. These observations question the long-standing paradigm that rivers are only of limited importance to the oceanic Fe cycle and indicate a refinement of budget and model representations is needed.

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1 Introduction

A large effort has been made to understand the role of iron (Fe) in marine ecosystems because of widespread Fe limitation or co-limitation of primary production across much of the global ocean (Browning and Moore, 2023). In the open ocean, atmospheric deposition (Conway and John, 2014; Duce and Tindale, 1991; Mahowald et al., 2005) and deep winter mixing (Achterberg et al., 2018; Rigby et al., 2020; Tagliabue et al., 2014) are thought to be the dominant sources of Fe supporting marine ecosystems. High-nitrate, low-chlorophyll (HNLC) zones, where Fe is the main limiting nutrient for primary production (Martin et al., 1990, 1994; Martin and Fitzwater, 1988), mainly occur because of low atmospheric Fe deposition (Jickells et al., 2005; Martin, 1990; Weis et al., 2024). Yet Fe source dynamics in shelf seas and inshore environments are far more diverse. In addition to atmospheric deposition, runoff (Aucour et al., 2003; Klunder et al., 2012; Zhang et al., 2019), submarine groundwater discharge (Rouxel et al., 2008; Windom et al., 2006), shelf sediment effluxes (Dale et al., 2015; Homoky et al., 2016; Severmann et al., 2010), and the cryosphere (Bolt et al., 2020; Lannuzel et al., 2016; Raiswell and Canfield, 2012) are major regional Fe sources. Shelf seas therefore often evidence much higher dissolved (<0.2 μm) Fe concentrations than offshore environments (GEOTRACES Intermediate Data Product Group, 2025).

Marine Fe dynamics are not only of interest because of the seasonal limitation of primary production; Fe is also a key cofactor for nitrogenase, the enzyme used by diazotrophs to fix N_2 (Zehr et al., 1997) and thus may also be a key agent affecting oceanic nutrient budgets on millennial timescales (Moore and Doney, 2007). Furthermore, Fe is a key driver of phosphorous and organic carbon dynamics in shelf sediments (Lalonde et al., 2012; Meyers, 2007). Changing marine Fe biogeochemistry through geological time therefore affects not only ocean productivity, but also the oceanic cycling of carbon, nitrogen, and phosphorus (Bjerrum and Canfield, 2002; Mills et al., 2004; Moore et al., 2009). Modelling Fe dynamics in the ocean is therefore deemed an important research task in order to understand interactions and feedbacks between Fe dynamics, marine primary production (Aumont et al., 2003; Fennel et al., 2003), the biological carbon pump (Jin et al., 2008; Parekh et al., 2006), N_2 fixation (Coles and Hood, 2007; Yao et al., 2022), and ocean deoxygenation (Dale et al., 2015; Wallmann et al., 2022).

Dissolved Fe dynamics are relatively well studied in rivers, with dFe concentrations typically 1 to 4 orders of magnitude higher than the sub-nanomolar concentrations found in the open ocean (Boyle et al., 1977; GEOTRACES Intermediate Data Product Group, 2025; Martin and Meybeck, 1979). Yet rivers are assumed not to function as a major dFe source to the ocean in almost all biogeochemical models representing the Fe cycle (Tagliabue et al., 2016). This is a well-reasoned omission based on extensive observations of how dFe concentrations normally change across salinity gradients. In river water, dFe concentrations range from 10–100 nM in alkaline systems, such as the Mississippi (Shiller and Boyle,

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1991) and Columbia (Bruland et al., 2008) rivers, to high micromolar concentrations in humic and fulvic acid-rich blackwater systems (Holliday and Liss, 1976; Ukotije-Ikwut et al., 2023; Zhang et al., 2020). If these dFe concentrations are multiplied by river discharge volumes, they indicate a large annual input into the global ocean. Assuming a relatively low average dFe concentration of 10—100 nM in river water, rivers worldwide deliver 0.4—4 Gmol dFe $year^{-1}$ to the ocean (Martin and Meybeck, 1979), in addition to a far larger quantity of particulate Fe. This dFe flux is comparable to modelled estimates of the total soluble Fe delivery from atmospheric deposition into the global ocean (e.g., 3.4 Gmol $year^{-1}$, Somes et al., 2021). However, calculating a gross riverine dFe flux from freshwater dFe concentration and runoff volume neglects an important caveat concerning how dFe concentrations change in estuaries. Almost all surveys of dFe dynamics in estuaries reveal a pronounced non-conservative loss of dFe across the salinity gradient (Boyle et al., 1977; Mosley and Liss, 2020; Sholkovitz, 1978).

2.0 Estuarine dFe removal

Whilst the process of dFe loss observed with increasing salinity in river estuaries is often referred to as an 'estuarine mixing' dynamic, this phenomenon is not limited to river estuaries because the process is triggered by increasing ion concentrations associated with increasing salinity (Boyle et al., 1977; Mayer, 1982). It is thus expected to be a universal phenomenon wherever freshwater enters the ocean (Bale and Morris, 1981; Mayer, 1982). The same phenomenon can be, for example, found beneath ice shelves and adjacent to glaciers where meltwater laden with dFe enters the ocean (Krisch et al., 2021; Schroth et al., 2014; Shen et al., 2024). In constructing regional dFe budgets, ~90—99% of riverine dFe is typically estimated to be removed from the dissolved phase, defined operationally by filtration (typically >0.2 µm), over the salinity gradient (Boyle et al., 1977; Holliday and Liss, 1976; Sholkovitz et al., 1978). However, removal factors of ~90—99% dFe are only crude approximations to account for estuarine dynamics in dFe budgets. In reality, there are notable divergences between different field surveys which have defined dFe estuarine removal factors from apparently 0 to >99% (Boyle et al., 1977; Bruland et al., 2008; Dai and Martin, 1995; Duinker and Nolting, 1976; Figueres et al., 1978; Guieu et al., 1996; Holliday and Liss, 1976; Hong and Kester, 1985; Mayer, 1982; Schroth et al., 2014; Wilke and Dayal, 1982; Zhang et al., 2015). Furthermore, the typical process via which an estuarine removal factor is derived from observed dFe concentrations infers an over-simplistic situation where one point-source of riverine dFe is diluted into homogenous saline waters with an assumption of no other overlapping dFe sources.

Estuarine dFe removal is commonly estimated either graphically (Fig. 1), or via a simple two endmember mixing model (Equation 1) (Conrad et al., 2019b). In Equation 1, dFe_{SW} and dFe_{RW} are the endmember dFe concentrations in seawater and river water, respectively; dFe_S is the dFe concentration at an intermediate salinity, S; and S_{SW} is the salinity of the seawater endmember. The river water endmember must be collected upstream of the estuary and the seawater endmember is ideally collected far enough

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offshore that it can be assumed it is not directly affected by riverine outflow. In reality, it is not always possible to collect these endmembers in rapid succession during a single field campaign and the properties of the low dFe offshore endmember may instead be prescribed with fixed, approximate values (e.g., S_{SW} = 35 and dFe_{SW} = 1 nM).

Equation 1 $$\text{Estuarine dFe removal} = 1 - \left(\frac{dFe_{SW}}{dFe_{RW}} + \frac{dFe_S - dFe_{SW}}{dFe_{RW}} \times \frac{1}{1 - {}^{S}/_{S_{SW}}} \right)$$

Equation 2 $$\text{Estuarine dFe removal} = \frac{\text{dFe export}}{Total\ estuary\ dFe\ inputs}$$

In many estuaries, the overlap of multiple dFe sources complicates the interpretation of dFe distributions across the salinity gradient derived using Equation 1 or graphical approaches based on the same assumptions. Estuarine dFe sources other than river water may lead to under-estimation of the derived 'removal factor' for riverine dFe and might be one reason why estuarine dFe removal appears to have high temporal and spatial variability. Equation 2 is more challenging to use than Equation 1 as it requires flux measurements rather than only dFe concentrations, but it accounts for multiple dFe sources. In Equation 2, dFe export out of an estuary is divided by total dFe inputs into the estuary which may include significant benthic and modest atmospheric components in addition to weighted freshwater outflow from multiple outlets.

Kongsfjorden (Svalbard), for example, is a shallow Arctic fjord that receives runoff from the River Bayelva and numerous smaller streams (Svendsen et al., 2002). The distribution of dFe at intermediate salinities in Kongsfjorden consistently suggests loss of ~90% of dFe (Shen et al., 2024; Zhang et al., 2015) from the River Bayelva (using Equation 1). This is similar to deductions from other geographically similar Arctic estuaries (van Genuchten et al., 2021; Schroth et al., 2011; Shen et al., 2024). However, runoff is not the only major dFe source to Kongsfjorden; a net benthic efflux of dFe into the fjord (2400—26000 mol day^{-1}, Herbert et al., 2020) is comparable in magnitude to dFe inputs from runoff (913—3770 mol day^{-1}, Shen et al., 2024). Interpreting the fjord as a system with one major source of dFe (runoff) and deducing dFe loss either from the dFe-salinity curve across the whole fjord, or from a comparison of dFe concentrations in fjord inflow and outflow, thereby considerably under-estimates the net removal of dFe occurring. The combined dFe input from benthic and riverine sources into Kongsfjorden is 2- to 30-fold higher than the input from rivers alone. Thus dFe removal in Kongsfjorden is likely within the range 94—99% (using Equation 2), rather than 90% as estimated using Equation 1, but cannot be precisely constrained without a more detailed dFe budget. When and where benthic dFe sources affect measured

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dFe concentrations in estuaries will depend not only on the magnitude of the benthic dFe efflux, but also the type of estuary and degree of stratification.

Despite the complexities in defining precise dFe removal factors, prolific dFe removal is clearly observed in many estuaries worldwide (Dai and Martin, 1995; Ruan et al., 2024; Schroth et al., 2014). The assumption that this renders riverine dFe supply irrelevant to offshore annual Fe budgets is therefore longstanding and widely applied in flux calculations (Boyle et al., 1977; Sholkovitz, 1978; Sholkovitz et al., 1978). This principle has thereby also underpinned the design of ocean models representing Fe as a micronutrient. Global ocean biogeochemical models that explicitly represent dFe almost universally assume riverine Fe supply can be ignored entirely for off-shelf budgets (Tagliabue et al., 2016). A 2016 comparison of 13 global ocean biogeochemistry models, for example, showed that only 4 included any riverine dFe source with corresponding global fluxes of 0.06, 0.34, or 2.5 Gmol dFe $year^{-1}$ (Tagliabue et al., 2016).

Although the hypothesis that rivers have no significant direct effect on offshore annual dFe budgets is widely applied, several newly discovered exceptions challenge the universality of this concept. GEOTRACES observations in both the Arctic (Charette et al., 2020; Laglera et al., 2019; Slagter et al., 2019) and South Atlantic (Gu et al., 2025; Hunt et al., 2022; Vieira et al., 2020) have revealed evidence of riverine dFe supply as a major, or dominant, contributor to regional offshore dFe budgets. These findings not only challenge a long-standing hypothesis concerning the role of rivers in marine Fe biogeochemistry, but also indicate a re-configuration of some of the basic assumptions underpinning ocean Fe models may be required.

3.0 The mechanism and extent of dFe removal in estuaries

The ionic strength of seawater is much higher than freshwater. As river water begins to mix with saline water, the increase in salinity corresponds to increasing concentrations of cations such as Na^{+}, Ca^{2+} and Mg^{2+}. In river water, a large fraction of the dFe present in the dissolved phase (<0.2 µm, defined by filtration) is associated with humic material in the form of colloids and organic complexes (Eckert and Sholkovitz, 1976; Pokrovsky and Schott, 2002; Stolpe et al., 2013). Critically, humic material contains functional groups with negative charges which thereby induce electrostatic repulsion between colloids (Mosley et al., 2003). Due to this energetic barrier, humic colloids in river water will not readily aggregate. However, at higher salinities, the increasing abundance of cations means that negatively charged functional groups on humic colloids are more easily neutralized. This removes the electrostatic repulsion between colloids and thus reduces the barrier to colloid aggregation (Mosley et al., 2003). Field observations and some process studies generally describe this process as being triggered by increasing salinity (Boyle et al., 1977; Fox, 1983; Sholkovitz, 1978). More detailed mechanistic studies show that

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some ions are more effective than others at triggering dFe removal (Eckert and Sholkovitz, 1976; Nowostawska et al., 2008). Nevertheless, in the context of estuaries, the concentration of all ions in seawater will increase in parallel. In rivers where the solubility of dFe is also promoted by lower pH than seawater, precipitation of dFe due to lower solubility at higher pH in seawater may also be a contributing factor (Elbaz-Poulichet et al., 1999). Changing temperature also exerts an effect on Fe solubility (Liu and Millero, 2002), but this is minor compared to the above effects in the context of estuaries.

As increasing cation concentrations across the salinity gradient are the main driving force behind the estuarine removal of dFe (Bruland et al., 2008; Holliday and Liss, 1976; Wilke and Dayal, 1982), non-conservative loss of dFe across salinity gradients is thought to be a universal phenomenon (Boyle et al., 1977) (Table 1). Both laboratory incubations and estuarine transects similarly demonstrate that the process is initiated at low salinities (<1) (Holliday and Liss, 1976; Hopwood et al., 2015; Wilke and Dayal, 1982) and can remove a majority of riverine Fe from the dissolved size fraction within minutes (Matsunaga et al., 1984; Mayer, 1982; Nowostawska et al., 2008). Concurrently, a majority of the humic material in river water is also removed, though this usually constitutes only a minor (<10%) fraction of riverine DOC (Dissolved Organic Carbon) which may behave more conservatively (Sholkovitz, 1976; Sholkovitz et al., 1978). Detailed mechanistic studies have further characterized the estuarine removal of dFe as a two-stage process. The first stage consists of a rapid flocculation of dissolved components which can be evident as reduced dFe concentrations within seconds (Nowostawska et al., 2008). The second stage consists of a slower aggregation of larger colloids and particles (>0.2 μm) to form progressively larger particles which more readily sink from the water column (Hunter and Leonard, 1988; Mayer, 1982). Colloidal aggregation thereby removes dFe from the dissolved phase, although not necessarily from the water column as particulate Fe (>0.2 μm) may, at least temporarily, remain in suspension (Gustafsson et al., 2000; Markussen et al., 2016; Wilke and Dayal, 1982). Nevertheless, a large fraction of the dFe flocculated within estuaries will ultimately be deposited in near-shore sediments (Fig. 2) (Jilbert et al., 2018; Wu and Luther III, 1996).

A more general dFe removal process that occurs elsewhere, and continues to control the distribution of dFe which is transported through an estuary, is scavenging. Scavenging is often broadly defined as the removal of dFe from the water column via a transfer to sinking particles. Although the exact definition varies between studies, the use of the term ‘scavenging’ often does not distinguish between cellular uptake of dFe, the passive absorption of dFe onto particle surfaces including particulate organic material, the precipitation of dFe to form Fe oxyhydroxides, or the aggregation of colloids to form particles which are no longer within the ‘dissolved’ size fraction (Bergquist et al., 2007). From a thermodynamic perspective, passive binding of dFe to particulate organic material or precipitation to form Fe oxyhydroxides are the most favourable of these processes in seawater (Gledhill et al., 2026). Scavenging is the main sink for dFe in the ocean and limits the extent to which coastal dFe sources can propagate offshore (Somes et al.,

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2021). The factors that control scavenging rates are not fully understood and have proven challenging to parameterize in models (Parekh et al., 2004; Somes et al., 2021; Tagliabue et al., 2016). This is perhaps partially because scavenging collectively refers to several mechanistically distinct processes (Gledhill et al., 2026). Nevertheless, scavenging should be understood as a process that continues to further reduce the dFe flux from rivers into the ocean after the timescale of estuarine mixing (Aguilar-Islas et al., 2013; Johnson et al., 1997; Mackey et al., 2002).

Region	River/estuary	Filter size / µm	Estuarine removal factor / %	Data source
Africa	Congo (Zaire)	1.2	85	(Figueres et al., 1978)
		0.45	75	"
		0.22	65	"
		0.05	55	"
		0.025	50	"
		0.2	90	(Vieira et al., 2020)
	Moulouya	0.22	95	(Tovar-Sánchez et al., 2016)
Europe	Beaulieu	0.45	85	(Holliday and Liss, 1976)
		0.40	68—92	(Fang, 1995)
		0.20	<60	(Hopwood et al., 2014)
	Rhine	0.45	94	(Duinker and Nolting, 1976)
	Kalix	0.22	>90	(Conrad et al., 2019b)
	Gironde	0.4	25	(Kraepiel et al., 1997)
	Danube	0.4	0—62	(Guieu and Martin, 2002)
Arctic	Lena	0.40	80	(Guieu et al., 1996)
	Ob	0.40	>80	(Dai and Martin, 1995)
	Yenisey	0.40	>80	(Dai and Martin, 1995)
	Nuup Kangerlua	0.2	88	(Hopwood et al., 2016)
		0.2	96	(Krause et al., 2021)
	Ameralik	0.2	97	(Krause et al., 2021)
	Bayelva	0.4	>90	(Zhang et al., 2015)
	Kongsfjorden (including the Bayelva)	0.22	46—97	(Schmidt et al., 2025)
	Kuloy	0.45	45	(Savenko et al., 2026)
North America	Copper	0.45	85	(Schroth et al., 2014)
	Ochlockonee	10-kD	97	(Powell et al., 1996)

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	North River	0.22	63—82	(Escoube et al., 2009)
	Sacramento	0.45	47—95	(Flegal et al., 1991)
	Peconic	0.45	>90	(Wilke and Dayal, 1982)
	Winyah Bay	0.2	80—90	(Hopwood et al., 2015)
	Cape Fear	0.2	91	(Hopwood et al., 2015)
	Saco	0.50	76—98	(Mayer, 1982)
	Connecticut	0.4	94	(Hong and Kester, 1985)
		0.10	99	"
		1.2	71	(Boyle et al., 1977)
		0.22	64	(Escoube et al., 2009)
		0.2	70—82	(Buck et al., 2005)
	Merrimack	1.2	54—71	(Boyle et al., 1977)
		0.5	>56	(Boyle et al., 1974)
	Parker	1.2	66	(Boyle et al., 1977)
	Mullica	0.7	96	(Boyle et al., 1977)
	Rappahannock	1.2	91	(Boyle et al., 1977)
	Mississippi	0.4	*Conservative*	(Shiller and Boyle, 1991)
	Hudson	0.4	*Conservative*	(Klinkhammer and Bender, 1981)
	Galveston Bay	0.45	64	(Wen et al., 1999)
	Columbia	0.45	81	(Lohan and Bruland, 2006)
	Saguenay fjord	0.45	93	(Yeats and Bewers, 1976)
South America	Comau	0.2	67	(Hopwood et al., 2020)
	Amazon	0.45	>95	(Sholkovitz, 1978)
		0.2	99	(Hollister et al., 2026)
		0.2*	94	(Gledhill et al., 2022b)
Oceania	Taieri	1.2	70—85	(Hunter, 1983)
Asia	Pearl	0.2	>95	(Ruan et al., 2024)
		0.4	81	(Zhang et al., 2019)
	Changjiang	0.4	98	(Zhu et al., 2018)
		0.22	40	(Wang and Liu, 2003)
		0.22	85	(Gao et al., 2026)
		0.22	57	"
		0.22	79	"
	Geum	0.4	>95	(Byrd et al., 1990)
	Bang Pakong	0.4	50—86	(Windom et al., 1988)
	Ariake Sea	0.2	>99	(Ikhsani et al., 2021)

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	Rajang	0.4	98	(Zhang et al., 2020)
	Maludam	0.4 0.45	*Conservative* *Conservative*	(Zhang et al., 2020) (Ukotije-Ikwut et al., 2023)
	Tanshui	0.4	*Conservative*	(Fang and Lin, 2002)
	Nakdong	0.2	90	(Lim et al., 2025)

Table 1. Estuarine removal factors calculated from measurements of dFe concentrations in different estuaries worldwide. When an estuarine removal factor was not estimated in the original data source, a factor was derived assuming a seawater endmember of salinity 35 and 1 nM dFe. *This study specifically constrained the distribution of dFe associated with dissolved organic material, determined via solid-phase extraction.

A close look at the many case studies which have characterized estuarine dFe removal worldwide reveals that the derived removal factors have an extremely broad range from apparently conservative dynamics (i.e., no evidence of net dFe removal), to >99% dFe removal (Table 1). A simple average of all estuarine transects defining dFe via filtration at 0.2 to 0.45 µm suggests mean (± standard deviation) removal of 72 ± 29% dFe (n = 53). Yet it may be more meaningful to report that where non-conservative dFe loss is evident (91% of 53 case studies) it averages an 80 ± 18% loss of dFe. In the other 9% of case studies no dFe removal is evident. Before further interpreting differences between calculated removal factors, there are several important caveats to note.

A major caveat is that derived estuarine dFe removal factors are sensitive to both the method used and the distribution of dFe data with respect to the range of salinities observed. To calculate estuarine dFe removal, a linear extrapolation can be used to predict a freshwater endmember from high-salinity dFe measurements (e.g., Fig. 1). The difference between this extrapolated zero-salinity endmember and a measured zero-salinity endmember deduces the net dFe removal within the estuary -assuming that the zero-salinity measurement is representative of all freshwater entering the estuary. This is similar to a graphical representation of Equation 1. For example, the measured dFe endmember for a survey of Cape Fear (Fig. 1) is 5.0 µM and the extrapolated endmember from salinities >10 is 840 nM (via linear regression), which indicates 83% removal of dFe at low salinities. Whichever derivation of a removal factor is used, removal factors are usually biased low if the lowest salinity observations within a dataset have already experienced some degree of mixing between river and saline water due to the rapid onset of dFe loss. Similarly, because dFe removal initiates at low salinities, it is also most evident graphically at low salinities. For practical reasons concerning the different spatial zones in an estuary that can be accessed logistically, estuarine dFe datasets often do not fully obtain samples across the salinity gradient present in quick succession. Datasets collected in an outer estuary, at high salinities, can observe close to

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conservative dFe distributions simply because most dFe removal has already occurred upstream. In regions where runoff volumes are low, or highly dispersed, even nearshore samples may only evidence high salinities which precludes derivation of a dFe removal factor. This is a key reason why there are no directly estimated estuarine dFe removal factors for Antarctica (Table 1), where salinities even a few metres away from runoff streams are usually >30 (Annett et al., 2015; Forsch et al., 2021; Krause et al., 2021).

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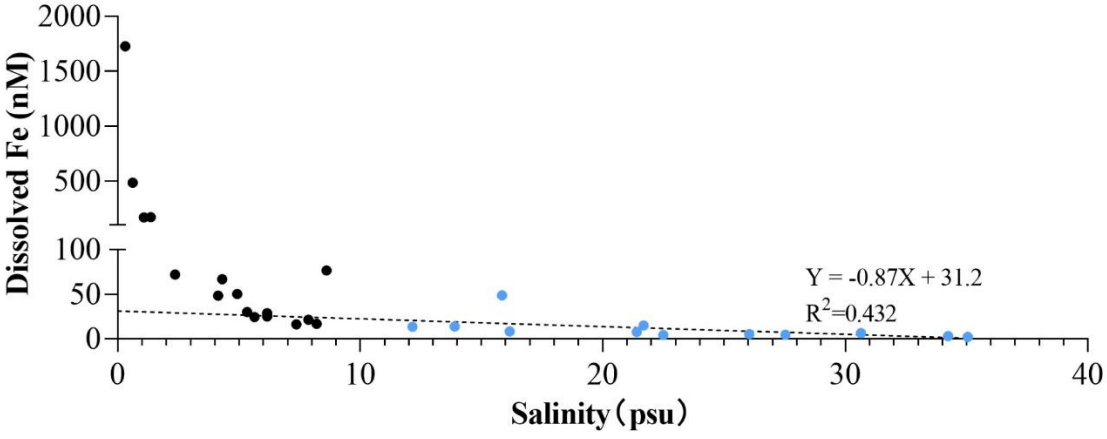
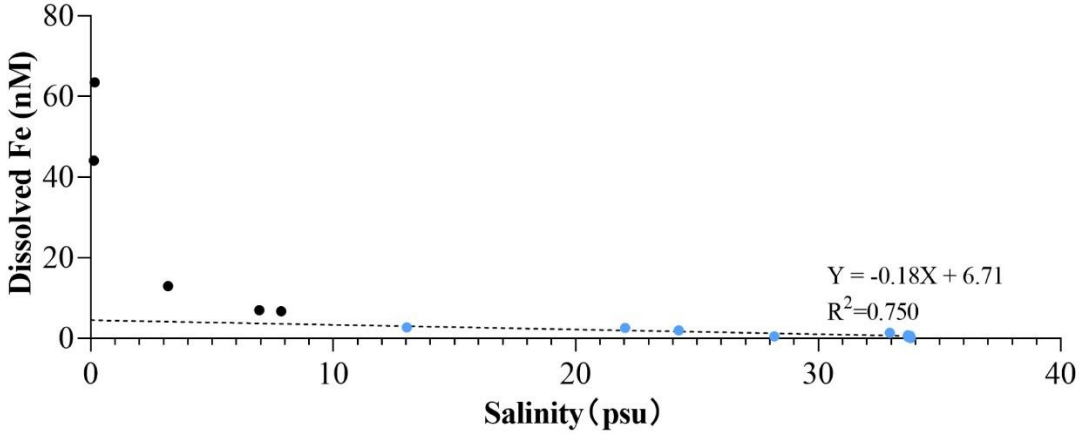
(a)



(b)



(c)

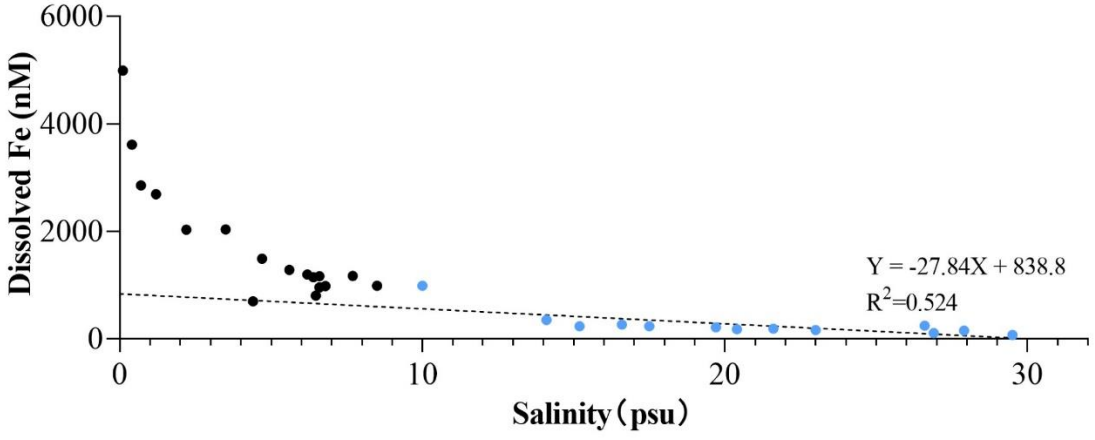


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Figure 1. Estuarine transects of three systems which show the commonly observed non-conservative removal of dissolved Fe with increasing salinity (a) the River Pará (Pará, Brazil), (b) the Pearl River (Guangdong, China), and (c) Cape Fear (North Carolina, USA). Dissolved Fe data in all cases covers a large range of salinities (Hollister et al., 2026; Hopwood et al., 2015; Ruan et al., 2024). A linear regression is shown for datapoints with salinity >10 (blue datapoints).

Before making comparisons between different estuary systems it should be further noted that there are significant variations in the derived dFe removal factors from different surveys within individual estuaries (Table 1). The Connecticut, Beaulieu and Changjiang are well studied rivers with multiple surveys reporting removal factors ranging from 64—99%, <60—92%, and 40-98%, respectively (Table 1). These ranges within each individual case study represent a considerable fraction of the total global variability in estuarine dFe removal. Nevertheless, a few interesting observations can be made from a global compilation of estuaries. First, there is no systematic difference based on filtration size (Table 1). Whilst several early studies suggested that smaller colloids are always more efficiently transported through estuaries (Figueres et al., 1978), comparing dFe trends using various filter sizes from <0.1 to 1 µm, this trend is not consistently observed across multiple surveys. This does not necessarily mean that smaller colloids are not more efficiently transported through estuaries, only that this is not a dominant control on observed removal factors at the global scale. Second, there are multiple reports of conservative dFe dynamics which include low salinity data and appear to be a notable violation of the hypothesis that dFe is always subject to non-conservative removal in estuaries (Table 1). Case studies with apparent conservative dFe dynamics are from diverse regions with little in common. The Tanshui is an anoxic estuary system (Fang and Lin, 2002) and thus the retention of dFe in this case is likely related to the high solubility of Fe(II) under anoxic conditions (Millero et al., 1987). The Maludam is a blackwater system with high dFe concentrations, high DOC concentrations and low pH (Ukotije-Ikwut et al., 2023; Zhang et al., 2020). Conversely, the Mississippi and Hudson rivers both have low freshwater dFe concentrations (Klinkhammer and Bender, 1981; Shiller and Boyle, 1991) with relatively low DOC and pH closer to neutral or slightly alkaline conditions (Cai et al., 2015; Kozar et al., 2023; Limburg et al., 1986). Whilst the methods used to obtain dFe data also vary, and studies using some spectroscopy-based methods (e.g., with ferrozine, Stookey, 1970) may not recover 100% of dFe, method differences appear only to be a minor cause of deviations in estuarine dFe dynamics as repeat surveys using the same methods still demonstrate considerably variation (Table 1).

Herein we have defined ‘dissolved Fe’ using a size fraction as all Fe <0.2 µm. This is the most common oceanographic definition of ‘dissolved Fe’ (although some studies use <0.45 µm, and earlier literature uses a broad range of filtration size cutoffs). Yet within the <0.2 µm size fraction, Fe does not have a uniform chemical speciation. As has been alluded to already, some details concerning the different

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components of dFe and their chemical dynamics are clearly required to fully understand dFe dynamics in the context of estuarine removal.

4.0 Dissolved Fe solubility and speciation across the river-to-ocean continuum

Dissolved Fe, defined by filtration at 0.2 μm, consists of a complex mixture of physically or chemically distinct species (Blain and Tagliabue, 2016; Bruland et al., 2001). These include 'free' Fe(III) ions, Fe(III) ions complexed by organic molecules, and colloids. Under most circumstances Fe(II) species also account for a minor fraction of dFe. Fe(III) ions in solution not associated with organic complexes are referred to as 'free' inorganic Fe, denoted 'Fe''. Fe′ can be directly taken up by microorganisms and is thus often a key focus of modeling studies or speciation calculations (Lis et al., 2015). Because Fe(III) solubility in seawater is very low under oxic conditions, around 0.01 nM (Liu and Millero, 2002), the concentration of Fe′ in oxic seawater is invariably low (Lis et al., 2015) with the vast majority of dissolved Fe(III) present as either complexes with organic ligands or colloids (Gledhill and Buck, 2012). Critically, there is overlap between the physical definition of colloids and the chemical definition of Fe bound to organic ligands thus these two categories are not exclusive.

Fe complexes are complex ions or coordination compounds which consist of an Fe ion surrounded by a ligand or multiple ligands. Ligands can be inorganic, or organic. In both cases they form coordinate bonds with the Fe ion. Strictly Fe′ exists as an inorganic complex in seawater, with the Fe ion surrounded by inorganic components of seawater. References to 'Fe complexes' or 'Fe ligands' (often denoted 'L') in seawater therefore usually specifically refer to Fe(III) bound to organic ligands (Gledhill and Buck, 2012; Hunter and Boyd, 2007; Whitby et al., 2020). Organic ligands may have one or multiple binding sites that can form coordinate bonds with Fe. Any ligand binding site-metal ion combination has a characteristic affinity, such that Fe(III) will, theoretically, bind organic ligand binding sites according to the most favorable thermodynamics. The capacity of organic matter to bind Fe ions is not only determined by the concentration of organic ligands and the number of binding sites on ligands, but also by ambient physico-chemical conditions including pH, temperature, and ionic strength. These factors affect the affinity of each binding site for Fe ions (Zhu et al., 2023). Furthermore, the kinetics of ligand exchange are related to both steric effects and affinities (Boiteau and Repeta, 2022).

Several frameworks have been proposed to represent the mixture of organic ligands in seawater. One of the conceptually simplest approaches is to operationally define different groups of organic ligands. For example, many studies define the continuum of organic molecules in seawater as a series of progressively weaker ligands (Bundy et al., 2014), or simplify this situation with two L categories; L_1 a class that represents the strongest Fe(III) complexation agents, followed by L_2, representing weaker Fe(III) ligands (Hunter and Boyd, 2007; Macrellis et al., 2001; Rue and Bruland, 1995). An alternative approach, which

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was initially developed for freshwater environments (Kinniburgh et al., 1996; Stockdale et al., 2015), is to represent the continuum of organic binding site affinities more explicitly, via describing their statistical distribution (Zhu et al., 2021a, b). Such an approach more completely represents the effective affinity of the binding sites at different Fe concentrations, and can thus theoretically determine the apparent solubility of Fe and the partitioning of Fe between dissolved and particulate phases at equilibrium under ambient environmental conditions (Gledhill et al., 2022a; Zhu et al., 2021b). A dynamic effective binding affinity allows dFe solubility to vary as a function of pH, temperature and DOC, which might be particularly important for understanding the mechanisms that underpin riverine Fe inputs to shelf and off-shelf waters (e.g., Gledhill et al., 2022b). Understanding the inherent assumptions, strengths and weaknesses of these different approaches to describe Fe speciation is necessary in order to address the causes of model-observation discrepancies in the context of river plumes.

In addition to the influence of organic ligands, dFe dynamics are also strongly influenced by Fe oxyhydroxide dynamics. Fe oxyhydroxide particles are readily formed in seawater when Fe hydroxide reaches its saturation state (Byrne and Kester, 1976; Stumm and Sulzberger, 1992). Iron oxyhydroxide formation and aggregation thus constitutes a key component of dFe scavenging, which removes Fe from the dissolved phase. As Fe oxyhydroxides are formed in situ, they are alternatively referred to as authigenic Fe mineral phases (Sofen et al., 2023; Tagliabue et al., 2023). The size continuum of organic material and Fe oxyhydroxides means there is no definitive filtration boundary that separates an organic complex from an Fe oxyhydroxide colloid and it is important to recognize that colloids may contain a mixture of Fe present as oxyhydroxides and Fe bound to organic material. A colloid is defined physically as a particle which has a diameter of 1 nm to 1 µm. Fe colloids can thus be formed from organic material with similar binding properties to the organic ligands which form Fe complexes and will include a diverse range of material. For example, viruses and small bacteria are included within this definition of Fe containing colloids (Bonnain et al., 2016). In some environmental contexts, Fe colloids are primarily inorganic, for example Fe oxyhydroxides formed from glacial weathering (Raiswell et al., 2006) and pyrite released from hydrothermal vents (Yucel et al., 2011) are inorganic species with low organic carbon content. However in many contexts, including rivers and estuaries, colloidal Fe is often a heterogenous mixture of Fe bound to organic molecules and Fe oxyhydroxides (Herzog et al., 2020a; Powell et al., 1996).

To further complicate dFe speciation, whilst Fe(III) is the most stable oxidation state of Fe under oxic conditions, a dynamic fraction of dFe usually exists as Fe(II) due to kinetic processes (Hansard et al., 2009; Sarthou et al., 2011). Photochemical processes (Barbeau et al., 2001; Rose and Waite, 2005) and effluxes into the water column from anoxic sediments (Hong and Kester, 1986; Lohan and Bruland, 2008) both lead to a fraction of dFe existing as Fe(II) in coastal environments. As dissolved Fe(II) rapidly oxidises to form Fe(III) via oxygen or H_2O_2 (Millero et al., 1987; Millero and Sotolongo, 1989), the half-

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life of dissolved Fe(II) is usually short in oxic seawater. Nevertheless, the limited available surveys suggest Fe(II) accounts for 5—30% dFe in estuaries (Hopwood et al., 2015; Yao et al., 2025) and may be dominant in estuaries with low oxygen, low pH, or high sewage input (Statham et al., 2012). The distribution of Fe(II) between 'free' ions, organic complexes, and colloids will differ from Fe(III) due its different organic ligand affinities.

Models attempting to represent Fe as a micronutrient in the ocean thus have to balance the complexity of the natural Fe cycle with simplicity in terms of its parameterized model representation (Tagliabue and Voelker, 2011). Whilst overly simplistic model frameworks may miss key Fe sources or processes relevant to how Fe interacts with other biogeochemical cycles, increasing model complexity does not necessarily lead to better model performance (Denman, 2003). Increasing complexity does however invariably require increasing computational resources and can also lead to further challenges in model interpretation.

5.0 Discovery of a pronounced offshore dFe plume in the Congo

It is an almost universal assumption in biogeochemical models with an Fe cycle module that rivers can be ignored in regional offshore Fe budgets. Yet GEOTRACES observations in both the Congo and the Transpolar Drift appear to challenge this notion indicating major model-observation discrepancies in the Arctic and South Atlantic. Here we will review the state of the art concerning dFe budgets in these regions, before comparing these observations to dFe dynamics in recently developed models and assessing the likely causes of regional model-observation discrepancies.

The Congo basin covers 13% of the landmass of Africa and is Earth's third largest river by discharge volume. Early work in the Congo estuary verified up to 85% removal of dFe (Figueres et al., 1978) at intermediate salinities (~5—15). Observed dFe distributions within the estuary are therefore similar to those observed in other large, tropical estuaries (Araujo et al., 2014). Yet, unexpectedly, an offshore GEOTRACES transect (GA08, 2015), which approximately followed the Congo Plume westwards off-shelf (Vieira et al., 2020), found elevated dFe concentrations extending >1000 km into the South Atlantic (Fig. 3). Within the low-salinity near-surface Congo Plume, dFe concentrations remained >15 nM up to 600 km from the river mouth and >2 nM 900 km from the river mouth (Vieira et al., 2020). When initially measured, these dFe concentrations were so high compared to other offshore regions worldwide (GEOTRACES Intermediate Data Product Group, 2025) that it was suspected they reflected inadvertent contamination. However, closer analysis demonstrated that trends in dFe were matched by ^{228}Ra, a conservative tracer of terrigenous inputs to the ocean which is determined independently (Vieira et al., 2020). The vertical distribution of dFe, with enrichment in the upper 10 m of the water column, particle tracking experiments (Gu et al., 2025), concurrent enrichment of other elements (Liu et al., 2023), and

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the dFe isotopic composition (δ^{56}Fe, Equation 3) (Hunt et al., 2022) all further corroborated a major riverine source for dFe within the Congo Plume.

δ^{56}Fe values (Equation 3) are the conventional notion for measurements of the isotopic ratio of the two most common isotopes of Fe (^{54}Fe which has an average abundance of 5.84%, and ^{56}Fe which has an average abundance of 91.76%). Samples which reflect the average crustal abundance have 0‰ δ^{56}Fe values and deviations from this can be informative about the sources and internal cycling of dFe (Fitzsimmons and Conway, 2023; Homoky et al., 2016; Hunt et al., 2022).

Equation 3 $$\delta^{56}Fe = \left(\frac{\left(\frac{^{56}Fe}{^{54}Fe}\right)_{sample}}{\left(\frac{^{56}Fe}{^{54}Fe}\right)_{standard}} - 1 \right) \times 1000$$

Flux calculations, using ^{228}Ra, derived an off-shelf dFe input from the Congo Plume to the South Atlantic of 0.68 ± 0.23 Gmol year^{-1}. For context, this is a larger input from the River Congo than all biogeochemical models, except PISCES (Aumont et al., 2015), put into the ocean from the combined effect of all rivers globally (Tagliabue et al., 2016). What factors might explain a high off-shelf dFe input from the Congo Plume? The River Congo is unusual as it is the only major river worldwide to enter the ocean in an eastern boundary upwelling region close to the equator. A combination of wind and regional scale circulation result in the propagation of the Congo Plume westwards off-shelf throughout much of the year, with little influence of the Coriolis effect (Hopkins et al., 2013; Martins and Stammer, 2022). At higher latitudes the Coriolis effect deflects river plumes crossing the shelf thus impeding or slowing off-shelf transfer of riverine material (Fig. 2). Alongshore coastal currents also commonly drive river plume deflection. Theoretically, a faster offshore transport reduces the time for scavenging of dFe within the Congo Plume. The fate of the Congo Plume is, for example, a stark contrast with the Amazon Plume, which is more commonly deflected to the northwest along the South American shelf towards the Caribbean (Coles et al., 2013) (Fig. 3).

A further notable feature of the Congo Plume is high observed δ^{56}Fe values. The seasonal δ^{56}Fe endmember for the River Congo corresponding to the GA08 transect is +0.33 ± 0.04‰ (Hunt et al., 2022), which is similar to δ^{56}Fe values for other organic carbon-rich rivers reported to date (Bergquist and Boyle, 2006; Escoube et al., 2009). Moving from the Congo estuary off-shelf, δ^{56}Fe values steadily increase up to +0.95 ± 0.06‰ (Hunt et al., 2022). Several processes could explain this fractionation. The most likely interpretation is a fractionation associated with organic ligands. If organic components are key to stabilizing dFe during off-shore transport (Buck et al., 2007; Bundy et al., 2014; Kritzberg et al., 2014), the preferential survival of an isotopically heavy Fe organic-bound phase could explain increasing δ^{56}Fe

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values moving offshore (Hunt et al., 2022). This hypothesis is testable. A dissolved organic material driven mechanism would likely require differences in both the concentration and composition of the organic carbon within the Congo Plume compared to the open ocean to significantly increase apparent Fe solubility from background concentrations of ~0.5 nM (Zhu et al., 2023) and thus impede authigenic Fe formation. Alternatively, or in parallel, there may be other mechanisms that slow the formation rate of authigenic Fe and thus keep dFe concentrations in the Congo Plume from reaching lower equilibrium concentrations. For example, elevated levels of Fe(II) have been identified as a contributing factor to non-equilibrium dFe conditions over the suboxic Peru shelf and slope (Zhu et al., 2021b). It is less clear what specific mechanism could be at play in the oxic Congo Plume, but photochemical processes in a stratified offshore river plume could at least plausibly contribute to the observed dFe stability (Breitbarth et al., 2009; Miller et al., 1995). Photochemistry is the dominant source of Fe(II) in the photic zone creating a diel cycle in dFe dynamics which is a strong influence on dFe kinetics in the upper few metres of the ocean (Barbeau, 2006; Croot and Heller, 2012; Lueder et al., 2020).

Whilst multiple lines of evidence support a large contribution of the River Congo to dFe supply in the South Atlantic, a complication in the derivation of fluxes is the possibility of overlapping Fe sources. This complication is not unique for the Congo Plume, as overlap between multiple dFe sources is common in many shelf environments worldwide (Boyd et al., 2012; Charette et al., 2016; Chen et al., 2023). In particular, atmospheric deposition (aerosol deposition and rainfall) into the salinity-stratified Congo Plume is likely increasingly important moving off-shelf (Gu et al., 2025; Liu et al., 2023). Direct measurements of rainwater dFe concentration suggest this is only a minor effect over the shelf, contributing ~0.02% of the total dFe input to the Congo Plume (Liu et al., 2023). However, rainfall off-shelf could contribute up to 25%–67% of dFe input (Gu et al., 2025). Any effect of rainfall on near-surface dFe concentrations is likely amplified by the strong stratification within the 3—20 m thick Congo Plume. Further work is needed to verify whether this is consistent with the observed heavy δ^{56}Fe fractionation.

6.0 Discovery of a pronounced offshore dFe plume in the Transpolar Drift

Transport of material from Siberia across the Arctic and further south into the North Atlantic is well-documented. As early as 1881 it was deduced that driftwood in southern Greenland originated in Siberia and thus must have been transported across the Arctic by natural means (Eggertsson, 1993). Three major Siberian rivers drain from the central Eurasian shelf into the Arctic; the Yenisei, Lena and Ob. Freshwater from these rivers can subsequently be advected across the Arctic in the Transpolar Drift, a near-surface current which passes from the Laptev and East Siberian Seas to northern Greenland via the North Pole (Fig. 3). A low-salinity near-surface layer in the current is concentrated in the upper ~60 m of the water

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column (Charette et al., 2020). The estimated timeframe for cross-Arctic transport in the Transpolar Drift has been assessed as 1.5 to 3 years for sea ice (Krumpen et al., 2019; Pfirman et al., 1997; Steele et al., 2004).

Early observations investigating trace metal dynamics in the Yenisei, Lena and Ob reported loss of >80% dFe across the salinity gradient similar to other estuaries worldwide (Dai and Martin, 1995; Guieu et al., 1996). Dissolved Fe concentrations at intermediate salinities (15—30) are 10 to 109 nM in the Lena (Guieu et al., 1996), up to 50 nM in the Ob, and up to 110 nM in the Yenisei (Dai and Martin, 1995). Later work has used both $\delta^{18}O$ and ^{228}Ra isotopic measurements to trace terrigenous inputs from these rivers across the Arctic (Charette et al., 2020; Kipp et al., 2023, 2018). In particular, the GEOTRACES sections GN01 and GN04 (both in 2015) were designed to cover an Arctic transect which would bisect the Transpolar Drift (GEOTRACES Intermediate Data Product Group, 2025). Both cruises successfully captured the high freshwater content of the Transpolar Drift, which exceeded 20% close to the North Pole (Charette et al., 2020). Similar to the Congo Plume, high offshore concentrations of 3.14 ± 0.97 nmol kg^{-1} dFe were found within a thin, near-surface layer (Zhang et al., 2021). These elevated concentrations extend >1500 km from the Siberian coastline (GEOTRACES Intermediate Data Product Group, 2025). Offshore concentrations of this magnitude would normally be considered erroneous in most contexts, yet here they are consistently associated with low salinities across two independent cruises conducted in parallel which verifies their oceanographic consistency (Charette et al., 2020). Furthermore, prior observations in the Arctic have also captured elevated dFe concentrations in the same surface layer. An earlier survey in 2012 reported elevated near-surface dFe concentrations in the same region, averaging 1.75 ± 0.97 nmol L^{-1} at latitudes >85 °N in the upper 50 m of the water column (Klunder et al., 2012).

How far elevated dFe concentrations associated with Transpolar Drift extend is unclear. Later GEOTRACES observations in Fram Strait (GN05, 2016) attributed elevated dFe concentrations of 1.02 ± 0.62 nmol L^{-1} at 79°N in the near-surface waters of the East Greenland shelf to Arctic outflow (Krisch et al., 2022). Whilst this is 3000 km downstream of the Siberian shelf, dissolved trace elements including cobalt, nickel and copper at 79°N still maintained strong correlations with freshwater content (Krisch et al., 2022), as is the case further north (Charette et al., 2020). A source of trace elements associated with the Siberian shelf at 79°N is further supported by a strong correlation between $^{228}Ra/^{226}Ra$ and freshwater content (R^2 0.91) (Krisch et al., 2022). Combined, this suggests a predominant role in cross-Arctic transport for controlling dFe distributions in Arctic outflow through Fram Strait rather than any other regional sources (Krisch et al., 2021). Nevertheless, the relatively high dFe concentrations of the East Greenland Current in Fram Strait are notably depleted compared to those observed further north, suggesting extensive dFe removal, likely in part due to biological drawdown (Charette et al., 2020; Klunder et al., 2012; Zhang et al., 2021).

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Several processes related to Fe biogeochemistry may influence dFe dynamics in the near-surface waters of the Transpolar Drift. Notably, the central Arctic remains under sea ice cover for most of the year which moderates primary production -and thereby biological dFe utilization (Ardyna et al., 2014)- and may also facilitate dFe exchange between sea ice and seawater. Sea ice formation can entrain dFe and conversely sea ice melt can re-release entrained dFe back into the water column (Lannuzel et al., 2016). Sea ice formed in shallow shelf environments might be a particularly prominent Fe source as high concentrations of dissolved and labile particulate Fe can be acquired both from the water column over winter and from erosion at the coastline (Hölemann et al., 1999; Measures, 1999). Sediment laden "dirty" sea ice can often be visually identified. Similarly, atmospheric deposition on sea ice between its formation and melt interlinks atmospheric and sea ice sources of dFe to the water column (Kadko et al., 2016; Lannuzel et al., 2016; Tovar-Sánchez et al., 2010). Furthermore, sea ice is not only a passive agent for Fe accumulation, advection and release. Meltwater ponds forming on sea ice over summer provide low salinity, high light environments with high particle loads which can favor dissolution of some elements such as manganese (Jensen et al., 2021). Early work noted high concentrations of dFe in "dirty" sea ice in inshore waters of the Laptev Sea (281 nmol kg^{-1}, Hölemann et al., 1999) and found reactive Fe concentrations of up to 20 nM in water samples carefully collected immediately adjacent (10—20 cm) to sea ice floes in regions with high sediment loading (Measures, 1999). However more recent work has found less evidence for a clear role of sea ice as a major dFe source to the Transpolar Drift. In the Laptev and East Siberian seas, sea ice was found to contain less dFe than the underlying water (Kanna et al., 2025). Similarly, on GN01, samples collected near the North Pole had dFe concentrations of 3.6 ± 2.9 nM for snow, 1.1 ± 1.0 nM for sea ice, and 3.0 ± 1.3 nM for the underlying seawater at the same locations (Marsay et al., 2018).

These observations do not preclude exchange of dFe between sea ice and the water column across the central Arctic, but suggest the input of sea ice melt is negligible as a net regional dFe source. This also implies that the atmospheric Fe deposition flux onto sea ice is relatively low. Furthermore, in meltwater ponds formed on the sea ice surface, dFe scavenging processes appear to predominate over dissolution of particulate Fe and thus limit the role of sea ice melt as a net source of dFe to the underlying water column (Jensen et al., 2021; Marsay et al., 2018). Atmospheric Fe fluxes derived for the Arctic from GN01 verify a low regional atmospheric deposition flux. Scaled to the entire Arctic, a dFe input of 2.1 ± 0.6 Mmol $year^{-1}$ is derived from the naturally occurring radionuclide beryllium-7 (Kadko et al., 2019). This is equivalent to 2% of the estimated off-shelf dFe transport in the Transpolar Drift (Charette et al., 2020).

The isotopic composition of dFe within the Transpolar Drift is distinct from other Arctic water masses and, unlike the Congo Plume, remains close to zero, averaging 0.02 ± 0.23‰ δ^{56}Fe (Zhang et al., 2021). This is interpreted as reflecting riverine inputs, which in the Arctic have a −0.11 ± 0.27‰ δ^{56}Fe endmember (Conrad et al., 2019a; Escoube et al., 2015). Snow (−0.48 ± 0.09 δ^{56}Fe), sea ice (−0.61 ± 0.35

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δ^{56}Fe) and melt ponds on sea ice (−0.61 ± 0.81 δ^{56}Fe) have more negative δ^{56}Fe compositions (Marsay et al., 2018). Isotopic measurements thus corroborate estimates of minimal dFe inputs from sea ice and atmospheric deposition over the Transpolar Drift flow path. The deduction that riverine-sourced Fe supplies almost all of the dFe within the Transpolar Drift therefore appears to be sound (Charette et al., 2020). Processes which impede scavenging below sea ice, rather than processes which continuously re-supply dFe into near-surface waters, appear to be key to understanding why the Transpolar Drift dominates regional dFe supply (Charette et al., 2020). Compared to other ocean basins, apparent Fe solubility is expected to be higher in the Arctic which is relatively less alkaline, cold and has high humic DOC concentrations- particularly in the Transpolar Drift (Slagter et al., 2019). All of these factors should theoretically reduce dFe scavenging. Studies in the western Arctic corroborate this hypothesis noting that, away from the shelf, a large fraction (>70%) of dFe is present in the <0.02 µm size fraction, which is low compared to the North Atlantic where a majority of dFe is in size fractions >0.02 µm (Jensen et al., 2020). This is thought to reflect the importance of DOC in the Arctic forming organic complexes with Fe.

7.0 Mechanisms to explain efficient off-shelf transport of riverine Fe

The magnitude of dFe export from individual rivers to off-shelf marine environments reflect a combination of two key processes which are not driven by the same factors. The first process is the extent to which dFe is removed in the estuary. The second process is the extent to which the riverine plume of dFe is advected off-shelf, as plumes which are confined to the shelf are inherently limited in their direct effect on off-shelf dFe concentrations. The factors determining temporal and spatial variations in the extent of dFe removal in estuaries are not clear. Although several hypotheses have been made, the inherent limitations in quantification of estuarine dFe removal should be considered throughout. Environmental factors such as seasonality (Gao et al., 2026; Hopwood et al., 2014; Mayer, 1982) and the residence time of water within an estuary (Bruland et al., 2008; Pokrovsky and Schott, 2002) are inferred to have some influence on dFe retention. Critically, the fact that a broad range of dFe removal factors are reported within individual estuaries (Table 1) suggests a variety of spatial and temporal factors are at play. These may include temperature dependent effects (Mayer, 1982), particle size associated effects (Dai and Martin, 1995; Figueres et al., 1978; Hong and Kester, 1985) and the nature of organic carbon in river water (Gustafsson et al., 2000; Krachler et al., 2010; Sholkovitz et al., 1978). Seasonal changes in estuarine dFe removal may relate to any combination of these factors.

Short water residence times in estuaries have been reported to increase dFe export (Bruland et al., 2008; Wu and Luther III, 1995). Given the seconds-to-minutes timescale of dFe flocculation at low salinities (Hunter and Leonard, 1988; Nowostawska et al., 2008), compared to the days-to-weeks residence time of water within estuaries (Cui et al., 2023; Du and Shen, 2016; Yuan et al., 2007), an effect of residence time on dFe removal may seem counterintuitive. However, the finding that decreased residence time

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allows increased dFe export might relate to the second stage of dFe removal where larger colloids aggregate and are removed from the water column. Explicit parameterizations of dFe scavenging and particle aggregation in the ocean usually have a scaling factor with particle load (Honeyman et al., 1988). That is at higher particle loads, scavenging is more efficient. As scavenging is not instantaneous, shorter residence times in estuaries and the more rapid dilution of dFe and particles into higher salinity waters may limit scavenging rates and thus allow a higher transfer efficiency from fresh to saline waters. The same principle might also be extrapolated to the shelf; faster transport and dispersion of a river plume off-shelf may reduce the dFe scavenging rate.

If rapid dilution is a mechanism to facilitate efficient retention of dFe in seawater, an interesting related case study is rain water. Although sparsely studied, dFe concentrations in rainfall are usually on the order of 10 nM (Kieber et al., 2001; Liu et al., 2023; Shelley et al., 2017). Critically, deposition of rainfall in the ocean occurs alongside rapid dilution. Whereas freshwater in an estuary is diluted to salinities >30 on timescales of hours to days, freshwater in rainfall can be diluted to salinities >30 on timescales of seconds. Whilst to our knowledge not explicitly demonstrated, there are indicators that rainfall is an efficient dFe delivery mechanism and this may partially relate to rapid dilution (Kieber et al., 2001; Willey et al., 2004, 2008). There are however also other critical differences comparing rain water to river water. Rain water pH is usually more acidic than river water, which combined with the high photon flux droplets of water experience in the atmosphere, means dFe in rain water can be mainly present as Fe(II) rather than Fe(III) (Kieber et al., 2003; Willey et al., 2008, 2009).

As particle surface area is a key driver of scavenging, differences in experimental protocol, particularly the filter size used to define ‘dissolved’ species, are also contributing factors to reported estuarine dFe removal rates (Dai and Martin, 1995; Figueres et al., 1978; Hong and Kester, 1985). This is especially the case for laboratory mixing experiments because the method used to simulate mixing may exert a strong effect on the observed particle and dFe dynamics (Hunter et al., 1997; Hunter and Leonard, 1988). When large particles are removed from solution in order to study a specific size fraction of Fe colloids, and to what extent this specific size fraction is removed over the salinity gradient, the overall scavenging rate of dFe is likely also reduced. Large particles are themselves a driving mechanism of both particle aggregation and dFe scavenging (Hunter and Leonard, 1988), so their removal should always result in less effective dFe removal than would be exhibited in the natural environment. Both estuarine transects (Table 1) and mixing experiments therefore have strengths and weaknesses and must be interpreted together. Estuarine transects obtain only snapshot images of highly dynamic systems and have inherent - and often unrealistic- assumptions when deriving a dFe removal factor. On the other hand, controlled mixing experiments offer reduced complexity and have proven useful for characterizing the specific mechanisms of dFe loss in estuaries, but are less environmentally realistic.

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Several hypotheses have been made concerning why a small minority of estuaries have low apparent dFe removal rates or approximate conservative mixing (Table 1). In defining apparent 'conservative' mixing within estuaries we are primarily concerned with estuaries which appear to have conservative mixing across a large part of the salinity gradient. As estuarine removal of dFe is almost invariably evident at low salinities (often <1), the distribution of dFe is generally expected to be more conservative at higher salinities. This principle can be illustrated by sub-sampling from an estuarine dFe dataset which covers the full salinity gradient (e.g., Fig. 1). Selecting data from higher salinities inevitably produces a stronger linear correlation between dFe and salinity. Non-conservative dynamics are therefore best assessed from datasets which include dFe measurements at zero, low (~1—10), and high (~25+) salinity. Apparent conservative dynamics at high salinities is not informative of dFe dynamics at low salinities.

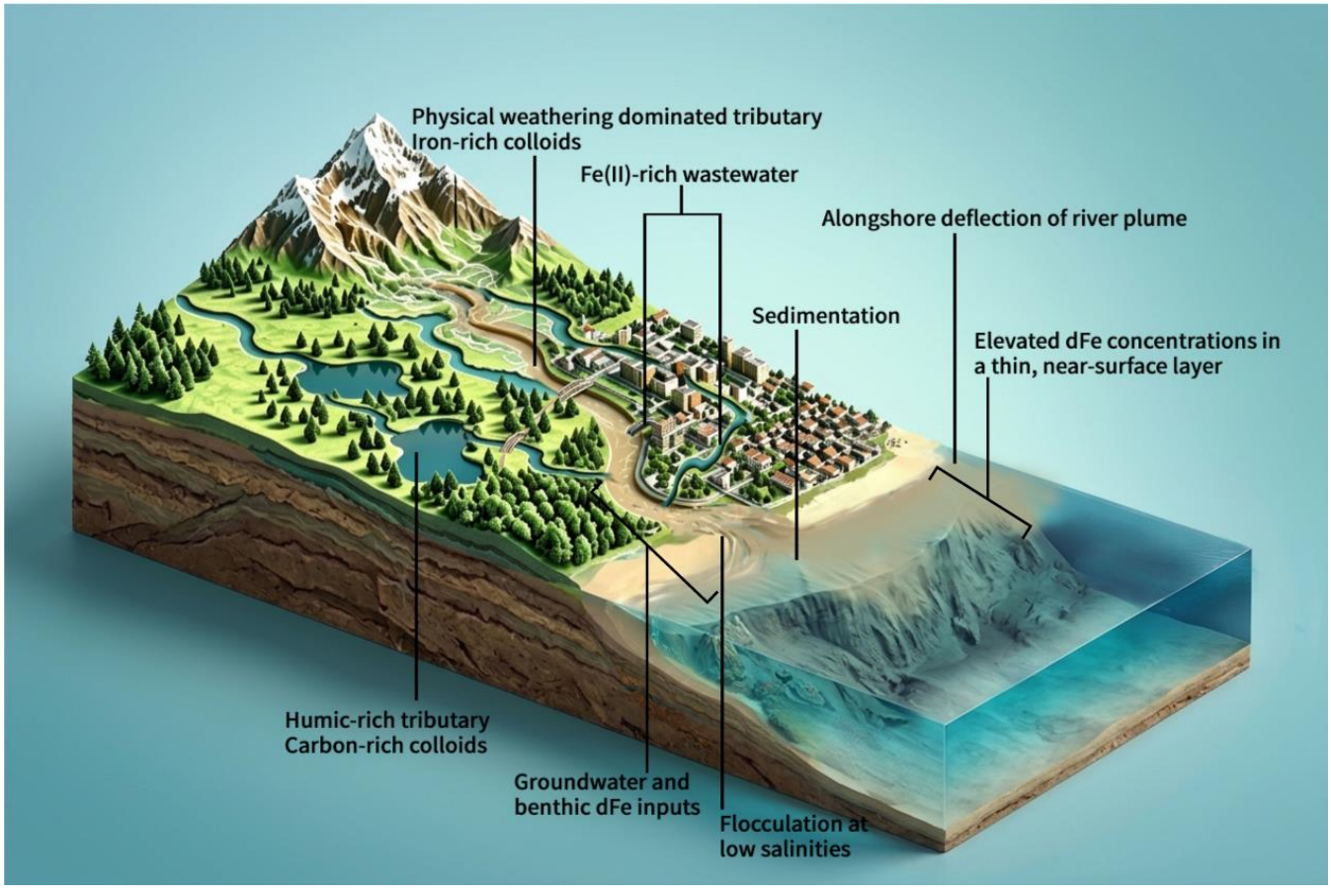

Figure 2. A concept diagram of the key processes which characterize dissolved Fe delivery from rivers to the ocean. Estuaries may integrate dissolved Fe inputs from different sources with different chemical properties. Removal of Fe from the dissolved phase is usually, but not always, evident at low salinities.

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Where river plumes enter the ocean, they are often deflected along the shelf. If the plume is stratified, rather than well-mixed, dFe concentrations may be elevated in a shallow, near-surface layer.

A subset of case studies worldwide do appear to show evidence of low dFe removal across broad salinity gradients (Table 1). An apparent conservative mixing of dFe has been demonstrated in the Mississippi Delta (Powell and Wilson-Finelli, 2003; Shiller and Boyle, 1991). The Mississippi is alkaline compared to average world river water with dFe concentrations ~30 nM (Shiller and Boyle, 1991). Some of the earliest estuarine dFe transects in the Merrimack and Parker rivers similarly deduced relatively low dFe removal of 54—71% and 66%, respectively (Boyle et al., 1977). These rivers have moderately high dFe concentrations, ranging 4—12 µM, and near-neutral pH (Boyle et al., 1977). One of the most commonly invoked hypotheses concerning the factors that impede dFe removal is that organic-rich colloids are less prone to removal (Krachler et al., 2005; Krachler and Krachler, 2021; Kritzberg et al., 2014). Thus, rivers with high organic carbon concentrations and high organic C:Fe ratios are suggested to be less prone to estuarine dFe flocculation (Khoo et al., 2022). Notably, this does not include any of the above case studies. High organic carbon concentrations are normally associated with peat dominated catchments, where DOC concentrations can be on the order of 1000 µM (Khoo et al., 2022). It is important to note that the hypothesis C:Fe ratios affect estuarine dFe removal usually refers to total organic C:Fe ratios, i.e. total suspended and dissolved Fe and organic C rather than specifically DOC:dFe ratios as it is the competition between all available Fe oxyhydroxide and organic material binding sites which affect the distribution of Fe. High DOC:dFe ratios can be found in both high and low dFe rivers. For example, of the three rivers in Figure 1, the Pearl River has the highest DOC:dFe ratio (>4000) compared to <200 for the Cape Fear and Amazon-Pará Rivers (Gledhill et al., 2022b; Hollister et al., 2026; Hopwood et al., 2015; Ruan et al., 2024; Ye et al., 2018). Yet dFe removal in the Pearl River is >99%. Similarly, the River Bayelva, a glacier-fed Arctic river where dFe readily aggregates, has a relatively low DOC range 98–167 µM, but a higher DOC:dFe ratio (>4000) than the Amazon (Zhang et al., 2015).

The River Maludam (Sarawak) is one example of a river with high DOC (300—4600 µM) and low dFe removal in the global compilation of surveyed estuaries (Ukotije-Ikwut et al., 2023; Zhang et al., 2020). Independent surveys on two occasions both noted no apparent loss of dFe in the estuary at intermediate salinities (Ukotije-Ikwut et al., 2023; Zhang et al., 2020). Whilst few other small humic-rich river estuaries are present within the global compilation of estuarine dFe surveys (Table 1), this type of river is relatively common in peat dominated regions. Both total and dissolved Fe concentrations are well correlated with DOC in many rivers worldwide (Bjorkvald et al., 2008; Neal et al., 2008; Neubauer et al., 2013) because of the formation of carbon-rich colloids (Batchelli et al., 2010; Cameron and Liss, 1984; Rose et al., 1998). These colloids drive the stabilizing influence of organic material on dFe load. Two distinct classes of Fe colloids are therefore often distinguished in rivers; carbon-rich colloids and Fe-rich colloids (Lyven et al., 2003; Stolpe et al., 2013). The former consist mainly of humic and fulvic bound

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Fe whereas the latter are primarily inorganic Fe-oxyhydroxides (Stolpe et al., 2010). Mixed phases also observed in many contexts (Herzog et al., 2020b; Neal et al., 2008). Mixing experiments support the hypothesis that organic-rich Fe colloids are less prone to flocculation than Fe-oxyhydroxide rich colloids (Herzog et al., 2020a; Kritzberg et al., 2014; Sanders et al., 2015). This means small humic-rich rivers could be a disproportionately large dFe source to the ocean compared to other rivers (Krachler et al., 2005, 2010, 2019), which is supported by observations in the Maludam (Ukotije-Ikwut et al., 2023; Zhang et al., 2020).

Examples of an extreme opposing scenario- rivers dominated by Fe-oxyhydroxide colloids with low organic carbon:Fe- can be found in glacier-fed catchments. The high dFe loads from subglacial bedrock weathering (Poulton and Raiswell, 2002) create Fe oxyhydroxides in these rivers which readily aggregate even in freshwater (Zhang et al., 2015) and are thus often associated with particle surfaces (Poulton and Raiswell, 2005; Raiswell et al., 2006). For the River Bayelva, 80% of dFe was found to aggregate along the 4 km river prior to further losses during estuarine mixing (Zhang et al., 2015). In the available studies of glacier estuaries (Table 1), dFe removal calculated from salinity gradients ranges from 85—97% (Hopwood et al., 2016; Krause et al., 2021; Schroth et al., 2014). Yet it should be noted that observations in the River Bayelva suggest a large degree of colloidal aggregation may also have occurred upstream of these estuarine measurements (Zhang et al., 2015). Observations of a rapid decline in dFe concentrations along the relatively short (4 km) River Bayelva, prior to further removal in the associated estuary, thereby raise an additional pertinent question concerning whether or not it is appropriate to generally assume a riverine dFe endmember entering an estuary is in a state of equilibrium with organic material. Unlike the ocean, the residence time of water in rivers globally is short, on the order of days. During this time pH, organic carbon concentration and the suspended particle load are subject to more pronounced changes in relative and absolute terms than in most marine contexts (Mulholland et al., 2015; Zhang et al., 2020). A key difference comparing dFe dynamics in some estuaries might therefore arise depending on whether or not dFe was approximately in thermodynamic equilibrium with ambient conditions -particularly organic carbon- before entering the estuary.

8.0 Implications of river plumes as major dFe sources to the ocean

The Congo and Transpolar Drift observations from GEOTRACES cruises present compelling evidence that some riverine plumes of dFe propagate off-shelf and constitute not only regionally significant, but sometimes regionally dominant dFe fluxes. In the Arctic, the Transpolar Drift carries 0.1 ± 0.05 Gmol dFe $year^{-1}$ off-shelf, compared to atmospheric deposition of 2.1 ± 0.6 Mmol dFe $year^{-1}$. In the South Atlantic, the Congo Plume carries 0.68 ± 0.23 Gmol dFe $year^{-1}$ off-shelf, compared to atmospheric deposition of 72 Mmol dFe $year^{-1}$. Both modelled and calculated Fe atmospheric deposition fluxes often have a high uncertainty due to propagated uncertainties on estimates of atmospheric dust deposition, dust

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Fe content, and Fe solubility (Jickells et al., 2016). Nevertheless, a comparison of the best available estimates clearly indicates that the Congo Plume and the Transpolar Drift are both highly likely to be regionally dominant dFe sources. Yet in most models these sources are either missing entirely, or deemed minor compared to atmospheric deposition in their respective areas of influence (Tagliabue et al., 2016).

An obvious question is where else in the world similar phenomena may be evident. At the global scale, there are clearly strong variations in the extent to which dFe is removed across the salinity gradient (Table 1). Many of these differences will be of little direct consequence to global Fe biogeochemistry models because of the small scale of individual river plumes compared to model grid cells (Fig. 3). For rivers to be evident as regional dFe sources on scales relevant to global ocean biogeochemical model grids they must be enriching oceanic regions that extend off-shelf. Particularly with smaller rivers, it is therefore important to distinguish between limitations which arise in model-observation comparisons because of model grid size, and limitations which arise because of how dFe is parameterized. For example, of the three studies presented to illustrate the classic non-conservative loss of dFe observed in many estuaries worldwide (Fig. 1: the Cape Fear, Pearl River Estuary, and the Amazon- Pará), only the Amazon- Pará is large enough to make a meaningful comparison within the ECCO-Darwin model framework (Savelli et al., 2026). The transition from low to high salinity in the Cape Fear and Pearl River estuaries occurs within too small a spatial frame for global model results to be meaningfully compared to observations (Fig. 3).

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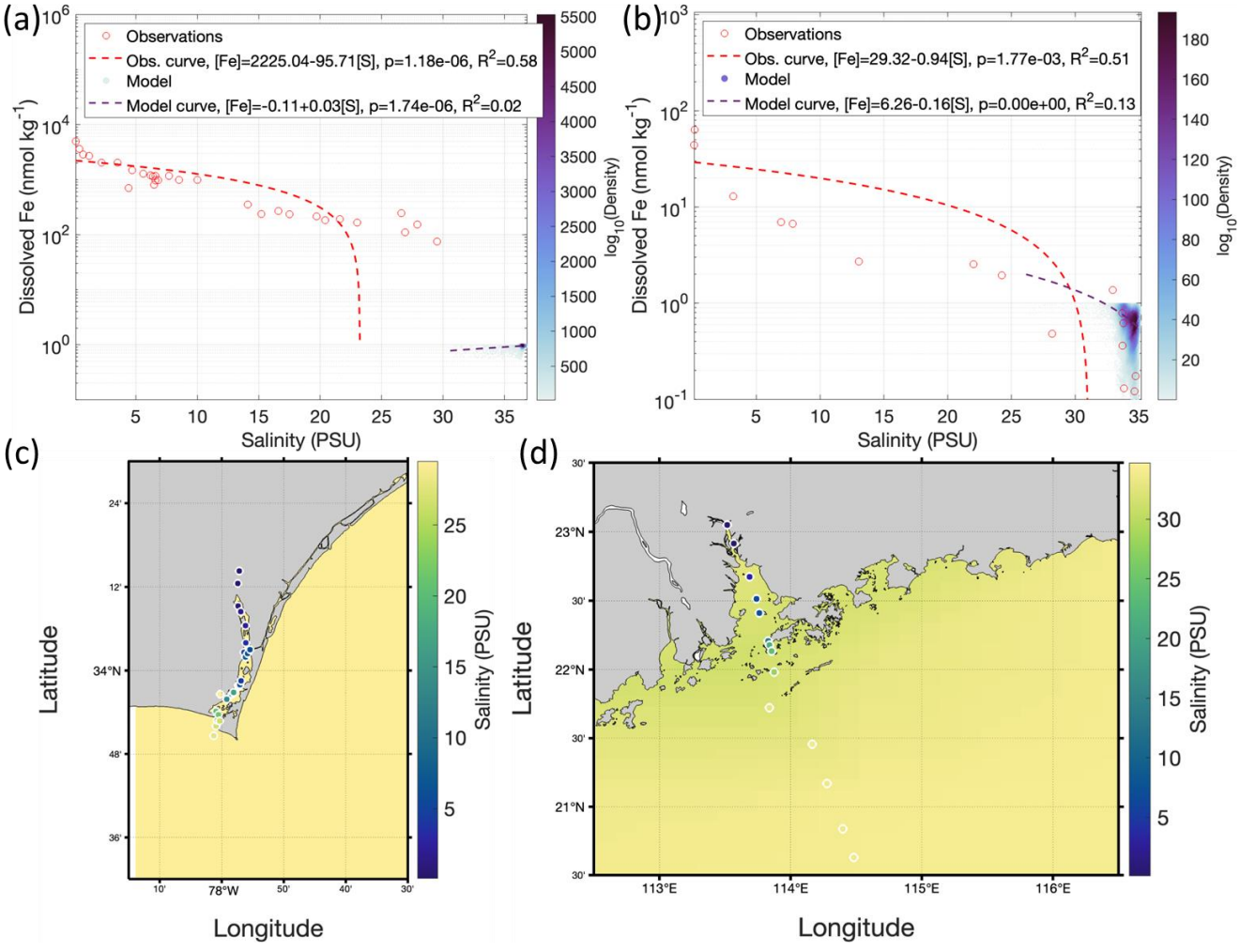

Figure 3. A comparison of model (ECCO-Darwin) and observational data from the Cape Fear and Pearl River Estuary (Savelli et al., 2026). (a) Dissolved Fe across the observed and model salinity gradient in the Cape Fear. (b) Dissolved Fe data across the observed and model salinity gradient in the Pearl River Estuary. (c) Comparison of model and observed salinity in the Cape Fear, (d) Comparison of model and observed salinity in the Pearl River Estuary. Regional dFe and salinity data from prior work (Hopwood et al., 2015; Ruan et al., 2024). Each per-river zoomed panel (c, d) re-grids the native 1° ECCO-Darwin outputs onto a 150×150 mesh.

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In the next section we will evaluate how dFe is represented in a recent model simulation, focusing on larger rivers. We will verify that dFe plumes associated with the Congo and Transpolar Drift remain absent, assess why this is the case, and evaluate how models could better represent riverine dFe supply.

8.1 Modeling Riverine Dissolved Iron Plumes in the Open Ocean

The representation of dFe associated with river plumes and riverine Fe advection offshore in global-ocean biogeochemical models is limited by the physical parameterization of freshwater plumes, and the parameterization of Fe biogeochemistry. The addition of riverine freshwater and associated solutes in coarse vertical and horizontal grid cells leads to a rapid numerical dilution, which drives weak Fe–salinity gradients in major river plumes compared to observations — irrespective of how well the model river dFe flux matches observations. This is observed in ECCO-Darwin, as it is in other global models, and remains the case for both large and small rivers (e.g., Figs. 4 and 5) (Savelli et al., 2026).

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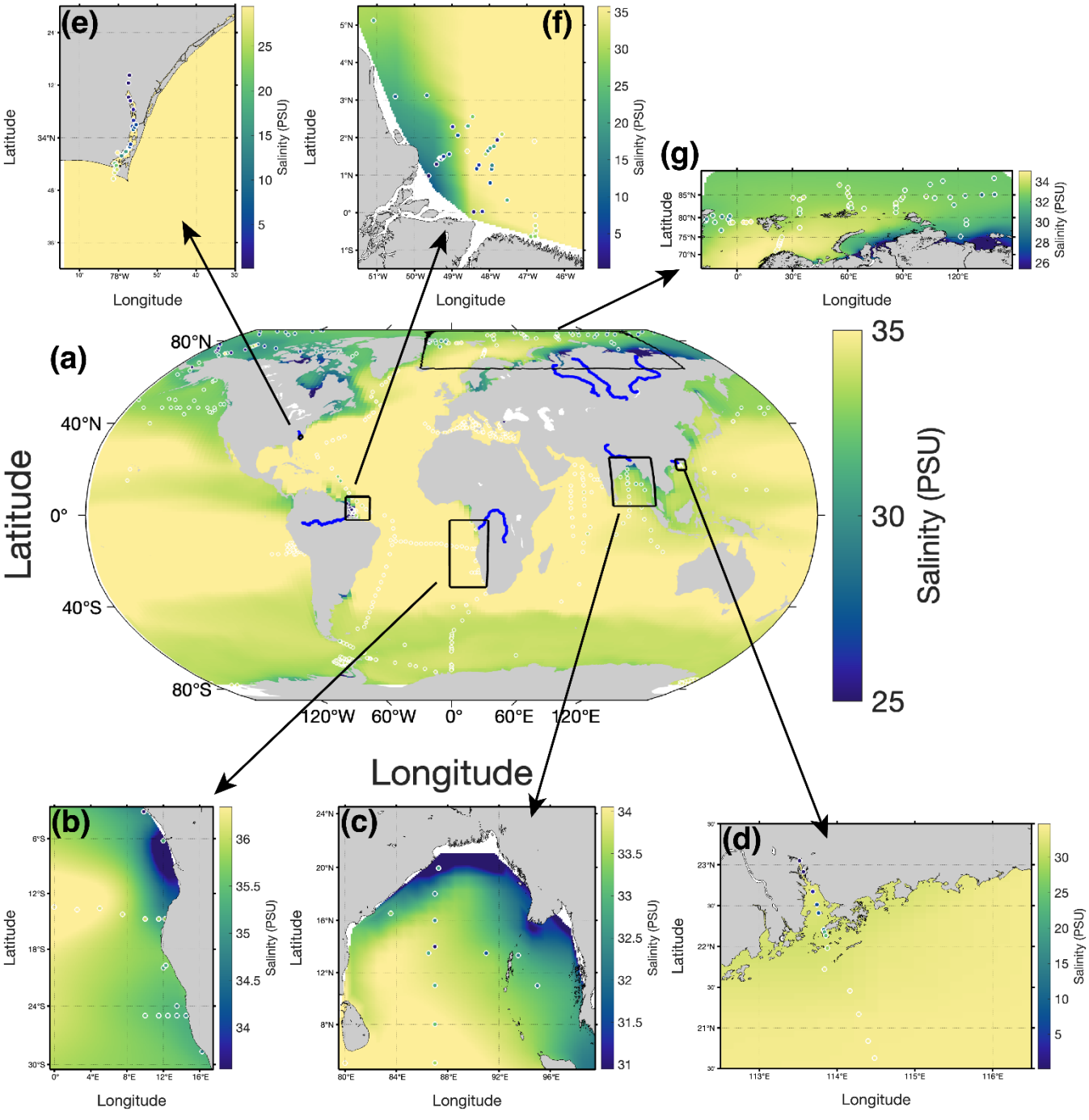

Figure 4. Global and regional surface salinity. Maps are time-mean model surface-ocean salinity simulated by ECCO-Darwin from 2000–2022 for the (a) global ocean, (b) Congo Plume, (c) Bay of Bengal, (d) Pearl River Estuary, (e) Cape Fear, (f) Amazon-Pará, and (g) Transpolar Drift domains (Savelli et al., 2026). Observations are represented by data points averaged over the surface layer (< 10

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m) from GEOTRACES (GEOTRACES Intermediate Data Product Group, 2025) and regional observations (Gledhill et al., 2022b; Hollister et al., 2026; Hopwood et al., 2015; Ruan et al., 2024). Each per-river zoomed panel re-grids the native 1° ECCO-Darwin outputs onto a 150×150 mesh.

Limitations in the parametrization of Fe biogeochemistry concern not only the riverine Fe source flux, but also how dFe concentrations are capped within models. After atmospheric dust deposition as the primary input, additional sources of Fe vary from one model to another (i.e., rivers, shelf sediment, and hydrothermal vents) (Tagliabue et al., 2016). Furthermore, most Fe models to date assumed constant ligand concentrations despite growing evidence for strong spatial variability, particularly in coastal and river-influenced waters (Gerringa et al., 2007; Laglera and van den Berg, 2009; Su et al., 2015). As rivers may be major ligand sources (Bundy et al., 2015; Powell and Wilson-Finelli, 2003; Slagter et al., 2019), a model ligand cap is likely to be a key reason why models universally appear to be missing the influence of the Transpolar Drift and the Congo Plume, even when riverine dFe inputs are explicitly included (Aumont et al., 2015; Tagliabue et al., 2016). The representation of Fe scavenging also differs widely among models depending on whether models use particle-concentration-dependent scavenging, if caps are imposed on dFe concentrations, and how Fe speciation is represented (Tagliabue et al., 2016; Tagliabue and Voelker, 2011).

While the data-assimilative global-ocean biogeochemistry ECCO-Darwin model (Carroll et al., 2020) successfully captures the salinity distribution of the surface ocean globally (Fig. 4), it still misses the dFe-salinity mixing gradient associated with many river plumes (Fig. 5) (Savelli et al., 2026). The absence of enriched dFe concentrations in the Transpolar Drift and the Congo Plume therefore remains a result common, to our knowledge, to all global biogeochemical models that explicitly parameterize Fe to date (Tagliabue et al., 2016). A key test of model skill is the predictive power of a model. In the context of dFe distributions, with a relatively low global data resolution, this can be exemplified as the ability of a model to match observed dFe concentrations in a dataset that was not used during model development or testing. Concerning, the high dFe concentrations in the Transpolar Drift and the Congo Plume, models could be argued to be deficient in skill as these features were not, to our knowledge, predicted by any biogeochemical models prior to their observation. Nevertheless, it is important to note that this absence partially reflects model grid size.

In ECCO-Darwin, rivers add only 0.005 Gmol Fe yr^{-1} dFe into coarse 1° × 1° and 10-m thick surface grid cells, leading to a quick dilution of surface river plumes and limited impact on regional Fe budgets. Additionally, in ECCO-Darwin, dFe is constrained by a prescribed 0.4 nM upper limit on Fe′ concentration (Savelli et al., 2026). While this threshold may be a reasonable assumption in the open-ocean where, combined with a prescribed constant ligand concentration (L_T, 1 nM), it is designed to prevent unrealistically high dFe concentrations, the model Fe′ and L_T caps clearly unrealistically limit

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dFe concentrations in the coastal ocean and river plumes (Fig. 5). As ECCO-Darwin defines the maximum stable dFe concentration as FeL + Fe′, there is effectively a global cap of 1.4 nM on dFe concentrations anywhere in this ocean model.

Use of a constant ligand concentration is common to most Fe model frameworks and will thus have a similar quantitative effect in most other reported model results to date (Aumont and Bopp, 2006; Moore and Braucher, 2008; Parekh et al., 2005). The imposition of this cap was a reasonable assumption given the evidence available at the time these formulations were devised (Hunter and Boyd, 2007; Rue and Bruland, 1995; Wu and Luther III, 1995), and remains a reasonable assumption in most of the open-ocean to date (GEOTRACES Intermediate Data Product Group, 2025; Somes et al., 2021; Zhu et al., 2023). However, this approach is not well suited to representing coastal dynamics where L concentrations may be considerably higher (Boye et al., 2003; Laglera and van den Berg, 2009; Mahmood et al., 2015). Critically, an unrealistically low cap on L at the coastline not only limits dFe concentrations, but also any lateral dFe fluxes towards the ocean interior (Hioki et al., 2014; Laglera et al., 2019; Slagter et al., 2017). Recently, there have been attempts to model variable ligand concentration in the open ocean (e.g., Lauderdale et al., 2020), and such processes combined with riverine sources might prove a significant advancement in biogeochemical model Fe cycling (Somes et al., 2021).

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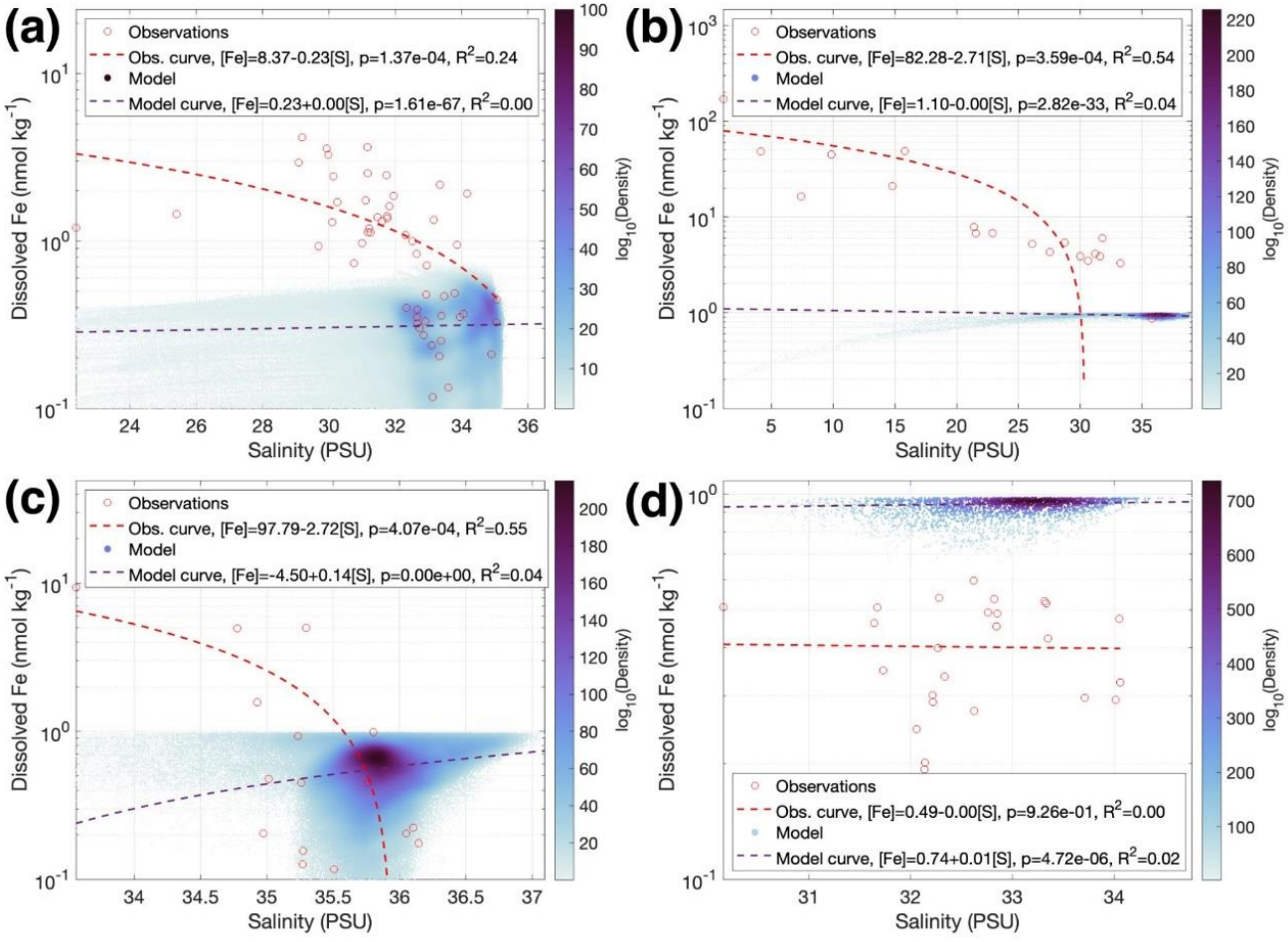

Figure 5. Iron and salinity comparison between observations and the ECCO-Darwin model for the (a), Transpolar Drift, (b) Amazon River plume, (c) Congo River plume and, (d) Bay of Bengal domains defined in Figure 1. The model curve is fit using points above the median density. Model points at capped concentration were removed from the analysis. Observations are from GEOTRACES (GEOTRACES Intermediate Data Product Group, 2025) and METEOR M147 cruise datasets (Gledhill et al., 2022b; Hollister et al., 2026).

A further subtlety, which is beyond the capability of most biogeochemical models, is that the affinity of organic material for Fe(III) does not only depend on the concentration of organic ligands, but also physical conditions. Ligand dynamics in seawater are often investigated via titrations (Buck et al., 2012; Hawkes et al., 2013; Ruzic, 1982) with ligand properties then defined in terms of a ligand concentration and affinity for Fe(III). Yet strictly these definitions are only valid under the conditions they are defined (e.g., one fixed pH, temperature and salinity) (Hudson et al., 2003). In the Arctic, the ocean is colder and less

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alkaline than the tropics, and so apparent Fe solubility will generally be higher in the Arctic than the tropical Atlantic or Pacific -even in the hypothetical (and unrealistic) circumstances where the concentration and nature of organic material were identical. Modeling this effect would require a more complicated Fe framework than a fixed ligand approach, as attempted by Lauderdale et al., (2020) and Somes et al., (2021), or a less computationally expensive redefining of 'L concentration' such that it is nudged according to this effect. One of the key aspirations for developing the apparent Fe solubility concept is that it may thereby be possible to derive regional apparent Fe solubility from common measurements such as DOC, pH, temperature and salinity (Zhu et al., 2021b, a, 2023) which could then be used in some model frameworks (Misumi et al., 2013; Tagliabue and Voelker, 2011). These parameters are available at much higher resolution in the ocean than estimates of ligand concentration and affinities based on titrations (Gledhill and Buck, 2012; Rue and Bruland, 1995; Wu and Luther III, 1995).

Improving the representation of riverine Fe in global ocean biogeochemistry models requires a combination of both physical and biogeochemical adjustments. First, representation of dFe plumes in global models would benefit from subgrid parameterizations or coast-responsive grids that better represent estuaries, plumes, and mixing without substantially increasing model complexity (Ward et al., 2020). The addition of river-associated Fe and L pools and plume-specific scavenging, or factors which represent this by adjusting dFe, would further improve the plume- and river-related Fe chemistry in models. Such developments would allow models to better reconcile the large riverine Fe fluxes inferred from observations in the Congo and Transpolar Drift with their currently-limited or negligible influence on simulated open-ocean Fe distributions (Savelli et al., 2026; Tagliabue et al., 2016). Adding a parameter to represent riverine input would be straightforward and could be scaled to either riverine freshwater volume or other river inputs (e.g., nutrients). However, the effect of this addition within individual models will vary depending on how ligands and scavenging are parameterized. Furthermore, adjusting how [L] is parameterized on a global scale may also require parallel adjustments to how scavenging is parameterized and which forms of modelled Fe are defined as bioavailable within the model framework (Tagliabue and Voelker, 2011).

In the most recent version of ECCO-Darwin (shown in Figures 4 and 5), scavenging is constrained as a function of particulate organic material (Equation 4). In Equation 4, the scavenging rate (r_{scav}) is defined using three parameters: τ_{scav} converts measured thorium-based scavenging rates into Fe scavenging rates, I_{scav} is the intercept of the scavenging power law, POM is particulate organic material, and e_{scav} is the exponent of the scavenging power law.

Equation 4 $$r_{scav} = \tau_{scav} I_{scav} POM^{e_{scav}}$$

This postulated example illustrates how any proposal to add increasing complexity in representation of dFe speciation or source terms needs to carefully weigh the resulting benefit for model-observation

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mismatches (if any) against the increase in computational resources required. A targeted and computationally efficient approach is likely required to improve the model representation of riverine Fe inputs. A key question, which has not yet been resolved, is whether other river plumes worldwide may be under-estimated as a component of regional offshore dFe budgets. The Congo and Transpolar Drift both result in high off-shelf dFe concentrations due a combination of physical and biogeochemical factors. At a global scale, rivers contribute vast quantities of dFe to the coastal ocean. In many regions, this input may be larger than expected in budgets which assume a universal 90–99% estuarine dFe removal due to much lower removal in some cases (Krachler et al., 2019; Kritzberg et al., 2014; Sanders et al., 2015). However, in global models the effects of most individual rivers on marine dFe distributions and concentrations are limited or negligible because of the spatial scale over which the resulting dFe plume is evident (Fig. 3). As multiple Fe sources drive generally high dFe concentrations in most shelf environments worldwide, models typically produce the best fits to observed dFe data in shelf seas under high-Fe-input, high-Fe-removal scenarios (Somes et al., 2021). A key question is therefore which river plumes worldwide are large enough to possibly perturb dFe concentrations offshore and to justify additional parameters in modelled Fe cycles at the global scale. Other than the Congo and the Transpolar Drift, there are only limited examples of global regions where other large rivers perturb off-shelf salinity (Fig. 6).

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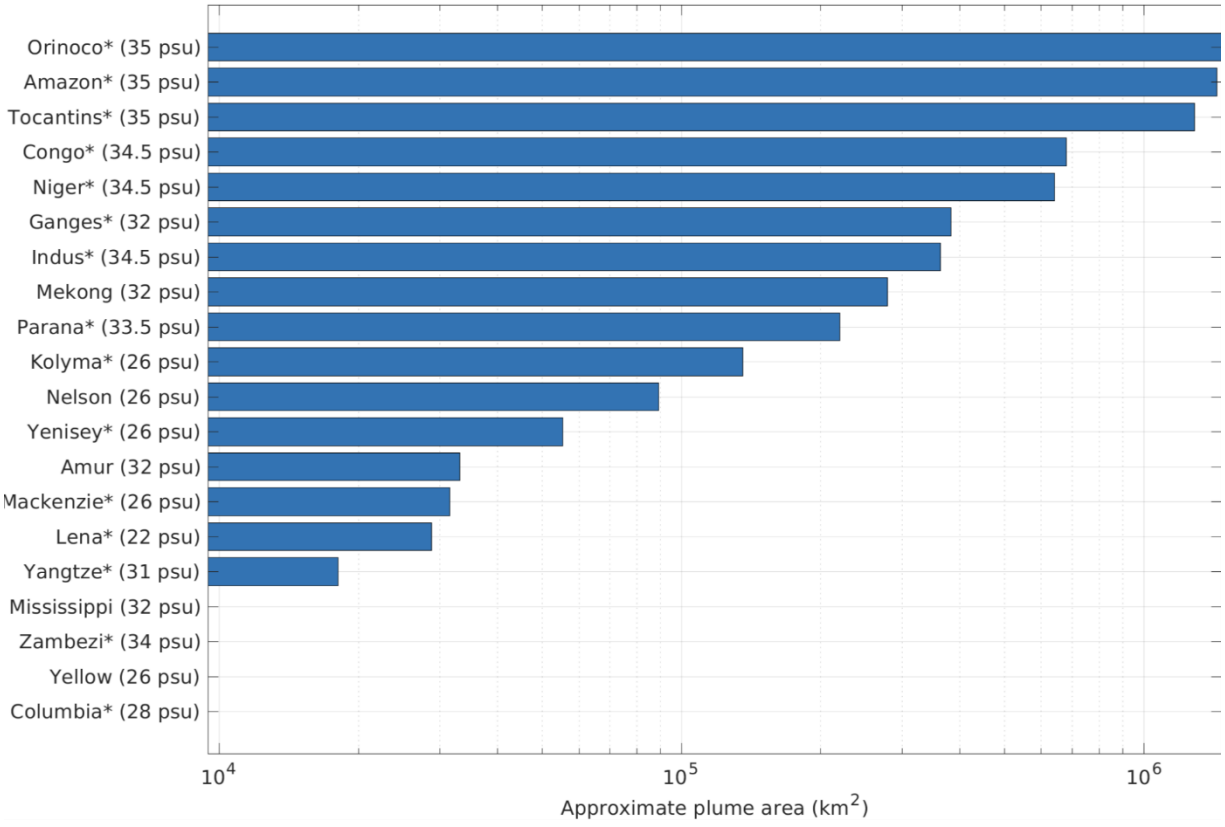

Figure 6. The largest river plumes globally by surface area in ECCO-Darwin. Approximate river-plume area (km²) is computed as the sum of native 1° model grid-cell areas where time-mean surface salinity falls below each river's reported plume-delineation threshold in literature for this specific or closely-related system(s) (Gouveia et al., 2019; Hickey et al., 2009; Hopkins et al., 2013; Jay et al., 2009; Osadchiev, 2017; Savin and Osadchiev, 2025; da Silva and Castelao, 2018; Son and Choi, 2022; Wang et al., 2011; Zeng et al., 2022). The salinity threshold used to delineate each river plume is indicated in parenthesis next to the river name. * Indicates rivers which discharge directly into the open ocean rather than enclosed shelf seas.

In ECCO-Darwin, there are only 10 river plumes globally which extend to surface areas $>10^4$ km^2 and only 16 which extend to areas $>10^4$ km^2. Of these, 4 discharge into the Arctic (the Kolyma, Yenisei, Lena, and Mackenzie), 4 discharge into the Atlantic from South America (the Orinoco, Amazon, Tocantins, and Parana), 2 discharge into the Atlantic from Africa (the Congo and Niger), 2 discharge into the Indian Ocean (the Ganges and Indus), 3 discharge into the enclosed seas of the western Pacific (the Mekong, Amur, and Yangtze), and 1 (the Nelson) drains into Hudson Bay. It should therefore be possible to take a focused approach in global models to more accurately represent Fe in the river plume regions which make the largest spatial contribution to marine dFe concentrations. In models which contain river

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discharge, this could be achieved by increasing the L cap in specific plumes by adding a riverine L and Fe source. Based on available evidence at the time of writing, adding Fe and L sources for 12 rivers which discharge directly into the Atlantic, Arctic and Indian Ocean (Fig. 6) would be the most computationally efficient way of reducing global model-observation dFe mismatches in river plumes. Furthermore, as several of these rivers appear to be under-surveyed with respect to trace metal observations, they could provide interesting case studies for further observations. Whilst plumes from the Amazon, Congo, and rivers feeding the Transpolar Drift have been subject to multiple surveys (Table 2), the biogeochemistry of several of the other largest river plumes worldwide are unconstrained. Notably, the Orinoco, Tocantins, and Niger offshore plumes are all relatively unsurveyed and not within the vicinity of any cross-basin GEOTRACES transects (GEOTRACES Intermediate Data Product Group, 2025).

A proposed framework for future exercises aiming to refine model representations of the marine Fe cycle is therefore to introduce dFe and ligands in 12 large river plumes. For the purposes of modeling, a reasonable assumption is that the dFe concentration in these plumes can be assumed to be Fe bound to organic ligands. Models could either universally add a riverine dFe source with a fixed Fe and L concentration over the 12 cases globally, or add a variable L concentration to approximately match the best available observations of each plume region – though several of these case studies lack offshore observations (Table 2). A more sophisticated, but computationally expensive, approach would be to allow variable ligand affinities i.e., not only varying ligand concentration (L), but also the binding affinities of ligands for Fe. A variable ligand concentration and affinity model with scavenging driven by Fe oxyhydroxide precipitation, rather than via particulate organic material (Equation 4), would more closely match our present understanding of the marine Fe cycle (Gledhill et al., 2026; Tagliabue et al., 2023). However, such an approach would also be computationally expensive and a marked departure from present model Fe cycles.

River	Dissolved Fe endmember (after estuarine removal) nM	Data sources
Amazon	26	(Hollister et al., 2026)
Congo	3900 ± 610 1250	(Vieira et al., 2020) (Figueres et al., 1978)
Yenisey	40—60 19*	(Dai and Martin, 1995) (Charette et al., 2020)
Lena	47	(Guieu et al., 1996)

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	19*	(Charette et al., 2020)
Ganges	790	(Su et al., 2024)

Table 2. A synthesis of dissolved Fe endmembers for case studies in estuaries included within the world's largest 12 river plumes, excluding rivers which drain into enclosed or interior seas. These endmembers are derived after estuarine removal processes and could be represented in models as an organic ligand (L) concentration in order to introduce a representation of rivers within existing frameworks of marine Fe biogeochemistry. *Derived from the Transpolar Drift which integrates river outflow from across the Siberian shelf.

An alternative specific approach would be to leverage the data-assimilative framework of ECCO-Darwin to better represent dFe concentrations in river plumes. The Green's function-based biogeochemical optimization could be used to perturb individual Fe-cycle controls (i.e., scavenging and ligand-complexation rate constants, sedimentary and atmospheric dFe solubility/flux, and the magnitude and estuarine-attenuation factor applied to riverine freshwater and dFe runoff, along with the initial dFe field) (Menemenlis et al., 2005). This suite of Green's functions could then be combined to identify the parameter and forcing combination that best reduces the model-data mismatch. Any similar optimization would need to rely on a relatively high global model resolution and observational datasets along the coast to constrain the model from river mouths to off-shelf ocean regions (Carroll et al., 2020; Savelli et al., 2026).

9.0 Conclusions

Estuarine mixing is a well-established phenomenon which removes Fe from the dissolved phase in estuaries (Boyle et al., 1977). Yet the extent to which dFe is removed within individual estuaries varies widely in space and time from apparent conservative behavior to >99% dFe removal. Variation in the extent of dFe removal likely reflects multiple factors, including the nature and concentration of organic material, estuary residence time, particle load, pH and dissolved oxygen. No single factor appears to explain the varying extent of estuarine dFe removal globally. However, it should be noted that the methods typically used to derive estuarine removal are imprecise and may often under-estimate the dFe removal occurring in estuaries which have multiple dFe sources. Nevertheless, a compilation of global estuarine transects suggest that a majority of estuaries evidence dFe loss averaging 80 ± 18% across the salinity gradient, and a minority of estuaries (9% of 53 case studies) do not evidence dFe removal.

The present generation of ocean biogeochemical models which explicitly include dFe have been designed following the assumption that rivers do not make significant contributions to annual offshore dFe budgets. Whilst this hypothesis is widely applied and has a strong theoretical basis, the Congo and the Transpolar

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Drift have both been extensively verified as major regional dFe sources to the South Atlantic and Arctic Ocean, respectively (Charette et al., 2020; Vieira et al., 2020). The elevated dFe concentrations associated with these river plumes were not predicted by prior models (Tagliabue et al., 2016) and remain absent from more recent model simulations (e.g., ECCO-Darwin, Carroll et al., 2020). The absence of these plumes does not solely arise because riverine input is ignored as an Fe source. Models which explicitly include a riverine dFe input still do not evidence either plume (e.g., PISCES, Aumont et al., 2015). To represent the complexity of dFe speciation in seawater, models typically invoke a fixed ligand concentration which caps dFe concentration to prevent unrealistically high modelled dFe concentrations. However, this cap also prevents lateral inputs of dFe from rivers which are associated with high dissolved organic material, and likely high ligand concentrations (Gerringa et al., 2007; Laglera et al., 2019; Su et al., 2015). Additionally, the coarse model grids of global models are generally unable to resolve river plumes and their associated mixing processes.

Representations of dFe in global biogeochemical models typically have moderately high complexity, reflecting numerous Fe sources and the dynamics of Fe speciation in seawater. Adjustments to better reflect riverine dFe sources must therefore balance the number of additional parameters (and computational cost) required with the resulting benefits for reducing observational-model mismatch (Tagliabue and Voelker, 2011). In the case of small rivers, rivers which discharge into semi-enclosed shelf seas, and rivers where the outflowing plumes are deflected to flow along-shelf, improving the representation of riverine Fe sources will not likely improve dFe model-observation mis-matches at the global scale. This is due to the input and scavenging of dFe occurring on scales which are sub-grid in models, and/or occurring in shelf seas where dFe concentrations can be reasonably approximated as approaching a state of saturation. Yet in cases where river plumes containing elevated (>1 nM) dFe proceed off-shelf, a more explicit representation of river dFe and ligand inputs is required for the associated dFe plumes to appear at all in models. As the number of these cases at a global scale is limited, a tailored regional approach including specific large river plumes (~12 globally) may allow a simpler parameterization than a generic global adjustment. This could be achieved by relaxing caps on dFe and ligand concentrations within these specific plume regions.

Code and data availability

All data sources are cited in the text. No new data is presented.

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Author contributions

MJH and RS drafted the first version of the text. RS visualized the model-observation comparison for ECCO-Darwin. The manuscript was then revised and edited with comments from all authors.

Competing interests

The authors have no potential conflicts of interest to declare.

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