Dissolved silicon isotope dynamics in large river estuaries

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Abstract

Estuarine systems are of key importance for the riverine input of silicon (Si) to the ocean, which is a limiting factor of diatom productivity in coastal areas. This study presents a field dataset of surface dissolved Si isotopic compositions ($\delta^{30}\text{Si}_{\text{Si(OH)4}}$) obtained in the estuaries of three of the world’s largest rivers, the Amazon (ARE), Yangtze (YRE), and Pearl (PRE), which cover different climate zones. While $\delta^{30}\text{Si}_{\text{Si(OH)4}}$ behaved conservatively in the YRE and PRE supporting a dominant control by water mass mixing, significantly increased $\delta^{30}\text{Si}_{\text{Si(OH)4}}$ signatures due to diatom utilization of Si(OH)$_4$ were observed in the ARE and reflected a Si isotopic enrichment factor $^{30}\epsilon$ of $-1.0\pm0.4\%$ (Rayleigh model) or $-1.6\pm0.4\%$ (steady state model). In addition, seasonal variability of Si isotope behavior in the YRE was observed by comparison to previous work and most likely resulted from changes in water residence time, temperature, and light level. Based on the $^{30}\epsilon$ value obtained for the ARE, we estimate that the global average $\delta^{30}\text{Si}_{\text{Si(OH)4}}$ entering the ocean is 0.2-0.3‰ higher than that of the rivers due to Si retention in estuaries. This systematic modification of riverine Si isotopic compositions during estuarine mixing, as well as the seasonality of Si isotope dynamics in single estuaries, needs to be taken into account for better constraining the role of large river estuaries in the oceanic Si cycle.
1. INTRODUCTION

The land-to-ocean silicon (Si) flux, mainly occurring via riverine discharge, is of great importance because it strongly stimulates diatom growth in coastal oceans, thereby significantly contributing to global carbon fixation (Laruelle et al., 2009; Treguer and De La Rocha, 2013; Frings et al., 2016). Estuaries, situated between freshwater and marine environments, are key components of the land-ocean aquatic continuum and are highly complex environments with distinct patterns of salinity, pH, nutrients, and turbidity (e.g., Edmond et al., 1985; Nelson and Dortch, 1996; Cai et al., 2004). Estuarine mixing alters the distributions of dissolved and particulate materials delivered by rivers through, for example, adsorption-desorption onto particles (e.g., Nguyen et al., 2019), mineral precipitation and dissolution (e.g., Singurindy et al., 2004), and uptake by organisms (e.g., DeMaster et al., 1996). Dissolved silicate (Si(OH)\textsubscript{4}) concentrations often deviate from conservative mixing behavior between river water and seawater in estuaries, which can be induced by both biotic and abiotic processes (e.g., Carbonnel et al., 2013; Treguer and De La Rocha, 2013). Diatoms incorporate Si(OH)\textsubscript{4} into their frustules during growth and export biogenic silica (bSi) to the sediments, thereby removing Si from the dissolved pool (e.g., DeMaster, 1981; Conley and Malone, 1992). In the sediments, diagenetic reactions via dissolution of bSi and formation of authigenic silicate minerals (i.e., reverse weathering) help to further preserve Si (e.g., Michalopoulos and Aller, 1995, 2004; Rahman et al., 2017). In contrast, the dissolution of fluvial amorphous silica (ASi) adds Si to estuarine environments, which has been demonstrated in both laboratory experiments (e.g., Oelkers et al., 2011; Jones et al., 2012) and field studies (e.g., Pastuszak et al., 2008; Carbonnel et al., 2013; Lehtimäki et al., 2013). Furthermore, anthropogenic activities may decrease (such as damming; Conley, 2002; Hughes et al., 2012) or increase (such as deforestation and climate warming; Conley et al., 2008; Laruelle et
al., 2009) Si(OH)$_4$ concentrations and impact the riverine Si flux to the estuaries.

Tropical and subtropical rivers are the major contributors of riverine Si input to the ocean (Zhang et al., 1999; Beusen et al., 2009). Taking into account the strong climatic control on the weathering regime and intensity, processes affecting Si in estuaries associated with changing climate zones are of particular interest. In addition, large river estuaries with high water and sediment discharge commonly exhibit not only high turbidity and complex physical circulation but also significant seasonal variability in nutrient dynamics and phytoplankton bloom development (DeMaster and Pope, 1996).

Despite their potential significance for global Si cycling, our knowledge of the role of large river estuaries is still limited (Weiss et al., 2015; Frings et al., 2016; Sutton et al., 2018). One reason is that the Si concentration distributions only partially reveal Si dynamics. Over the past two decades, the stable isotopic composition of Si ($\delta^{30}$Si) has been developed as a powerful tool for identifying Si sources and tracking Si biogeochemical processes over various temporal and spatial scales (e.g., Varela et al., 2004; Zhang et al., 2019). In comparison to extensive studies conducted in rivers, lakes, and the ocean (Sutton et al., 2018, and references therein), information on factors controlling dissolved Si isotope compositions ($\delta^{30}$Si$_{\text{Si(OH)}_4}$) in estuaries is sparse and data have so far only been reported for four estuaries worldwide (Hughes et al., 2012; Delvaux et al., 2013; Weiss et al., 2015; Zhang et al., 2015). In the tropical Tana River Estuary, Si(OH)$_4$ concentrations decrease linearly with increasing salinity, whereas $\delta^{30}$Si$_{\text{Si(OH)}_4}$ signatures remain stable due to the absence of processes fractionating Si isotopes (Hughes et al., 2012). A notable increase of $\delta^{30}$Si$_{\text{Si(OH)}_4}$ has been observed to occur during diatom growth in the tidal freshwater zone of both the Scheldt River (Delvaux et al., 2013) and the Elbe River estuaries (Weiss et al., 2015). Heavier $\delta^{30}$Si$_{\text{Si(OH)}_4}$ signatures induced by biological utilization also occur at high salinities.
in the Yangtze River Estuary in summer (Zhang et al., 2015). Given the large importance of estuaries, integrated efforts are necessary for the development of a more comprehensive understanding of the global Si cycle (Sutton et al., 2018).

In this study, we investigate for the first time surface water $\delta^{30}$Si$_{\text{Si(OH)4}}$ distributions and their controlling processes in the estuaries of three of the world’s largest rivers, namely the Amazon River (1st) in the tropical zone, the Yangtze River (or Changjiang, 5th) in the temperate zone and the Pearl River (or Zhujiang, 13th) in the subtropical zone, including both the embayment and adjacent shelf (Fig. 1). The relationship between $\delta^{30}$Si$_{\text{Si(OH)4}}$ and salinity is investigated in each estuarine system to distinguish between chemical and biological fractionation effects and conservative mixing. Given that these rivers represent more than one fifth of the global freshwater discharge to the ocean, their Si isotope dynamics will shed new light on the importance of estuarine processes in the oceanic Si cycle.

2. MATERIALS AND METHODS

2.1. Study area

**Amazon River Estuary (ARE).** The Amazon River, covering over 20° of latitude and extending longitudinally across 3,000 km, is the largest river in the world (Nittrouer and DeMaster, 1996). It discharges 5.8×$10^{12}$ m$^3$ yr$^{-1}$ of freshwater with peak flow in June and minimum flow in November, which is approximately 20% of the global river water discharge (Meade et al., 1985; DeMaster and Pope, 1996). It also delivers 1.1-1.3×$10^9$ ton yr$^{-1}$ of suspended sediments to its lower reaches, contributing up to 7% of the global riverine sediment input to the ocean (Meade et al., 1985). The ARE is located in the low-latitude tropical zone where the freshwater plume from the river interacts with the North Brazil Current and is transported to the northwest (Milliman and Boyle, 1975; Johns et al., 1998). It is not strongly anthropogenically influenced and thus relatively low in nutrient and
cation contents (DeMaster and Pope, 1996), though recent studies have shown human-induced perturbations in the southern and eastern portions of the Amazon River drainage basin (Davidson et al., 2012; Latrubesse et al., 2017). The Si input from the ARE is the major source of Si(OH)$_4$ to the adjacent shelf with a smaller contribution from shoreward advection of offshore waters (Michalopoulos and Aller, 2004). Primary productivity, dominantly driven by diatoms (DeMaster et al., 1996), is highest in an intermediate zone between the turbid nutrient-rich Amazon plume waters inshore and the clear nutrient-poor marine surface waters offshore (Smith and Demaster, 1996).

Yangtze River Estuary (YRE). After a total of 6,300 km of eastward flow to the East China Sea, the Yangtze River supplies $9.2 \times 10^{11}$ m$^3$ yr$^{-1}$ of freshwater and $4.7 \times 10^8$ ton yr$^{-1}$ of sediments to the ocean (Wang et al., 2015). More than 70% of the freshwater discharge occurs in the flood season (May-October) (Zhang et al., 2015). The YRE, located in the temperate climate zone (e.g., Patra et al., 2012), is characterized by high nutrient contents due to anthropogenic eutrophication and high cation contents due to high weathering rates. The riverine fluxes of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphate (DIP) are estimated to be $9.50 \times 10^5$ and $2.63 \times 10^4$ ton yr$^{-1}$ (Liu et al., 2009). The Si(OH)$_4$ flux has decreased sharply after the construction of large reservoirs in the Yangtze River drainage basin, from $2.72 \times 10^5$ in the 1960s to $2.13 \times 10^5$ ton yr$^{-1}$ in the 1980s. In 2002, ~13% of the total Si(OH)$_4$ flux was fixed by phytoplankton within 162 big reservoirs before entering into the East China Sea (Li et al., 2007). On the other hand, Gao et al. (2012) pointed out no significant changing trend of Si(OH)$_4$ concentrations and fluxes near the YRE mouth since 1960s, suggesting that the long-term variability of Si(OH)$_4$ loads by the Yangtze River needs further investigation. Nevertheless, application of chemical fertilizers has increased N and P fluxes and enhanced N:Si and P:Si ratios since the 1980s. This has significantly
increased the abundance of non-siliceous algae over diatoms off the YRE (Li et al., 2007).

Pearl River Estuary (PRE). The Pearl River drains an area of 452,000 km² and reaches the South China Sea after 2,214 km southward flow. It is a large subtropical river located in a highly populated and industrialized area (e.g., Zhang et al., 1999). It discharges 1.6×10¹¹ m³ yr⁻¹ of freshwater and 8.5×10⁷ ton yr⁻¹ of sediments into the South China Sea via three estuaries, among which the Lingdingyang, known as the PRE, receives 50-55% of the freshwater discharge (Harrison et al., 2008). Approximately 80% of the freshwater discharge occurs in the wet season (April-September) and only 20% in the dry season (October-March) (Zhang et al., 1999; Cai et al., 2004). With the rapid economic development and urbanization of the upper PRE, anthropogenic loads of nutrients have dramatically increased in the last few decades. From 2001 to 2008, for example, the total ammonium discharge from Guangdong Province increased from 9.0×10⁴ to 12.2×10⁴ ton (He et al., 2014). However, the phytoplankton biomass is not as high as one would expect from the high level of nutrients, probably due to dilution by river discharge, estuarine circulation, and/or vertical mixing (Harrison et al., 2008). Moreover, diatom blooms in the PRE are seasonally highly variable and confined to spatially limited locations associated with suitable coupled physical-biological conditions (Lu and Gan, 2015).

2.2. Sampling and analyses

2.2.1. Sampling

Sampling in the mixing zone of the ARE was carried out during R/V Meteor Cruise M147 (Amazon-GEOTRACES) in May 2018, when the monthly discharge was 6.1×10¹¹ m³ (data from Óbidos observation station; http://www.ore-hybam.org). The samples were taken along a section covering the complete salinity gradient between the riverine endmember and open seawater. The ship’s conventional stainless steel Conductivity-Temperature-Depth (CTD) rosette equipped with
24-Niskin bottles was only briefly submerged at the surface in an effort to avoid vertical mixing and allow sampling of the undisturbed uppermost freshwater layer. Water for δ⁴⁰Si₂(H₂O)₄ analyses was sampled into 20 L cubitainers and filtered through 0.45 μm Nucleopore filters within a few hours after collection. Samples at stations M147_55-F (surface salinity of 35.0) and M147_56-F (surface salinity of 30.0) on the shelf (Table 1) were taken with a towed fish and treated the same way. All samples were subsequently acidified to pH~2 with concentrated ultrapure HCl to prevent adsorption of metals to the walls of the bottles. Surface water samples were also collected for analyses of nutrients (DIN (nitrate plus nitrite), DIP, and Si(OH)₄) and chlorophyll a (Chl-a). In addition to this cruise to the ARE, Si(OH)₄ concentration and δ³⁰Si₂(H₂O)₄ data were also collected at a single upstream station at zero salinity in November 2013 and at other stations on the shelf in February 2012 (see Text A2 for details).

Sampling in the YRE was carried out in March 2015, when the monthly discharge was 5.4×10¹⁰ m³ (data from Datong observation station; http://www.mwr.gov.cn). Sampling in the PRE was carried out in August 2012, when the monthly discharge was 2.7×10¹⁰ m³ (data from Wuzhou observation station; http://www.mwr.gov.cn). In both estuaries, ~150 ml of surface water was collected with Niskin bottles attached to a rosette sampler and immediately filtered through nitrocellulose acetate filters (0.45 μm pore size and 47 mm diameter) into acid pre-cleaned polyethylene bottles for δ³⁰Si₂(H₂O)₄ analyses. Samples were subsequently acidified to pH~2 with distilled concentrated HCl (0.1% v/v) and stored at room temperature in the dark until analysis in the laboratory. Surface water samples were also collected in the YRE and PRE for analyses of nutrients (DIN (nitrate plus nitrite), DIP, and Si(OH)₄), Chl-a, and total suspended matter (TSM).

2.2.2. Si isotope analyses
Si isotopic compositions were measured on a Nu Plasma HR multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Nu Instruments™, Wrexham, UK) at GEOMAR, Kiel and are reported in ‰ deviations from the international Si standard NIST Reference Material 8546 (or NBS28) (δ$^{30}\text{Si}$=[$(30\text{Si}/28\text{Si})_{\text{sample}}/(30\text{Si}/28\text{Si})_{\text{standard}}-1] \times 1000$).

(1) Sample treatment

$\text{Si(OH)}_4$ in all ARE samples collected in May 2018 was pre-concentrated and separated from the major matrix elements using a two-step brucite coprecipitation technique (Reynolds et al., 2006), with low-salinity samples pre-treated with Mg$^{2+}$ addition (Zhang et al., 2015), which was further purified using cation-exchange chromatography (Georg et al., 2006). For the YRE and PRE, $\text{Si(OH)}_4$ in samples with low concentrations (<40.0 μmol L$^{-1}$; Table 1) was pre-concentrated via brucite coprecipitation before cation-exchange chromatography, while $\text{Si(OH)}_4$ in other samples with high concentrations (>40.0 μmol L$^{-1}$; Table 1) was directly purified using cation-exchange chromatography given that their $\text{Si(OH)}_4$ content was sufficiently high for measurement on the MC-ICP-MS. Recent work has shown that Si isotope measurements on MC-ICP-MS are susceptible to anions or organic compounds in the matrix (e.g., van den Boorn et al., 2009; Hughes et al., 2011). However, the Nu Plasma HR MC-ICP-MS at GEOMAR is less sensitive to these matrices. Ehlert et al. (2016) did tests in order to check the matrix effect from anions and dissolved organic matter on pore-water Si isotopic compositions using the same instrument, which showed no significant matrix effects.

(2) Mass spectrometry

Each purified sample solution was analyzed three to four times in a single measurement session using a standard-sample-standard bracketing technique, resulting in sample reproducibilities between ±0.03 and ±0.31‰ (2 standard deviations, 2SD$_{\text{bracketing}}$; Table 1). For
most of the samples, purification and determination of isotopic compositions were repeated on two
or three days and the duplicate measurements indicate very good reproducibilities between ±0.01
and ±0.23‰ (2SD\textsubscript{repeated}; Table 1).

Repeated measurements of the standard reference materials IRMM-018 and Big Batch gave
average $\delta^{30}\text{Si}$ values of $-1.45±0.15$‰ (2SD\textsubscript{repeated}, n=5) and $-10.70±0.14$‰ (2SD\textsubscript{repeated}, n=5)
during measurements of the ARE samples collected in May 2018, and of $-1.39±0.15$‰ (2SD\textsubscript{repeated},
n=7) and $-10.67±0.19$‰ (2SD\textsubscript{repeated}, n=8) during measurements of the YRE and PRE samples.
All these values are in good agreement with those obtained during a previous interlaboratory
comparison (Reynolds et al., 2007). An average $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ value of $1.79±0.29$‰ (2SD\textsubscript{repeated}, n=3;
with coprecipitation) for the seawater standard ALOHA\textsubscript{300} was obtained during running the ARE
samples. Average $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ values of $1.27±0.17$‰ (2SD\textsubscript{repeated}, n=9; with coprecipitation) and
1.41±0.18‰ (2SD\textsubscript{repeated}, n=8; without coprecipitation) for the seawater standard ALOHA\textsubscript{1000} were
obtained during running the ARE samples and the YRE and PRE samples, respectively. These
values are within analytical error identical to or slightly higher than the consensus values
(1.68±0.35‰ for pre-concentrated ALOHA\textsubscript{300} and 1.24±0.20‰ for pre-concentrated ALOHA\textsubscript{1000})
obtained in the GEOTRACES inter-calibration study (Grasse et al., 2017). The long-term external
reproducibility for the replicate measurements of an in-house seawater matrix standard was ±0.20‰
(2SD, n=16), which represents the error bars of the majority of the field $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ data of our
study. For few samples with 2SD\textsubscript{repeated} larger than ±0.20‰, the 2SD\textsubscript{repeated} was used as error bars
of $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ (Figs. 3b, d, f, A4b, d, A5, and A6). We contend that there might be a tendency
towards slightly heavier $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ for samples without than with coprecipitation and further
comparisons should be conducted carefully. However, the offset of 0.14‰, as shown by our
measurements of ALOHA1000 using both pre-treatments, is within the long-term external reproducibility of ±0.20‰. More information on data quality can be found in Text A1.

2.2.3. Analyses of other parameters

In the ARE, salinities of the discrete surface water samples taken with the towed fish were determined with a hand-held conductivity meter (WTW LF330) and those taken with the CTD rosette were determined with a hand-held conductivity meter (WTW 3110) and corresponding probe Tetracon 325 to ensure comparability of all data. Nutrient concentrations in the water samples were analyzed following classical colorimetric methods, using a SEAL QuAAtro continuous flow Auto-Analyzer (Hydes et al., 2010). Chl-a concentrations were determined after extraction into cold (−20°C) acetone by high performance liquid chromatography with spectrophotometric detection (Van Heukelem and Thomas, 2001). In the YRE and PRE, salinities of surface water samples were determined with a SBE25 CTD (Sea-Bird) attached to a rosette sampler and was compared with salinity of discrete samples measured by a Multi 340i multi-parameter meter (WTW). Nutrient concentrations in the water samples were analyzed using a Nutrient Auto-Analyzer (SKALAR Sanplus System) for the YRE and a Technicon AA3 Auto-Analyzer (Bran-Luebbe, GmbH) for the PRE. The precisions for DIN, DIP, and Si(OH)₄ concentrations were ±1%, ±2%, and ±3%, respectively (1SD; Du et al., 2013). Chl-a concentrations were determined using a Turner fluorometer after extraction of the membrane samples with 90% acetone (He et al., 2014). TSM concentrations were determined by drying in an oven at 50°C and weighing the quartz microfiber membranes used for filtering (Zhai et al., 2017).

2.3. Si isotope fractionation model

Si isotope fractionation during Si(OH)₄ consumption can be described using either a Rayleigh or a steady state model (Cao et al., 2012, and references therein). The Rayleigh model describes a
closed system without further Si(OH)$_4$ input from external sources:

\[ \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{obs}} = \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{ini}} + 30 \epsilon \times \ln f \]  

(1)

\[ f = \frac{[\text{Si(OH)}_4]_{\text{obs}}}{[\text{Si(OH)}_4]_{\text{ini}}} \]  

(2)

The subscript “obs” and “ini” denote measured $\delta^{30} \text{Si}_{\text{Si(OH)}_4}$ and Si(OH)$_4$ values and initial $\delta^{30} \text{Si}_{\text{Si(OH)}_4}$ and Si(OH)$_4$ values, respectively, with the latter being equal to conservative $\delta^{30} \text{Si}_{\text{Si(OH)}_4}$ and Si(OH)$_4$ values predicted by a two-endmember mixing model ($\delta^{30} \text{Si}_{\text{Si(OH)}_4, \text{con}}$ and $[\text{Si(OH)}_4]_{\text{con}}$; Eqs. A3 and A4; Text A3). The term $f$ indicates the fraction of remaining dissolved Si(OH)$_4$ in solution relative to the initial concentration. The isotopic enrichment factor $30 \epsilon$ is thus estimated as:

\[ 30 \epsilon = \frac{\delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{obs}} - \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{ini}}}{\ln f} = \frac{\delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{obs}} - \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{ini}}}{\ln [\text{Si(OH)}_4]_{\text{obs}}/\ln [\text{Si(OH)}_4]_{\text{ini}}} \]  

(3)

In contrast, the steady state model describes an open system with a continuous supply of Si(OH)$_4$ from external sources:

\[ \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{obs}} = \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{ini}} - 30 \epsilon \times (1 - f) \]  

(4)

In this case, $30 \epsilon$ is calculated as:

\[ 30 \epsilon = \frac{\delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{ini}} - \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{obs}}}{1 - f} = \frac{\delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{ini}} - \delta^{30} \text{Si}_{\text{Si(OH)}_4}_{\text{obs}}}{1 - [\text{Si(OH)}_4]_{\text{obs}}/[\text{Si(OH)}_4]_{\text{ini}}} \]  

(5)

By combining the two-endmember mixing model (Text A3) and the Si isotope fractionation models, we are able to distinguish chemical or biological effects on Si concentrations and isotopic compositions from pure conservative mixing.

3. RESULTS
3.1. Surface distribution of salinity, \(\text{Si(OH)}_4\), and \(\delta^{30}\text{Si(OH)}_4\)

In all three estuaries, surface salinities generally increased from the upper reaches or the mouth (<1.0) to the adjacent shelf (Fig. 2a, e, j), reflecting estuarine mixing between the fresh river waters and the saline seawaters. Salinities at the outermost offshore stations were 35.0, 34.0, and 31.1 for the ARE, YRE, and PRE (Table 1), suggesting the dominance of oceanic shelf water in the ARE and YRE and the still significant influence of river plume water in the PRE during the high discharge season in August.

Surface \(\text{Si(OH)}_4\) concentrations generally decreased from the upper estuaries to the shelf (Fig. 2b, f, k) reflecting high riverine input of nutrients to the coastal shelf areas. The \(\text{Si(OH)}_4\) concentrations (0.6-150.2 \(\mu\text{mol L}^{-1}\) for the ARE, 9.2-106.3 \(\mu\text{mol L}^{-1}\) for the YRE, and 14.9-166.7 \(\mu\text{mol L}^{-1}\) for the PRE) are overall comparable between the three estuaries (and adjacent shelf areas) with slightly higher values observed in the upper PRE near zero salinity. The \(\delta^{30}\text{Si(OH)}_4\) signatures were significantly heavier in surface seawaters than in the river waters (3.0 vs. 1.2‰ for the ARE, 2.6 vs. 1.7‰ for the YRE, and 1.8 vs. 1.3‰ for the PRE; Fig. 2c, g, l; Table 1), with the largest increase observed in the ARE. The highest surface \(\delta^{30}\text{Si(OH)}_4\) value at the outermost offshore station in the PRE is lower than those of the ARE and YRE, largely due to the still higher proportion of the low-\(\delta^{30}\text{Si(OH)}_4\) river plume water indicated by its lower salinity. Note that \(\delta^{30}\text{Si(OH)}_4\) was not measured at salinity of 35.0 in the ARE due to the extremely low amount of dissolved Si in the surface seawater, and 3.0‰ reflects the \(\delta^{30}\text{Si(OH)}_4\) value measured at a salinity of 30.0.

3.2. Surface distribution of TSM and Chl-a

The TSM concentrations ranged from 0 to 120 \(\text{mg L}^{-1}\) in the YRE with the maximum concentrations observed at salinities of 7.5 to 16.0 (Fig. 2h), whereas they were significantly lower in the PRE with a maximum of up to 60 \(\text{mg L}^{-1}\) observed at a salinity of 6.5 (Fig. 2m). This
indicates the development of a turbidity maximum zone (TMZ, TSM >10 mg L\(^{-1}\)) at low salinities directly following the freshwater regions in both estuaries. Diatom growth is suppressed in the TMZ of estuaries due to light limitation (Edmond et al., 1985). TSM concentrations were much higher than 10 mg L\(^{-1}\) over the entire salinity range in the YRE (Fig. 2h), as well as at most stations with salinities <11.8 in the PRE (Fig. 2m). Unfortunately, no TSM data were collected during cruise M147 to the ARE. Previous studies have demonstrated, however, that the TMZ occurs at salinities below 17.0 (DeMaster and Pope, 1996).

In the ARE, Chl-a concentrations were lower than 3 µg L\(^{-1}\) in the freshwater zone with salinities <4.0 and increased to a maximum of 14 µg L\(^{-1}\) at a salinity of 15.0. Chl-a remained at high levels in the mixing zone at mid-salinities from 20.0 to 28.0 (Fig. 2d), suggesting abundant phytoplankton growth downstream of the TMZ. Consistent with the high turbidity, Chl-a concentrations were overall lower than 3 µg L\(^{-1}\) in the YRE (Fig. 2i), indicating largely reduced phytoplankton growth during the sampling period. In the PRE, Chl-a concentrations were distinctly elevated in the upper stream at salinities <1.0 and the highest value of 11 µg L\(^{-1}\) was observed at the freshest upstream station (Fig. 2n). This high Chl-a region clearly located upstream of the TMZ was likely induced by transport of freshwater algae from the drainage basin (He et al., 2014) and/or in situ biological production due to the high nutrient content and relatively low TSM (Anderson, 1986). Chl-a concentrations decreased rapidly in the TMZ of the PRE, but then higher Chl-a (>4 µg L\(^{-1}\)) were subsequently observed again at salinities of 16.5 and 24.0 (Fig. 2n), indicating enhanced phytoplankton growth at mid-salinities with reduced TSM.

Overall, in all three estuaries, phytoplankton growth generally increased towards the outer parts of the estuaries, where the decrease in nutrient levels is compensated for by the increase in water transparency and thus light availability.
4. DISCUSSION

4.1. Differences in $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ signatures of river water endmembers between estuaries

The Si(OH)$_4$ concentration and $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ value at zero salinity of the ARE amounted to 150.2 $\mu$mol L$^{-1}$ and 1.2±0.2‰, respectively, in May 2018 (field measurements at station M147_66-1; Table 1), and reached 125.3 $\mu$mol L$^{-1}$ and 1.3±0.2‰, respectively, in November 2013 (field measurements at station River; Table A1). Therefore, our data show a consistent $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ composition of the river water endmember despite differing Si(OH)$_4$ concentrations, sampling locations, and sampling periods. A $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ signature of 1.8±0.2‰ (Si(OH)$_4$ concentrations of 102.7 $\mu$mol L$^{-1}$) for the river water endmember in the YRE (the averages of field measurements at stations C4, C5, C6, and C7) is within error consistent with 1.6‰ provided by Zhang et al. (2015). Our $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ value of 1.4±0.2‰ (Si(OH)$_4$ concentrations of 143.8 $\mu$mol L$^{-1}$) for the river water endmember in the PRE (the averages of field measurements at stations P04, A01, A02, A03, and A04) is comparable to that of the ARE but lighter than that of the YRE. Such differences in $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ signatures of various river water endmembers most likely resulted from stronger fractionation in the Yangtze River catchment induced by a combined effect of relatively high weathering intensity, biological utilization, and anthropogenic activities (Text A4; Zhang et al., 2003; Li et al., 2007; Ding et al., 2014; Frings et al., 2016). Note that the uncertainties of $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ values for the river water endmembers, based on the selected field measurements, derived either from the propagation of their analytical errors (i.e., the long-term external reproducibility of ±0.2‰ or 2SD$_{\text{repeated}}$ if they are larger than ±0.2‰) or from the standard deviation of all field measured $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ values, which are 0.2 or 0.2‰ in the ARE, 0.1 or 0.04‰ in the YRE, and 0.1 or 0.04‰ in the PRE, respectively. We thus conservatively use the long-term external reproducibility of 0.2‰ for the Si isotope analyses as the uncertainties of $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ endmember values.
4.2. Si isotope dynamics during estuarine mixing

The relationship between the dissolved phase and salinity is widely used to interpret the biogeochemical behavior of a given element during estuarine mixing between river water and seawater. In this study, the water mass compositions at near zero salinity and at the highest salinity are selected as the two endmembers in each estuary (Fig. 3). Estimations of Si(OH)$_4$ concentrations and δ$^{30}$Si$_{\text{Si(OH)}_4}$ values for the river water endmember are introduced in subsection 4.1. In the ARE, salinity and Si(OH)$_4$ concentration for the seawater endmember were 35.0 and 0.6 μmol L$^{-1}$, respectively, based on the field measurements at station M147_55-F (Table 1). δ$^{30}$Si$_{\text{Si(OH)}_4}$ at this station was estimated to be 3.2±0.3‰ using a linear relationship between δ$^{30}$Si$_{\text{Si(OH)}_4}$ and ln(Si(OH)$_4$) based on available data in the ARE in May 2018 (δ$^{30}$Si$_{\text{Si(OH)}_4}$=(3.01±0.29)−(0.31±0.08)×ln(Si(OH)$_4$), R$^2$=0.81; Fig. A5), with the uncertainty propagated from that of the intercept and slope. In the YRE, salinity, Si(OH)$_4$ concentration, and δ$^{30}$Si$_{\text{Si(OH)}_4}$ values for the seawater endmember were 33.8, 10.3 μmol L$^{-1}$, and 2.4±0.2‰ based on the averages of field measurements at stations A06-9 and A06-11 (Table 1). In the PRE, salinity, Si(OH)$_4$ concentration, and δ$^{30}$Si$_{\text{Si(OH)}_4}$ values for the seawater endmember were 31.1, 14.9 μmol L$^{-1}$, and 1.7±0.2‰ based on the field measurements at station F415 (Table 1). A sensitivity test using open ocean seawater endmembers is carried out, which shows that our selection and estimation of seawater endmembers above are valid (Text A5 and Fig. A6). Note that here, we conservatively use the long-term reproducibility of 0.2‰ to represent the uncertainties of δ$^{30}$Si$_{\text{Si(OH)}_4}$ endmember values for predicting the conservative estuarine mixing, except for the ARE seawater endmember, the uncertainty of which is larger at 0.3‰ (Figs. 3 and A6). Clearly, Si biogeochemistry differs between the three estuaries when comparing field measurements along the salinity gradient with the predicted two-endmember conservative mixing following Eqs. A1-A4.
4.2.1. Amazon River Estuary: biological fractionation during diatom growth

The Si(OH)₄ concentration of 150.2 μmol L⁻¹ at zero salinity in the ARE is close to the annual average value of 163 μmol L⁻¹ observed at Óbidos observation station (Moquet et al., 2016), suggesting that our zero salinity sample represents a realistic river water endmember. Significant removal of Si(OH)₄ corresponding to elevated δ³⁰SiSi(OH)₄ that cannot be explained by mixing is observed over the entire salinity range (Fig. 3a, b), reflecting preferential utilization of Si(OH)₄ with lighter Si isotopic composition. Both DIN (Fig. 4a) and DIP (Fig. 4b) generally show significant removal at salinities >10.0 in the ARE, indicating strong nutrient uptake by phytoplankton as evidenced by high Chl-a concentrations (up to 14 µg L⁻¹; Fig. 2d). Applying Eqs. A1-A4, we obtain the expected initial Si(OH)₄ and δ³⁰SiSi(OH)₄ values for every single measurement within this salinity range. Based on these data, calculated Si(OH)₄ consumption (1-f; Eqs. 2 and A3) ranged from 6% at low salinity of 4.0 to 44±7% (n=6) at mid-salinities of 6.7-27.3 and to 94% at high salinity of 30.0 (Table A2). This is consistent with an overall increasing trend of Si(OH)₄ depletion from the inner to the outer shelf (DeMaster et al., 1996). The average isotopic enrichment factor $^{30}\epsilon$ is estimated to be $-1.0±0.4‰$ following the Rayleigh model (Eq. 3) or $-1.6±0.4‰$ following the steady state model (Eq. 5).

Culture experiments (De La Rocha et al., 1997; Milligan et al., 2004; Sutton et al., 2013; Meyerink et al., 2017; Meyerink et al., 2019) have discovered a range of $^{30}\epsilon$ ($-0.54$ to $-2.09$ ‰) with an average of $-1.1‰$ during Si(OH)₄ utilization by diatoms. Field studies (e.g., Reynolds et al., 2006; Beucher et al., 2008; Fripiat et al., 2011; Cao et al., 2012, 2015) have validated this value in different oceanic systems. Our estimates in the ARE, assuming either a closed or an open system, agree well with this consensus value, supporting a major role of diatoms in controlling the Si
isotope signatures. Previous studies have shown that diatoms are the predominant primary producers on the Amazon shelf, which control Si(OH)₄ distributions and removal (e.g. DeMaster et al., 1996), as well as the corresponding Si isotope fractionation. However, it is difficult to distinguish between Rayleigh or steady state models, and we contend that reality is between these two situations.

In addition to diatom productivity, the process of reverse weathering in sediments is significant in the ARE (Michalopoulos and Aller, 1995, 2004; Rahman et al., 2016), during which the formation of authigenic aluminosilicate from the dissolving bSi, preferentially removes lighter Si isotopes from the pore-water resulting in heavy δ³⁰Si₅Si(OH)₄ signatures of up to 2.0‰ (Tatzel et al., 2015; Ehlert et al., 2016). This process and associated fractionation effect, however, primarily occurs in the sediments. Aller et al. (1996) and DeMaster and Pope (1996) showed that for most Amazon shelf sediments, the diffusive Si flux out of the seabed is minimal, implying that the heavy pore-water signatures are generally not released to the bottom waters in significant amounts. Hydrographic evidences collected during cruise M147 suggest that the surface waters were highly stratified and vertical mixing was very weak. It is thus unlikely that pore-water δ³⁰Si₅Si(OH)₄ would affect the Si isotopic compositions of the surface waters (Chou and Wollast, 2006). As a consequence, the observed non-conservative behavior of both Si(OH)₄ and δ³⁰Si₅Si(OH)₄ most likely reflects preferential utilization of lighter Si isotopes during diatom growth in the outer parts of the Amazon River plume. Note that dissolution of fluvial ASi might add Si(OH)₄ with light δ³⁰Si₅Si(OH)₄ into the surface water (Frings et al., 2016), which might lower the apparent Si(OH)₄ removal and Si isotope fractionation during diatom growth.

Field data collected in February 2012 also reveal significant removal of Si(OH)₄ corresponding to elevated δ³⁰Si₅Si(OH)₄ at mid- and high salinities of 15.5-29.1 in the ARE,
independent of the selected river water endmembers (Text A2 and Fig. A4a, b). The average isotopic enrichment factor $^{30}\epsilon$ is estimated to be $-1.0\pm0.4\%$ following the Rayleigh model or $-1.4\pm0.5\%$ following the steady state model. Both values are consistent with those obtained in May 2018, suggesting that the seasonal variability of Si isotope fractionation during diatom growth is small in the ARE.

4.2.2. Yangtze River Estuary: seasonal variability due to changing hydrological conditions

Both surface Si(OH)$_4$ concentration and isotope distributions fit the two-endmember mixing very well in the YRE (Fig. 3c, d) supporting its conservative behavior during the sampling period in late winter. Measured DIN and DIP concentrations were apparently higher than those predicted from conservative mixing (Fig. 4c, d). We contend that these deviations most likely result from the uncertainty of the river water DIN and DIP endmembers. The close correlations between DIN ($R^2=0.98$) and DIP ($R^2=0.97$) and salinity over the entire salinity range essentially suggest exclusive mixing control (Fig. 4c, d). Unlike the ARE, biological effects on Si dynamics are thus negligible, which is supported by the observed low Chl-a concentrations in the YRE (Fig. 2i).

Zhang et al. (2015) reported $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ distributions in the YRE for two other seasons (Fig. 5a-d): the dry season of March 2012 with a monthly discharge of $7.0\times10^{10}$ m$^3$ and the wet season of July 2011 with a monthly discharge of $1.3\times10^{11}$ m$^3$ (data from Datong observation station; http://www.mwr.gov.cn). These data are included here to assess the seasonal Si dynamics in the YRE. It is noteworthy that Zhang et al. (2015) depicted the same conservative behavior of Si isotopes in the same dry season of March 2012 (Fig. 5a, b). Despite a comparable Si(OH)$_4$ concentration range of 5-110 $\mu$mol L$^{-1}$ between the two sampling campaigns, $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ values in this study (1.7-2.6\%) are overall higher than those of 1.5-2.0\% in Zhang et al. (2015), which is ascribed to a heavier seawater endmember in the former. This large difference between the
seawater endmember values (2.6 vs. 1.7‰) might be a consequence of stronger Si isotope fractionation prevailing during our sampling period, or it likely simply reflects the high temporal and spatial variations in the dynamic shelf system of the East China Sea. In the wet season of July 2011, the river water endmember had Si(OH)₄ concentrations and δ³⁰Si_{Si(OH)₄} signatures similar to those in March 2012, while the δ³⁰Si_{Si(OH)₄} of 2.1‰ for the seawater endmember was heavier, even at lower salinities (Fig. 5c, d; Zhang et al., 2015). More importantly, elevated δ³⁰Si_{Si(OH)₄} signatures corresponding to decreased Si(OH)₄ beyond the mixing control were observed at high salinities of 24.5 to 30.0 (Fig. 5c, d), which suggests significant Si isotope fractionation during diatom growth in the wet season.

The absence of significant Si(OH)₄ utilization at high salinities in late winter before the beginning of spring diatom bloom may be attributed to water temperatures lower than those at which most diatoms can survive in the YRE (Zhang et al., 2015). Moreover, Zhai et al. (2017) addressed the key role of water residence time in constraining biogeochemical processes in the YRE, which would influence the nutrient retention time for developing phytoplankton growth and Si(OH)₄ utilization in estuaries (Kemp et al., 2005). Therefore, the residence time of surface waters in the optimal-growth zone (low turbidity and high nutrients) at high salinities needs to be taken into account, which largely depends on the direction and intensity of the trade winds (Lentz, 1995). If the prevailing winds have a component opposite to the flow direction of the river plume, the waters will reside longer in the optimal-growth zone favoring phytoplankton growth (DeMaster et al., 1996). During the sampling periods of this study and Zhang et al. (2015), southeasterly wind prevailed over the shelf neighboring the YRE in July 2011 and weaker northeasterly wind prevailed in March 2012 and 2015 (Fig. 6). The southeasterly wind in summer is generally in the opposite direction of the Yangtze River flow (towards the southeast), which shifts towards the northeast.
outside of the YRE mouth. In contrast, the northeasterly wind in winter is overall in the same
direction of the plume flow enhancing its offshore transport. In this context, the longer retention
time of nutrients favors diatom growth during the summer in the YRE, suggesting that the changing
water residence time to some extent contributes to the different seasonal behavior of Si.
Unfortunately, data of the residence time of the Yangtze River plume were not collected in both
this study and Zhang et al. (2015), which warrants further investigation.

4.2.3. Pearl River Estuary: dominant control by mixing during the sampling period

Surface water Si(OH)₄ concentrations at low salinities between 0.0 and 1.6, as well as DIN
and DIP, varied within a relatively large range (Figs. 3e and 4e, f), likely suggesting local controls
on the variability in the complex upper PRE. However, the corresponding δ³⁰Si_{Si(OH)₄} signatures
were essentially constant (Fig. 3f). We thus take the average of these values as the river water
endmember for each parameter. Beyond the TMZ at a salinity of 6.5 (Fig. 2m), Si(OH)₄, DIN, and
DIP concentrations generally decreased along the two-endmember mixing curve suggesting
overall conservative behavior, despite DIP concentrations showing relatively large deviations
probably resulting from the uncertainty of river water endmember values (Figs. 3e and 4e, f).
Within analytical error, δ³⁰Si_{Si(OH)₄} values agree with corresponding mixing predictions (Fig. 3f).
The overall conservative distributions of both nutrients and Si isotopes likely point to low
phytoplankton growth during estuarine mixing, even in the offshore areas outside of the mouth of
the PRE, where both nutrients and light were available in sufficient amounts.

Note that relatively high Chl-a concentrations (>4 μg L⁻¹) were observed at mid-salinities of
16.5 and 24.0 (Fig. 2n) suggesting increased phytoplankton growth, which was, however,
insufficient to induce observable removal of any nutrients. One possible reason for the apparently
minimal biological utilization of Si(OH)₄ is the short residence time of surface waters in the PRE
due to high river discharge and fast flow, which is indicated by the still low salinity of 31.1 for the
selected seawater endmember at the outermost station (Fig. 2j). This not only limited the diatom
growth but also diminished the signal of potential nutrient removal. Subtle changes of Si(OH)₄ and
δ³⁰Si_{Si(OH)₄} induced by diatom utilization in the large Si(OH)₄ pool may have been masked by
strong physical mixing. Lu and Gan (2015) also pointed out that the water residence time plays an
important role for the development of phytoplankton blooms during summer in the PRE.

4.3. Differences in Si isotope behavior during estuarine mixing: passage versus reactor

Estuaries can either act as passages of terrestrial Si from the continents to the oceans
characterized by conservative behavior of Si or as biogeochemical reactors inducing non-
conservative behavior during estuarine mixing and potentially modifying their riverine input fluxes
and isotope compositions (Officer, 1979; Zhai et al., 2017). This is supported by the contrasting Si
isotope distributions in the large estuaries investigated in this study (i.e., the YRE and PRE acting
mainly as passages and the ARE acting mainly as a reactor), as well as significant seasonal
variations of δ³⁰Si_{Si(OH)₄} in the YRE (i.e., a passage in winter and a reactor in summer; Zhang et
al., 2015), which need to be taken into account for a comprehensive understanding of estuarine Si
dynamics and ultimately also the oceanic Si cycle.

Changing diatom productivity in different seasons seems to mainly determine whether an
estuary is a passage or a reactor for riverine Si input. However, the mechanisms controlling diatom
productivity differ between estuarine systems and climate zones. Besides water residence time,
water temperature and light availability also limit diatom growth in the YRE located in the
temperate climate zone, in which the primary production rates vary seasonally by nearly two orders
of magnitude (Ning et al., 1988). Similarly, surface waters of the Elbe River Estuary also showed
a notable increase of δ³⁰Si_{Si(OH)₄} during diatom growth in October relative to in December,
indicating a biologically-controlled seasonal variability of Si dynamics in this temperate estuary (Weiss et al., 2015). The PRE, located in the subtropical climate zone, is characterized by dynamic hydrology and biogeochemical processes primarily due to the seasonal variability of the Asian monsoon, river discharge, tidal forcing, and even anthropogenic interferences (Cai et al., 2004). This implies that the PRE varies between passage and reactor of Si as reflected by its seasonally variable and spatially confined diatom blooms (Lu and Gan, 2015).

In contrast, the tropical setting and huge size of the Amazon drainage basin minimize changes in freshwater discharge, water temperature, and light availability both within and between years (Nittrouer and DeMaster, 1996). Correspondingly, previous studies only observed small seasonal variations of bSi standing stock, Chl-a concentrations, and the average primary production rate in the optimal-growth zone during an annual cycle (DeMaster et al., 1996), suggesting that the ARE acts as a “continuous reactor”, in which diatom growth throughout the year induces strong fractionation of Si isotopes. Our field data collected during two cruises in different seasons showing consistent Si isotope fractionation also support this argument (Text A2). However, not all tropical estuaries display the same pattern. For example, the Indian tropical estuaries show different monsoonal regimes and significant diatom uptake was only identified during winter (i.e., dry period, northeast monsoon season; Mangalaa et al., 2017). In the tropical Tana River Estuary, $\delta^{30}\text{Si}_{\text{Si(OH)4}}$ remained stable along the salinity gradient because of the almost complete absence of processes fractionating Si isotopes (Hughes et al., 2012).

Estuaries acting as a reactor can efficiently filter and remove riverine Si before it reaches the ocean. This retention is expected to be greater than that of other nutrients because Si is recycled through dissolution of diatom frustules, which is a slow process relative to bacterial remineralization of N and P (Chou and Wollast, 2006). Pioneering work showed that nearly 50%
of the riverine Si(OH)_4 flux is removed due to extensive diatom growth in the ARE mixing zone (Milliman and Boyle, 1975) and that 20-40% of the riverine Si(OH)_4 flux is buried as bSi in the sediments (Edmond et al., 1981; Shiller, 1996). This is, however, inconsistent with the low bSi content in the Amazon shelf sediments (0.2-0.4 wt% bSi) estimated by DeMaster et al. (1983), which suggested that burial of bSi can account for only a few percent of the riverine Si(OH)_4 flux. Consequently, the efficiency of Si retention in high-productivity estuaries was questioned by DeMaster (2002), who argued that a substantial flux of bSi would be exported from the shelf by lateral advection and to a great extent re-dissolve in open ocean waters. Later on, studies (e.g., Michalopoulos and Aller, 2004) pointed out that a large amount of Si may be trapped in deltaic sediments as rapidly formed authigenic clays, little of which would dissolve using the classical bSi-leaching method by DeMaster (1981). Awareness of the substantial underestimation of the quantity of early diagenetic alteration products of bSi was thus raised, in particular in the large tropical estuaries such as the Amazon delta (Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008). By modifying the bSi-leaching procedure and applying diagenetic models, Michalopoulos and Aller (2004) estimated a bSi burial of ~22% of the riverine Si(OH)_4 flux in the ARE. Recently, Rahman et al. (2016, 2017) used cosmogenic ^32\text{Si} at natural activity levels to determine biologically-produced bSi trapped in rapidly formed authigenic clays and suggested that ~50% of the riverine Si(OH)_4 flux may be buried in the Amazon delta.

In this study, Si(OH)_4 removal in the ARE is estimated to be 47-55% at mid- and high salinities of 15.5-29.1 in February 2012 (Text A2) and 44±7% at mid-salinities of 6.7-27.3 in May 2018 based on the two-endmember mixing model (Text A3). We thus follow the latest study (i.e., Rahman et al., 2016, 2017) and take 50% as the filtering capacity of Si(OH)_4 in the ARE. Combined with the isotopic enrichment factor $^{30}\varepsilon$ of $-1.0±0.4‰$ or $-1.6±0.4‰$ obtained in the ARE, the
$\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ signatures entering the Atlantic Ocean from the ARE increase by 0.7±0.2‰ following the Rayleigh model (Eq. 1) or 0.8±0.2‰ following the steady state model (Eq. 4). Note that a part of bSi formed during Si(OH)$_4$ removal might be exported and re-dissolve in the open ocean, which would release light Si isotope signatures into the surrounding water. In this context, the estimated increase of 0.7-0.8‰ is most likely an upper limit.

4.4. Implications for the Si isotopic composition of the global riverine input to the ocean

Globally, Frings et al. (2016) adopted a low filtering capacity of 10% based on earlier work of DeMaster (2002) and estimated an increase of ~0.1‰ in riverine $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ signatures entering the ocean. However, Treguer and De La Rocha (2013) re-estimated the estuarine removal flux of Si to be 1.5±0.5 Tmol yr$^{-1}$ consisting of bSi deposition and its storage via authigenic clay formations, which is consistent with the preservation flux in proximal coastal zones (~1.4 Tmol yr$^{-1}$) estimated by Laruelle et al. (2009). We thus adopt the global estuarine filtering capacity of ~22% in Treguer and De La Rocha (2013). Assuming that all the estuarine Si removal induces Si isotope fractionation and applying the isotopic enrichment factor $^{30}\varepsilon$ of −1.0±0.4‰ or −1.6±0.4‰ obtained in the ARE, the increase of riverine $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ signatures entering the ocean globally is estimated to be 0.2±0.1‰ (Rayleigh model; Eq. 1) or 0.3±0.2‰ (steady state model; Eq. 4). We contend that this is a first order estimation, which needs further constraints, while several on-going studies suggest that the global estuarine Si removal flux of 1.5±0.5 Tmol yr$^{-1}$ is likely an underestimation. For example, Rahman et al. (2017) revisited Si sink in different delta systems and pointed out a higher sedimentary Si storage flux of 3.5-3.9 Tmol yr$^{-1}$ as authigenic clay in tropical and subtropical deltas. In this context, our estimation of 0.2-0.3‰ probably represents a lower limit of the increase in $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ by global estuaries. This also suggests that the estuarine reactors potentially exert a much larger influence on riverine Si isotope fluxes than previously
thought.

5. CONCLUSIONS

δ\(^{30}\)Si\(_{(OH)4}\) in the ARE, YRE, and PRE displayed significant differences in distribution patterns, reflecting the role of large river estuaries as either a passage or a reactor in delivering riverine Si to the ocean. While conservative mixing between river water and seawater primarily modulated both surface Si(OH)\(_4\) concentrations and δ\(^{30}\)Si\(_{(OH)4}\) signatures in the YRE and PRE presented in this study, significant Si isotope fractionation during diatom growth was observed over the entire salinity range in the ARE. We estimate isotopic enrichment factors \(^{30}\varepsilon\) of −1.0±0.4‰ (Rayleigh model) or −1.6±0.4‰ (steady state model) in the ARE, both of which are within error consistent with the consensus average value of −1.1‰ in various oceanic settings. Applying these \(^{30}\varepsilon\) values, we re-evaluate the influence that estuaries exert on the land-to-ocean Si isotope fluxes on a global scale and suggest that the present riverine δ\(^{30}\)Si\(_{(OH)4}\) input signature into the ocean is elevated by 0.2-0.3‰ compared to scenarios without estuarine diatom productivity. In addition, distinct seasonal variations of Si isotope behavior in the YRE are found by comparing our data to previously reported measurements. This seasonality and its underlying causes require future examination in large river estuaries for comprehensively understanding their impacts on the global Si cycle and the Si isotope mass balance.
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Table 1. Salinity, dissolved silicate (Si(OH)$_4$) concentrations, and dissolved silicon isotopic compositions ($\delta^{30}$Si$_{Si(OH)4}$) in the surface waters of the Amazon, Yangtze, and Pearl River estuaries and adjacent shelf areas. “Bracketing measurement” denotes $\delta^{30}$Si$_{Si(OH)4}$ analysis for a sample on a single day. “Mean” denotes the average $\delta^{30}$Si$_{Si(OH)4}$ based on repeated bracketing measurements from different days. “Final reported data” present $\delta^{30}$Si$_{Si(OH)4}$ of the mean except that for two samples measured once, $\delta^{30}$Si$_{Si(OH)4}$ of bracketing measurement was used.

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<th>Long. (°E)</th>
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<th>$\delta^{30}$Si$<em>{Si(OH)4}$ (‰ ± 2SD$</em>{bracketing}$)</th>
<th>Mean $\delta^{30}$Si$<em>{Si(OH)4}$ (‰ ± 2SD$</em>{repeated}$)</th>
<th>Final reported data $\delta^{30}$Si$_{Si(OH)4}$ (‰ ± 2SD)</th>
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<td>−47.79</td>
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<td>16.3</td>
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<td>1.75 ± 0.15</td>
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<td>M147_56-F*</td>
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<td>3.02 ± 0.17</td>
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<td><strong>Pearl River Estuary (August 2012)</strong></td>
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<td>C1</td>
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<td>113.54</td>
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<td>A01</td>
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<td>A02</td>
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<td>113.70</td>
<td>0.9</td>
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<td>1.44 ± 0.10</td>
<td>1.45 ± 0.13</td>
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<td>A03</td>
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<td>113.71</td>
<td>1.6</td>
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<td>22.52</td>
<td>113.75</td>
<td>1.3</td>
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<td>1.38 ± 0.16</td>
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<td>113.76</td>
<td>6.5</td>
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<td>8.1</td>
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<td>11.8</td>
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<td>A08</td>
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<td>16.5</td>
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<td>1.77 ± 0.17</td>
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<td>113.94</td>
<td>25.2</td>
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<td>1.71 ± 0.21</td>
<td>1.70 ± 0.03</td>
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<td>1.73 ± 0.08</td>
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<td>114.01</td>
<td>31.1</td>
<td>14.9</td>
<td>1.76 ± 0.20</td>
<td>1.60 ± 0.15</td>
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</table>

§‰ ± 2SD_{bracketing} is the average δ^{30}\text{Si}_{\text{Si(OH)4}} together with 2 standard deviations estimated from the bracketing measurements on a single day.

† ‰ ± 2SD_{repeated} is the average δ^{30}\text{Si}_{\text{Si(OH)4}} together with 2 standard deviations estimated from the repeated bracketing measurements from different days.

† 2SD for the final reported data represents the long-term external reproducibility of ±0.20‰, except that for few samples with 2SD_{repeated} larger than ±0.20‰, the 2SD_{repeated} was used.

* \text{Si(OH)4} in the samples was pre-concentrated via brucite coprecipitation before cation-exchange chromatography.
**Figure Captions**

**Figure 1.** Bathymetric map showing the locations of sampling stations in the Amazon, Yangtze, and Pearl River estuaries and adjacent shelf areas.

**Figure 2.** Surface distributions of salinity (a, e, and j), dissolved silicate (Si(OH)₄; b, f, and k), dissolved silicon isotopic compositions (δ⁳⁰Si(Si(OH)₄); c, g, and l), total suspended matter (TSM; h and m), and chlorophyll a (Chl-a; d, i, and n) in the Amazon (upper), Yangtze (middle), and Pearl (below) River estuaries and adjacent shelf areas.

**Figure 3.** Dissolved silicate (Si(OH)₄) concentrations and dissolved silicon isotopic compositions (δ⁳⁰Si(Si(OH)₄)) distributions along salinity gradients in the Amazon (a and b), Yangtze (c and d), and Pearl (e and f) River estuaries. The solid lines in each panel predict the conservative mixing for Si(OH)₄ or δ⁳⁰Si(Si(OH)₄) between the river water and seawater endmembers, which are selected according to field measurements at the lowest and highest salinities (squares). One exception is that the δ⁳⁰Si(Si(OH)₄) value of seawater endmember in the Amazon River Estuary is estimated based on a linear relationship between δ⁳⁰Si(Si(OH)₄) and ln(Si(OH)₄) (Fig. A5). In panels (b), (d), and (f), the error bars of the field δ⁳⁰Si(Si(OH)₄) data are the long-term external reproducibility of ±0.20‰ or the 2 standard deviations estimated from the repeated measurements if they are larger than ±0.20‰. The dashed lines above and below the corresponding solid line indicate errors deduced from the uncertainty in estimating the δ⁳⁰Si(Si(OH)₄) endmember values.

**Figure 4.** Dissolved inorganic nitrogen (DIN, nitrate plus nitrite) and dissolved inorganic phosphate (DIP) distributions along salinity gradients in the Amazon (a and b), Yangtze (c and d), and Pearl (e and f) River estuaries. The solid lines in each panel predict the conservative mixing for DIN or DIP between the river water and seawater endmembers, which are estimated according to field measurements at the lowest and highest salinities (squares). In panels (c) and (d), the
dashed lines and equations indicate the linear regression analysis for all data points over the entire salinity range.

**Figure 5.** Dissolved silicate (Si(OH)_4) concentrations and dissolved silicon isotopic compositions (δ³⁰Si_{Si(OH)₄}) distributions along salinity gradients in the Yangtze River Estuary in March 2012 (a and b) and July 2011 (c and d). Data were previously published in Zhang et al. (2015). The solid lines in each panel predict the conservative mixing for Si(OH)_4 or δ³⁰Si_{Si(OH)₄} between the river water and seawater endmembers, which are selected according to field measurements at the lowest and highest salinities (squares). In panels (b) and (d), the error bars of the field δ³⁰Si_{Si(OH)₄} data are the 2 standard deviations reported in Zhang et al. (2015). The dashed lines above and below the corresponding solid line indicate errors deduced from the uncertainty in estimating the δ³⁰Si_{Si(OH)₄} endmember values, which is the long-term external reproducibility of ±0.10‰ for the Si isotope analyses in Zhang et al. (2015).

**Figure 6.** Monthly average wind velocity vectors around the Yangtze River Estuary in July 2011 (a), March 2012 (b), and March 2015 (c). The wind field is extracted from the reanalysis dataset of ERA-Interim (https://www.ecmwf.int/en/forecasts/datasets/archive-datasets/reanalysis-datasets/era-interim).
Figure 3.
Figure 4.
Figure 5.
Figure 6.