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Progress in Earth and Planetary Science (2022) 9:22
https://doi.org/10.1186/s40645-022-00479-2

Progress in Earth and Planetary Science

RESEARCH ARTICLE Open Access

Refining the contribution of riverine particulate release to the global marine Nd budget

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Abstract

The release of neodymium (Nd) from particles along continental margins may contribute to losses in the global of Nd budget. The Changjiang River, which carries a heavy load of total suspended matter, empties into the East China Sea, and a strong particulate–seawater interaction process occurs along the salinity gradient. In the low-salinity region ($S < 2.0$), strong removal of dissolved rare earth elements (dREEs) occurs, but the Nd isotope values are uniform. At mid- and high-salinity ($S = 2.0$–28.0 and $S > 28.0$) areas, the dREE concentrations increase slightly. An Nd isotope mass balance indicates that the release of particulate matter is a source of dREEs in the Changjiang estuary. The release rate of particulate Nd (Nd_{SPM}) to the dissolved Nd pool in Changjiang estuary is higher than other estuaries, such as Amazon estuary. Composite all river data available from the previous studies indicate that 5800–9200 Mg per year of Nd is released to global marine waters from riverine particles. This estimated quantity is on the same order of magnitude as the calculated global Nd release flux based on the case study in the Amazon estuary. Our study indicates that to better constrain the global Nd budget, it is required to consider the release rate of Nd_{SPM} in different rivers due to the significant difference among various rivers, but with very limited available data as of now.

Keywords: Particulate release, Nd budget, Rare earth elements, Changjiang estuary

1 Introduction

Studies of the behavior of rare earth elements (REEs) and neodymium (Nd) isotopes as well as the sources and sinks of these elements are important for understanding the process of Nd cycle in the oceans. Although rivers are the main source of Nd in the ocean, the transport pathway of REEs requires further research because estuaries modify the elements that rivers input into oceans (Frank 2002; Goldstein and Hemming 2003; van de Flierdt et al. 2004; Lacan and Jeandel 2005; Tepe and Bau 2015; Merschel et al. 2017a, b). In the early stage, the magnitudes of both the flux of Nd from riverine and aeolian leads to a calculated Nd residence time in the ocean on the order of ~ 5000 yr (Bertram and Elderfield 1993). However, the Nd isotope provides strong evidence that the residence time of Nd is shorter than the global turnover time of the ocean (1000–1500 yr; Broecker and Peng 1982). This discrepancy in the Nd mass balance (which some researchers have termed the "Nd paradox") indicates there is a missing source of Nd in the ocean (Bertram and Elderfield 1993; Jeandel et al. 1995; Goldstein and Hemming 2003; van de Flierdt et al. 2004).

The search for the origin source of the missing Nd has attracted the attention of many researchers who have proposed a number of explanations. In 2007, Johannesson and Burdige tried to balance Nd budget in the ocean emphasizing the importance of the role of submarine groundwater discharge (SGD). Kim and Kim (2014) demonstrated that the REE fluxes through SGD were two to three orders of magnitude higher than diffusion from bottom sediments and atmospheric dust

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fallout in the subsequent study. In addition, pore fluid was also considered to be one of the sources of neodymium in the ocean (Abbott et al. 2015). Later, a subsequent landmark study by Rousseau et al. (2015) showed that the particulate fraction makes up the missing term in the Nd budget of global marine seawater. Although Nd release from particulates has been shown to be a significant source of dissolved marine Nd, the Nd release rate from suspended particulate matter (SPM) varies among different river estuaries. For example, the fraction of Nd released from SPM by partial dissolution (Nd_{SPM}, given in [%]) in the Amazon estuary is 0.94 ± 0.25% (Rousseau et al. 2015), but no Nd release from particulate phases has been found in the Lena River (Laukert et al. 2017). Significant differences among various rivers may be related to the pH and the concentrations of SPM and dissolved organic carbon (DOC) of the water (Pearce et al. 2013; Merschel et al. 2017b; Laukert et al. 2017; Paffrath et al. 2021). Experimental results have shown that the rate of Nd release from particulates is positively correlated with the surface area of the reacting sediments and ranges from 0.04 to 0.38% (Pearce et al. 2013). Thus, studying the Nd_{SPM} for different estuaries is important for improving our understanding of the marine Nd budget.

Estuaries are regions with active particulate–seawater interactions. Almost all trace metals exhibit nonconservative behavior due to the destabilization of mixed colloids during mixing with sea water in estuaries (Eckert and Sholkovitz 1976; Hoyle et al. 1984; Rousseau et al. 2015). It has been suggested that in most rivers, Nd is efficiently removed from seawater in low-salinity areas (e.g., > 70% in the Gironde estuary, 88% in the Great Whale estuary, 90% in the Amazon estuary, and 79% in the Changjiang estuary; see Rousseau et al. 2015 Table 1; Wang and Liu 2008) and the Nd concentration rebounds in mid- and high-salinity areas. These phenomena can be explained by the coagulation process of riverine colloid matter in low-salinity areas and the release of Nd from suspended materials in mid- and high-salinity areas (Li et al. 2005; Wang and Liu 2008; Rousseau et al. 2015).

The Changjiang River is the third largest river in the world, with a water discharge of 940 $km^3\ yr^{-1}$ and high concentrations of total suspended matter (Wong et al. 1998; Chen et al. 2002; Zhang 2002; Li et al. 2007; Meybeck and Ragu 2012), that strongly influences local biogeochemical cycling. The Changjiang River is the largest river discharging into the East China Sea (ECS), contributing approximately 60% of water in the eastern ECS and affecting the Tsushima Strait during the flooding season (Lee et al. 2014; Che and Zhang 2018). A previous study by Wang and Liu (2008) showed that in the 0–6.0 salinity range, > 70% of dREEs were removed from solution due to salt-induced coagulation of river colloids. The dREE concentrations increased again in the 8.0–19.0 salinity range, which was attributed to release from particulate matter. A vigorous release process in the estuarine mixing area could cause the Changjiang River to significantly impact on the biogeochemistry of adjacent seas, such as the ECS, the Sea of Japan, and even as far as the northwest Pacific Ocean. In this study, we quantify the flux of dissolved Nd_{SPM} in the Changjiang estuary instead of addressing the detailed driving mechanisms of particulates. The findings of this study enable us to explain the significance of particle–seawater interaction and more accurately assess the contribution of marginal seas to the marine Nd balance.

2 Materials and methods

2.1 Study area and sampling

Surface freshwater and seawater samples from the Changjiang (Datong) and estuary were collected during the high discharge season in August 2015 (included datasets from seven published Nd isotopic as reported by Che and Zhang 2018) (Fig. 1). Upon collection, water was filtered through a 0.40-μm Whatman membrane (Nuclepore Polycarbonate, 111707-Whatman) and acidified to a pH of ~ 2 with high-purity HCl (30%, Merck Suprapur). A volume of 15–20 L of each sample was placed in an acid-cleaned bottle for Nd isotope composition analysis, and 500 mL of each sample was used to determine the REE concentration. The filter membranes were cryopreserved to determine the SPM. The REE concentrations and Nd isotope compositions determined for the filtered water samples were considered to be dissolved-phase measurements ($Nd_{<0.45\ \mu m}$). An unfiltered water sample was directly acidified to a pH < 2 with hydrochloric acid directly after sample collection and then filtered through a 0.40-μm Whatman membrane in a cleanroom to determine the acid-soluble REE concentrations ($Nd_{>0.45\ \mu m}$). The above-mentioned processes were also carried out

Table 1 Average Nd concentration in the groundwater of different areas

Area	Average concentration (pmol kg^{-1})	References
Bangdu Bay Jeju Island	2899	Kim and Kim (2011)
Hwasun Bay Jeju Island	2448	Kim and Kim (2011)
Pearl River estuary	2573	Yuan et al. (2013)
Changjiang estuary	3606 ± 690	Data estimated in this study
Jiangyin (well water)	1054 ± 485	This study

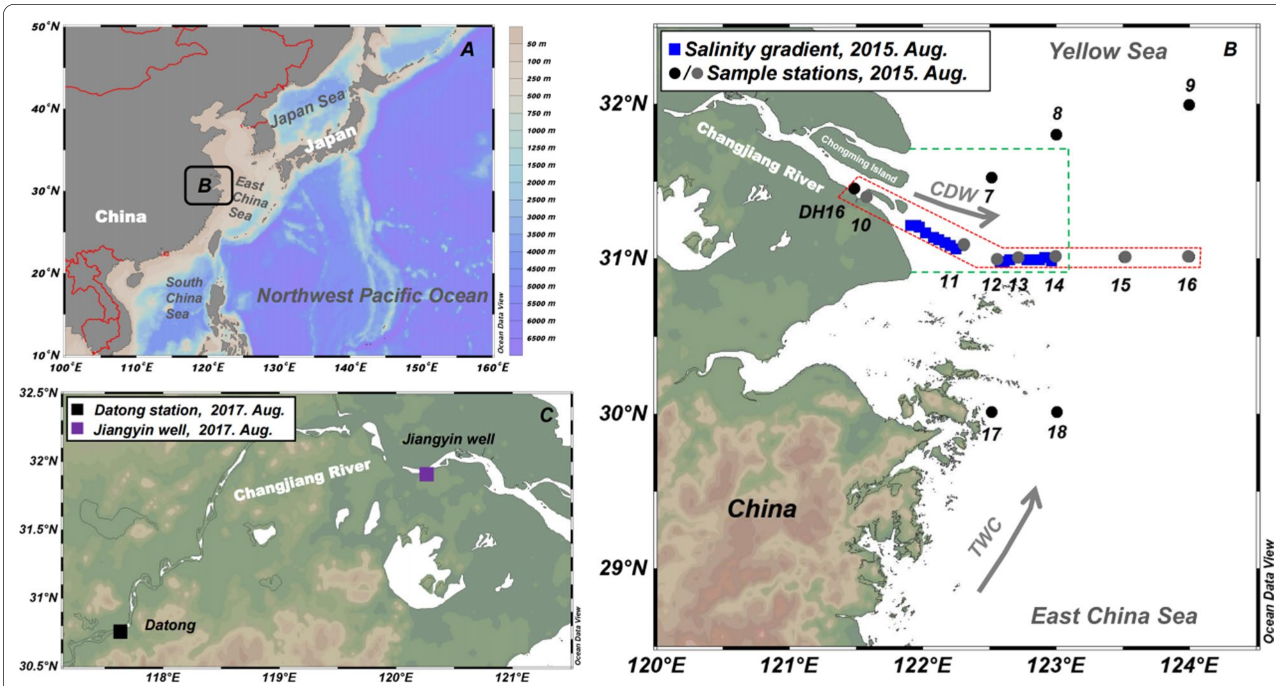

Fig. 1 Sampling map (**A**) and stations in the Changjiang River (black square in Fig. **C**), Jiangyin well (purple square in Fig. **C**), the Changjiang estuary (Fig. **B**; black circles; gray circles refer Nd isotopic published stations as reported by Che and Zhang 2018), the salinity gradient (Fig. **B**; blue squares); CDW and TWC indicate Changjiang diluted water and Taiwan warm current, respectively. Green dotted line in the map B shows the study area for calculation of the Nd budget (approx. 8455 km^2). Red dotted line (Fig. **B**) is the main area where Nd_{SPM} in the Changjiang River mixing zone was explored

using rainwater (between stations 13 and 17) and groundwater samples (Jiangyin well water) (120.262°E, 31.938°N), where all samples were collected in August 2017.

The analytical procedures for the measurement of the REE concentrations and Nd isotopic compositions in this paper are from the works of Persson et al. (2011), Hatje et al. (2014), Che et al. (2018), and Liu et al. (2022). The data on dissolved REE concentrations were measured by ICP-MS (Thermo iCAP-Q) with a precision of better than 4% and a reagent blank of less than 2%, based on the results of replicated measurements. Nd isotope measurements were made on Nu plasma I and II instruments at the Key Laboratory of Environmental Geochemistry. Corrections were made for instrumental mass bias using a value of $^{143}Nd/^{144}Nd = 0.7219$. The Nd isotopic compositions can be expressed by $\varepsilon_{Nd} = (^{143}Nd/^{144}Nd_{measured}/^{143}Nd/^{144}Nd_{CHUR} - 1) \times 10{,}000$, where CHUR represents the Chondritic Uniform Reservoir, with a value of 0.512638 (Jacobsen and Wasserburg 1980), and $^{143}Nd/^{144}Nd$ measured represents the measured value.

2.2 Calculation

2.2.1 Mass balance on water and salinity

The hydrography in the study area is largely controlled by the Changjiang River discharge, exchanges with the ECS and Yellow Sea (YS), and the open ocean current (including the Taiwan Warm Current (TWC) and Kuroshio Water (KW)). Given that the deepwater of the TWC mainly comprises the subsurface water of the Kuroshio Current (Chao 1990; Yang et al. 2011), we assumed that the water in the study area was directly governed by the Changjiang River and KW in August. Riverine inputs, precipitation, groundwater, evaporation, and exchanges between the studied area and other waters were accounted for in the water budget. The water budget was calculated for the continental shelf using the Land–Ocean Interactions in the Coastal Zone (LOICZ) approach (Swaney et al. 2011) as follows:

$$\left(V_Q + V_P + V_G + V_X + V_O\right) + (V_E + V_R - V_X) = 0 \quad (1)$$

$$\left(S_Q V_Q + S_P V_P + S_G V_G + S_O V_O + S_{ECS} V_X\right) + \left(S_E V_E + S_R V_R - S_{CJE} V_X\right) = 0 \quad (2)$$

where V is the water volume (km^3 d^{-1}), S is the salinity, and the subscripts indicate the riverine input (Q), atmospheric deposition (P), groundwater input (G), exchanges between the study area and open sea (X), other flow volume (O), evaporation (E), and residual flow volume (R). S_{CJE} and S_{ECS} are the salinities in the Changjiang estuary area and outer seas, respectively. As the salinity in the river, rainwater, and other terrestrial waters was generally zero, the water exchange between the study area and the outer seas was calculated using the following formula:

$$V_X = S_R V_R / (S_{CJE} - S_{ECS}) \tag{3}$$

where V_X is the water volume exchange between the study area and the open sea, S_R is the mean salinity of 22.4 in the study area, and V_R is the residual flow volume. S_{CJE} and S_{ECS} were 0.1 and 30.1, respectively, in August 2015.

2.2.2 Quantitative estimates of the Nd budget

A mass balance was performed on the Changjiang estuary to explore the effects of Nd processes in the river estuary. The Nd inputs into the Changjiang estuary include river inputs (F_Q), groundwater input (F_G), atmospheric inputs (F_P), ECS inflow ($F_{R\ ECS}$), and Y_S inflow ($F_{R\ YS}$). The Nd outputs include evaporation (F_E), the outflow to the ECS ($F_{X\ ECS}$), and the residual outflow to the YS ($F_{X\ YS}$).

The dissolved Nd flux for the different processes F_{Nd} was calculated based on the measurement data for the samples:

$$F_{Nd} = V \times c \tag{4}$$

where V represents the volume of the river, atmospheric input, and water exchange with groundwater and water output discharge and c is the dissolved Nd concentration.

2.2.3 Nd isotope mass balance

First, Formulas 5 and 6 were used to calculate the mixing proportion of different water masses considering the salinity:

$$f_{ECS\ vol} = (S_M - S_{CJ})/(S_{ECS} - S_{CJ}); \tag{5}$$

$$f_{CJ\ vol} = 1 - f_{ECS\ vol}; \tag{6}$$

Next, we calculated the theoretically conserved Nd concentration in the ECS using Formulas 7 and 8:

$$[Nd]_{T\text{-}theor} = f_{ECS\ vol} \times [Nd]_{ECS} + (1 - f_{ECS\ vol}) \times [Nd]_{CJ}; \tag{7}$$

$$[Nd]_{ECS\text{-}theor} = f_{ECS\ vol} \times [Nd]_{ECS}; \tag{8}$$

Finally, a quantitative mass balance was formulated based on the Nd fractions from different sources (Formulas: 9–11):

$$f_{Nd\ ECS} = [Nd]_{ECS\text{-}theor}/[Nd]_M; \tag{9}$$

$$f_{Nd\ CJ} = [\varepsilon_{Nd\ M} - \varepsilon_{Nd\ SPM} - f_{Nd\ ECS}(\varepsilon_{Nd\ ECS} - \varepsilon_{Nd\ SPM})] / (\varepsilon_{Nd\ CJ} - \varepsilon_{Nd\ SPM}); \tag{10}$$

$$f_{Nd\ SPM} = 1 - f_{Nd\ ECS} - f_{Nd\ CJ}. \tag{11}$$

where $f_{CJ\ vol}$ and $f_{ECS\ vol}$ denote the calculated salinity fraction for each endmember; $[Nd]_{ECS\text{-}theor}$ and $[Nd]_{T\text{-}theor}$ are the theoretical conservations of the Nd concentration; $f_{Nd\ ECS}$, $f_{Nd\ CJ}$, and $f_{Nd\ SPM}$ are the Nd fractions in the ECS, the Changjiang River, and the SPM, respectively; and $[Nd]_{ECS}$, $[Nd]_{CJ}$, S_{ECS}, S_{CJ}, $\varepsilon_{Nd\ ECS}$, $\varepsilon_{Nd\ SPM}$, and $\varepsilon_{Nd\ CJ}$ are the endmembers of the Nd concentration, salinity, and Nd isotopic composition in the ECS, Changjiang River, and SPM, respectively; and $[Nd]_M$, S_M, and $\varepsilon_{Nd\ M}$ are the measured values of the Nd concentration, salinity, and Nd isotopic composition measured at the sampling stations, respectively.

3 Results and discussion

3.1 Significance of estuaries as modulators of REEs in seawater

Numerous works of estuarine research studies suggest that the coagulation process of riverine colloid matter in low-salinity areas and the release of suspended materials in mid- and high-salinity areas are the main factors affecting the REE fractionation in the estuaries (Elderfield et al. 1990; Pearce et al. 2013; Rousseau et al. 2015). A similar phenomenon was discovered in the Changjiang River along the salinity gradient, where all of the REE distributions show strong nonconservative behavior. The concentrations of dREEs (Nd, samarium (Sm), and ytterbium (Yb) are representative LREEs, MREEs, and HREEs, respectively) decreased rapidly in the low-salinity area ($S < 2.0$) and increased slightly in the mid-salinity area ($S = 2.0$–28.0), despite appreciable scattering (Fig. 2). In the low-salinity area ($S < 2.0$) of the Changjiang estuary, the $[Nd/Yb]_N$ decreased rapidly and more than 89 ± 5% of dissolved LREE (Nd) was removed, such that the Nd concentration decreased from 295.7 pmol kg^{-1} to a minimum of 30.2 pmol kg^{-1} (Fig. 2A, C). Approximately 85% of the dissolved MREEs and 60% of the dissolved HREEs were removed in this region (Fig. 2B). The percentage removal of dissolved REEs shows a large decrease in the concentrations of a range of REEs, from LREEs to HREEs. However, in the area of the Changjiang estuary where the salinity ranges from 2.0 to 28.0, there was a noticeable increase in the concentration of dissolved REEs, of 140% for HREEs and 240% for LREEs and MREEs. The slight increase in $[Nd/Yb]_N$ corresponded to preferential release from LREEs to the dREE pool.

The endmember of the dissolved phase ε_{Nd} for the Changjiang freshwater was determined at the Datong station, which is approximately 500 km from the area in the

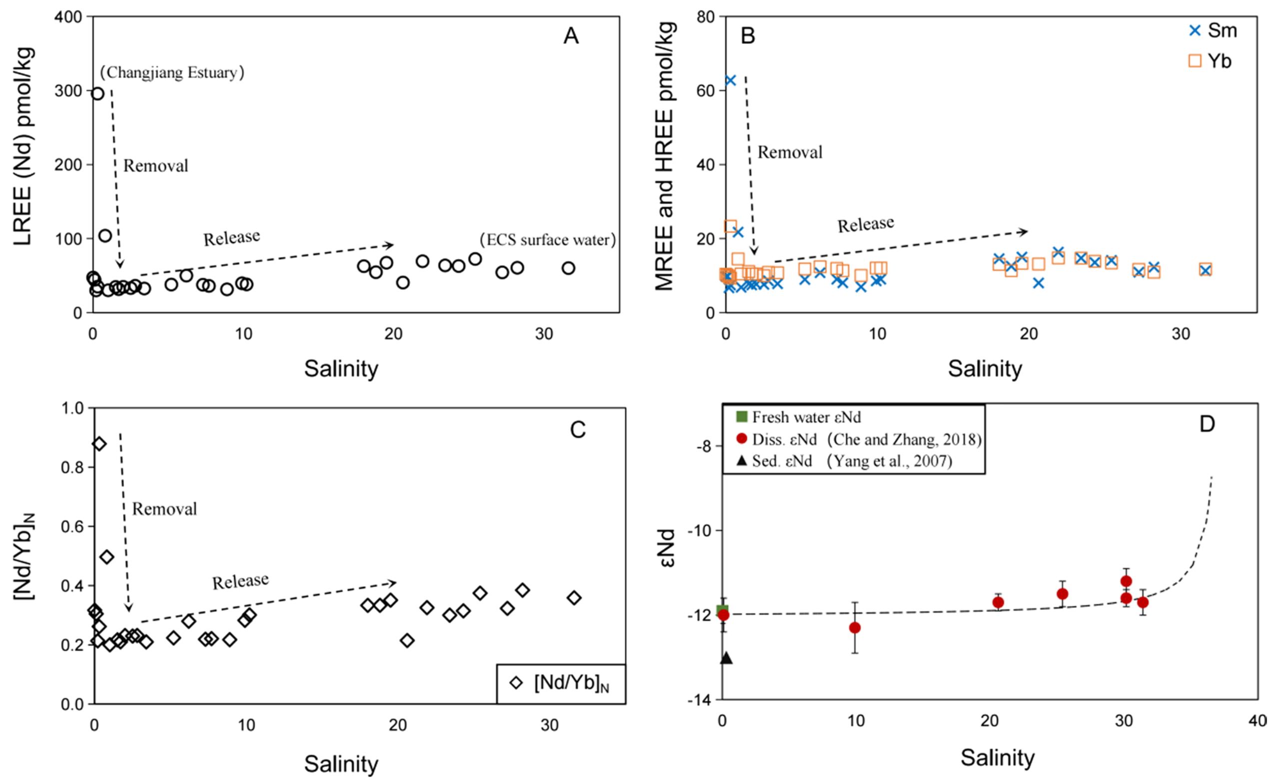

Fig. 2 Distribution of dissolved Nd (**A**), Sm and Yb (**B**) in surface water along the Changjiang estuary salinity area. **C** and **D** represent the relationship between $[Nd/Yb]_N$, or Nd isotopic and salinity, respectively. The black-dashed line in the **D** is the conservative theoretical dissolved Nd mixing curve

estuary with zero salinity; the sampling results for the channel of the Changjiang River in August 2017 showed that $\varepsilon_{Nd} = -11.9 \pm 0.3$ and $S = 0.0$. No difference in the ε_{Nd} signatures between the freshwater and the estuary water ($S = 0.1$, $\varepsilon_{Nd} = -12.0 \pm 0.3$) was observed at the mouth of the estuary (Che and Zhang 2018), indicating that an essentially uniform ε_{Nd} distribution was maintained (Fig. 2D). For regions where the salinity increased to 28, the Nd isotopes and dREE served as conservative tracers of the mixing of water masses (Che and Zhang 2018).

3.2 Importance of the effect of particle–seawater interactions on the dREE compositions in the mid-salinity regions

3.2.1 Neodymium budget for the Changjiang River Estuary

Considering the results of previous studies and the above-mentioned findings, a mass balance on the water and salinity was performed to calculate the dissolved Nd balance in the Changjiang estuary. The details of the calculation are presented below.

3.2.1.1 Changjiang River fluxes By taking the contribution of Nd = 182.4 pmol kg^{-1} at the Changjiang River mouth and an annual river discharge of approximately 913.9 km^3 yr^{-1} (Ministry of Water Resources of the People's Republic of China, http://www.mwr.gov.cn/), we obtained a Changjiang River fluxes of 24.0 Mg yr^{-1} for Nd. This value should be regarded as mean annual flux because of the Nd content including the winter data (Wang and Liu 2008) in November 1998 and summer data in this study. According to the above-mentioned analytical results, the total transport of effectively dissolved Nd from the Changjiang River was 2.6 ± 0.2 Mg yr^{-1}, for an Nd removal rate in the river estuary of approximately 89%.

3.2.1.2 Groundwater fluxes Since its discovery, groundwater has been regarded as an important source in the REE balance in seawater (e.g., Johannesson and Burdige 2007). Several investigators have pointed out that the Nd concentration of the groundwater is approximately 100 times that of the surrounding seawater (Kim and Kim 2011; Yuan et al. 2013). Few Nd data have been reported in the groundwater of the Changjiang estuary; however, groundwater can be inferred to play a significant role in the Changjiang estuary from the Jiangyin well water data (1054 ± 485 pmol kg^{-1}; $n = 2$)

and previous published data (3606 ± 690 pmol kg^{-1}) (Table 1). In this study, we used an annual average water flow of 72 $km^3\ yr^{-1}$ and an Nd concentration of 1054–3606 pmol kg^{-1} in groundwater to roughly estimate the total annual input flux of groundwater to the estuary as (11.0–37.4) ± 6.0 Mg yr^{-1} (Gu et al. 2012). This estimated Nd content in groundwater is also within the concentration range summarized by Johannesson and Burdige (2007). Based on the observations, 89% of Nd was removed during estuary mixing, from which we estimated that the effective groundwater flux of dissolved Nd to the study area was (1.2–4.1) ± 0.7 Mg yr^{-1}. Notably, however, the groundwater fluxes have a large part recirculated seawater and a small part fresh groundwater (Gu et al. 2012). The actual Nd contribution from fresh groundwater to the Changjiang estuary should be lower than the estimate given above. We will explore the large uncertainty introduced by the diverse range of the Nd contents in a future work, especially for the contribution of SGD on the ocean dissolved Nd budget.

3.2.1.3 Atmospheric fluxes By taking the average Nd concentrations in filtered rainwater in the spring (Nd = 199.9 pmol kg^{-1} (unpublished data)) and summer (Nd = 24.3–33.3 pmol kg^{-1}) (Zhang and Liu 2004) (avg. Nd = 86.0 ± 98.5 pmol kg^{-1}), an average annual precipitation of 1600 mm (based on the rainfall in Shanghai), and an oceanic area of 8455 km^2, we obtain an atmospheric wet deposition flux of 0.17 ± 0.19 Mg yr^{-1} Nd. However, the effects of anthropogenic activities and dust storms on river estuary areas also influence the Nd concentration in the surface seawater. In addition, there is a large amount of uncertainty in the atmospheric dry deposition input estimate, because only data for the spring have been reported, and no seasonal variation data have been published. The estimated contribution of atmospheric dry deposition to marine dissolved Nd was 0.05 ± 0.02 Mg yr^{-1} [Nd = 135.9 ± 49.9 pmol kg^{-1}; $n = 6$; sedimentation rate = 1 cm s^{-1} (Duce et al. 1991; Kadko et al. 2020)]. Ultimately, the total annual input (including wet and dry deposition) to the study area was approximately 0.22 ± 0.19 Mg yr^{-1}, indicating a nonsignificant contribution from atmospheric deposition to the Changjiang estuary.

3.2.1.4 Transport fluxes The LOICZ model was employed to estimate the transport flux of dissolved Nd from the Changjiang estuary to the ECS and the YS during the survey year (Table 2). By taking the mass balance of the water and salinity model, the average salinity in the study area ($S = 22.4$) and the salinity of the ECS and Changjiang estuary endmembers (30.1 and 0.1, respectively) were used to estimate the water volume exchange between the Changjiang estuary and ECS ($V_{X\ ECS}$) and YS ($V_{X\ YS}$) and the residual flow volumes ($V_{R\ ECS}$ and $V_{R\ YS}$). The outputs of dissolved Nd from the Changjiang estuary to the ECS were found to be five times higher than those from the YS.

Overall, the results indicate that the total transport of effectively dissolved Nd in the Changjiang estuary area was 4.1–7.0 ± 0.9 Mg yr^{-1}, of which 2.6 ± 0.2 Mg yr^{-1} was from rivers, 1.2–4.1 ± 0.7 Mg yr^{-1} was from groundwater, and 0.22 ± 0.19 Mg yr^{-1} was from the atmosphere (including wet and dry deposition) (Tables 1, 2). Here, we have neglected the effect of atmospheric dry deposition on marine dissolved Nd because the dry deposition flux was less than 2% of the total dissolved Nd flux (0.05 ± 0.02 Mg yr^{-1}, $n = 5$; deposition rate = 1 cm s^{-1}), although dust is one type

Table 2 Estimates of dissolved Nd fluxes for rivers, atmosphere, and groundwater and water exchange between the ECS and YS

Processes	Area	Annual average		
		Water discharge ($km^3\ yr^{-1}$)	Nd (pmol kg^{-1})	Flux (Mg yr^{-1})
River input (F_Q)	Changjiang River	913.9[a]	182.4	24.0
Atmospheric input (F_P)		0.12[b]	86.0/135.9	0.3
Groundwater input (F_G)		72[c]	1054–3606	(11.0–40.3) ± 5.0
Water exchange (F_X)[e]	ECS ($F_{X\ ECS}$)	517.2	57.6[d]	4.3
	YS ($F_{X\ YS}$)	97.9	64.5	0.9
Water output (F_R)[e]	ECS ($F_{R\ ECS}$)	729.6	57.6[d]	6.1
	YS ($F_{R\ YS}$)	138.0	64.5	1.3

[a] Ministry of Water Resources of the People's Republic of China (2015)

[b] Li et al. (2011)

[c] Gu et al. (2012). The exchange rates between the study area and the YS ($F_{X\ YS}$) and the ECS ($F_{X\ ECS}$) are based on data reported by Liu et al. (2003)

[d] The concentration is 57.6 pmol kg^{-1} in the south YS and 64.5 pmol kg^{-1} in the ECS (Che and Zhang 2018)

[e] The loading of the residual outflows and exchange outflows to the YS (26%, 10%, 5%, Ave. = 14%) and ECS (74%) was estimated from the corresponding water discharges (Liu et al. 2003)

of particulate matter. However, the flux of dissolved Nd in the estuary (2.8–5.7 Mg) was clearly lower than the total flux input to the ECS and YS (9.8 ± 0.9 Mg yr^{-1}), which implies that the additional sources of dissolved Nd should exist in the observation area (Fig. 3).

3.2.2 Fraction of Nd released from suspended particulate matter

In addition, an Nd isotope mass balance was performed to quantify the additional flux of dissolved Nd in the Changjiang estuary. The three main sources of dissolved Nd were the Changjiang River ($\varepsilon_{Nd\ CJ}$), the mixing shelf water of the ECS ($\varepsilon_{Nd\ MSW}$), and the particulate matter ($\varepsilon_{Nd\ SPM}$), with corresponding isotope values of − 11.9, − 11.3 (Che and Zhang 2018), and − 13 (Yang et al. 2007), respectively; here, as few data have been reported for ε_{Nd} of particulate matter, we used ε_{Nd} of the sediment instead. The endmembers of the Nd concentrations for the Changjiang River and the mixing shelf water were $[Nd]_{CJ}$ = 295.7 pmol kg^{-1} and $[Nd]_{MSW}$ = 28.9 pmol kg^{-1}, respectively. The specific calculation method is detailed in "Nd isotope mass balance" section.

We estimated that approximately 1.3 ± 0.3% of Nd_{SPM} was released to the dissolved Nd pool in the estuary based on the above-mentioned calculations (28.4 pmol kg^{-1} of Nd released from particles to the dissolved pool at zero salinity, and a particulate $Nd_{>0.45\ \mu m}$ concentration of 2247 pmol kg^{-1}). Our result is higher than those reported for other estuaries (Pearce et al. 2013; Rousseau et al. 2015; Laukert et al. 2017), which is probably because particulate–seawater interactions are stronger in the Changjiang River (Wang and Liu 2008). In addition, a relatively high SPM (500–1000 mg L^{-1}) could enhance the release rate in the Changjiang River, because the proportion of fine particulates in the river sediment flux impacts the release rate of Nd from the particulate phase (Pearce et al. 2013). By contrast, no REEs were released from the particulate phases in the Lena River because of the low amounts of SPM (33 mg L^{-1}) (Laukert et al. 2017).

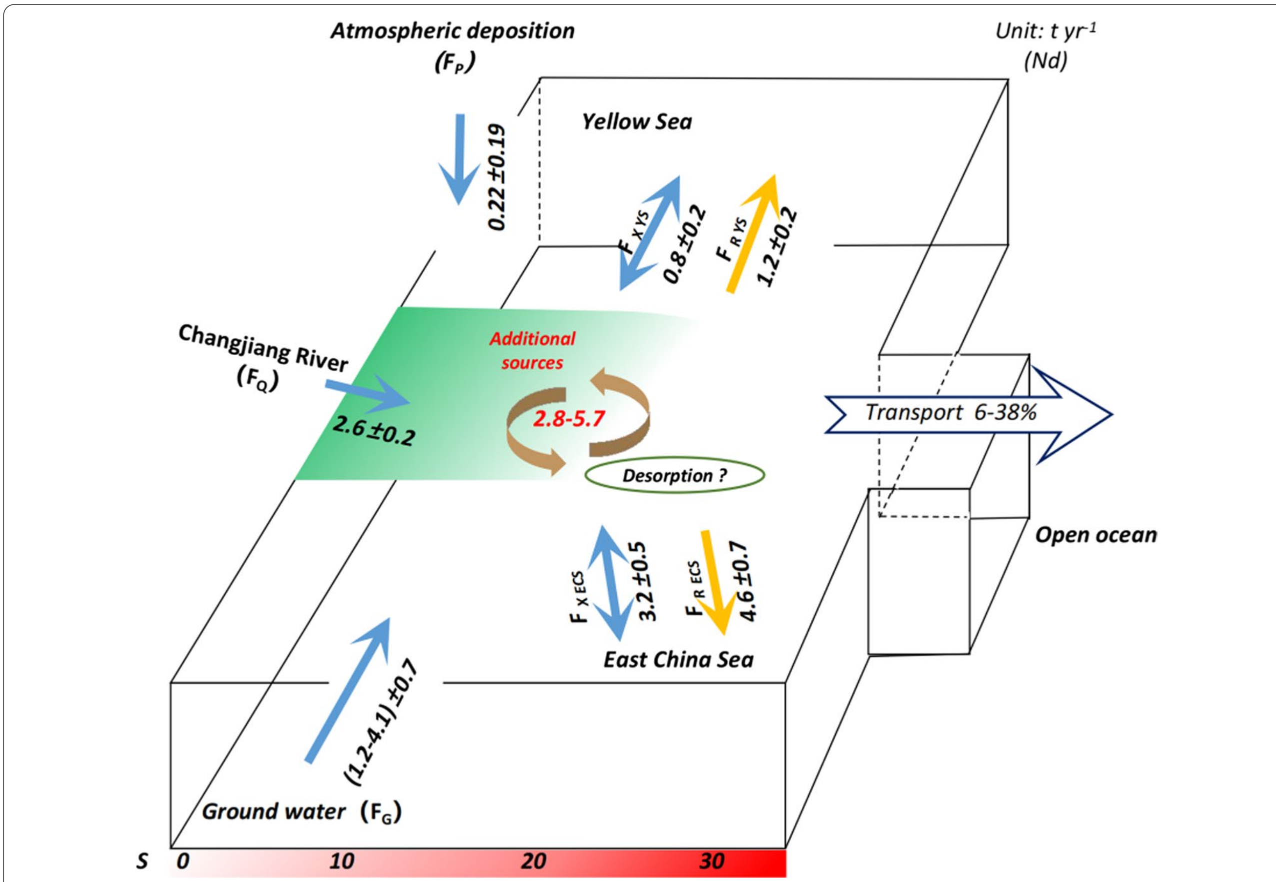

Fig. 3 Flux of effectively dissolved Nd in the Changjiang estuary (unit: t yr^{-1}). Numbers represent Nd concentration fluxes. F_Q: river inputs; F_G: groundwater discharge; F_P: atmospheric wet deposition; $F_{X\ YS}$: exchange flow between the Yellow Sea and the Changjiang estuary; $F_{X\ ECS}$: exchange flow between the East China Sea and the Changjiang estuary; $F_{R\ YS}$: residual outflow to the Yellow Sea; $F_{R\ ECS}$: residual outflow to the East China Sea. Red-stripe area represents the salinity gradient

The Changjiang River Nd_{SPM} flux to the ECS was estimated based on the detailed Nd observations in this study. Using an Nd concentration of 35.6 mg kg^{-1} for the Changjiang sediment and a total river suspended flux of 4.8×10^8 Mg yr^{-1} (Meybeck and Ragu 2012) yielded an Nd_{SPM} flux of 17,000 Mg yr^{-1}. We calculated that about 1.3% of the 17,000 t yr^{-1} Nd_{SPM} flux (220 Mg yr^{-1}) was released from the SPM to the dissolved Nd pool in the Changjiang estuary. However, the flux of dissolved Nd from the Changjiang River to the ECS is approximately 4.8 ± 0.7 Mg yr^{-1}, because approximately $80 \pm 3\%$ of river suspended and $89 \pm 5\%$ of the dissolved Nd flux was removed in the low-salinity area of the estuary. These results indicate that Nd release from lithogenic sediments is an important additional contributor to REEs in the dissolved budget of the ocean.

If the dissolved Nd concentrations and Nd removal were constant throughout the year, these results would roughly account for the imbalance in the Nd budget imbalance in the Changjiang estuary. It is difficult to consider the effects of Nd concentrations and the Nd isotope compositions determined in this study. The maximum contribution of the Nd concentration and Nd isotope composition to the Nd_{SPM} release rate were approximately $\pm 0.1\%$ and $\pm 0.7\%$, assuming variations in the Nd concentration and Nd isotope composition to be $\pm 10\%$ and ± 0.3, respectively. Seasonal variations in the release of Nd from particles in the Changjiang estuary will be considered in a future study.

3.3 Quantitative estimates of the Nd flux in Chinese marginal seas and global ocean

Finally, the Nd budget of China's marginal seas was roughly assessed based on our observations of Nd_{SPM} release. The total river sediment flux for nine Chinese rivers is approximately 1.8×10^9 Mg yr^{-1} (Meybeck and Ragu 2012). Thus, we estimate that approximately 770 Mg yr^{-1} of Nd was released from Chinese river sediments to coastal marine waters. (The mean river $Nd_{sediment}$ concentration is 33 ± 12 mg kg^{-1} (Kim and Kim 2014) and the Nd_{SPM} release of the rivers is $1.3 \pm 0.3\%$.) According to previous studies, approximately 6–38% of Nd is transported to adjacent ocean basins such as the Sea of Japan and the North Pacific Ocean via the ocean circulation (Che and Zhang 2018). We calculated that approximately 46–290 Mg of Nd is transported annually through the northern South sea (Table 3), the ECS, and the YS to adjacent seas, which is in agreement with a previous report (295 ± 240 Mg yr^{-1}) (Lacan and Jeandel 2005).

We categorized the world's rivers into three groups according to the SPM: SPM < 40 mg L^{-1}, 40 < SPM < 500 mg L^{-1}, and SPM > 500 mg L^{-1} (Meybeck and Ragu 2012), and recalculated the global marine Nd budget by incorporating the data obtained for the Amazon estuary ($0.94 \pm 0.25\%$), the Lena River (none), and the Changjiang estuary ($1.3 \pm 0.3\%$). The final estimated results showed that approximately 5800–9200 Mg yr^{-1} of Nd is released in marginal seas, which is closer to the global missing Nd flux of 5500–11,000 Mg per year than a previous estimate (Rousseau et al. 2015). Considering the global riverine sediment flux to the oceans is $1.85 \pm 0.16 \times 10^{16}$ g yr^{-1}, the rivers with an SPM concentration greater than 500 mg L^{-1} account for 83% of the total sediment flux and the rivers with an SPM concentration between 40 and 500 mg L^{-1} account for 16.8%. The range of the total flux is calculated using the range of the error in the release rate. And the final estimated results show that approximately 7500 ± 1700 t yr^{-1} of Nd is released in marginal seas (Table 3). In this study, a synthesis of river data for the northwest Pacific Ocean, the South and North Atlantic Oceans, and the Arctic Ocean demonstrated that particulate release is significant for balancing the dissolved marine Nd budget. To confirm the contribution of the particulate release from the margins to the ocean, it is necessary to obtain more Nd_{SPM} release data from various estuaries with different geochemical properties, such as the composition and particulate surface area. In addition, submarine groundwater discharge

Table 3 Nd_{SPM} release rate in different estuaries and dissolved Nd_{SPM} flux to the ocean

Contact area	SPM discharge Mg yr^{-1}	Nd_{SPM} release rate %	Nd sediment concentration mg kg^{-1}	Water masses mixing	Nd flux Mg
Chinese rivers	1.8×10^{9} [a]	1.3 ± 0.3	33 ± 12 [c]	6–38% [d]	46–290
World river					
$1.85 \pm 0.16 \times 10^{16}$ [a]	1.53×10^{16}	1.3 ± 0.3	33 ± 12 [c]		5800–9200
	0.31×10^{16}	0.94 ± 0.25 [b]			

[a] Meybeck and Ragu (2012)

[b] Rousseau et al. (2015)

[c] Kim and Kim (2014)

[d] Che and Zhang (2018)

and sediment pore water may be a potential source of dissolved Nd, but these contributions require further study.

4 Conclusions

Considerable dREE removal and uniform Nd isotope signatures were observed in low-salinity regions of the Changjiang estuary. In the mid-salinity region of the estuary, an Nd mass balance yielded an estimated Nd release rate higher than the available published data. Our results indicate that the flux of Nd release from riverine particulates to the seawater pool (5800–9200 Mg per year) close to the global missing Nd flux of 5500–11,000 Mg per year is also on the same order of magnitude as that reported by Rousseau et al (2015). This study provides direct evidence for exploring the Nd cycle process in the estuaries, and the result suggests that the release of dissolved Nd from riverine particles should be considered a "missing source" constraint on the Nd mass balance in ocean waters. Moreover, particulate–seawater interactions appear to be an important geochemical control and should thus be considered in coastal environments when assessing the cycle of trace elements.

Abbreviations

SPM: Suspended particulate matter; DOC: Dissolved organic carbon; ECS: East China Sea; REE: Rare earth element; CDW: Changjiang diluted water; TWC: Taiwan warm current; KW: Kuroshio water; LOICZ: Land–ocean interactions in the coastal zone; LREE: Light rare earth element; MREE: Middle rare earth element; HREE: Heavy rare earth element.

Acknowledgements

We thank the captain and crew of the Zhedaiyuyun and researchers for taking seawater samples during cruises and performing onboard sample processing. We would especially like to thank Professor Dr. Tristan C. C. Rousseau for contributing to the Nd mass balance model calculation. We would also like to thank Wenkai Guan, Jie Liang, and Hailong Zhang for assistance in the laboratory and with sampling. We are grateful to the anonymous reviewers for their helpful comments and suggestions. This paper is dedicated to the memory of Huijun He, an outstanding scientist who sadly passed away on September 3, 2021.

Author contributions

JZ proposed the study subject, conceived and designed the study, and was the project administrator. HC carried out the experimental study and wrote the manuscript. QL and HH conceived the study and participated in discussion on the manuscript. ZZQ analyzed and interpreted the data. All authors read and approved the final manuscript.

Funding

This study was partially supported by the National Natural Science Foundation of China (Grant Nos. NSFC-41890801, 4191154007, 41906038, and 41530965); the Key Laboratory of Marine Ecology and Environmental Science and Engineering, SOA (Grant No. MESE-2019-04); the Pilot National Laboratory for Marine Science and Technology (Qingdao) (Grant No. JCZX202019); JSPS KAKENHI Grant Nos. JP20H04319 and 15H05821.

Availability of data and materials

The datasets generated and analysed during the current study are available in the [Data Publisher for Earth & Environmental Science] repository, (https://doi.org/10.1594/PANGAEA.939705; https://doi.org/10.1594/PANGAEA.939706; https://doi.org/10.1594/PANGAEA.939708).

Declarations

Ethical approval

Our research does not involve human participants, or tissue or animals. The datasets generated and analysed during the current study are available in the [Data Publisher for Earth & Environmental Science] repository, [https://doi.org/10.1594/PANGAEA.939705,939706,939708].

Competing interests

The authors declare that they have no competing interests.

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Received: 13 October 2021 Accepted: 3 April 2022
Published online: 21 April 2022

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