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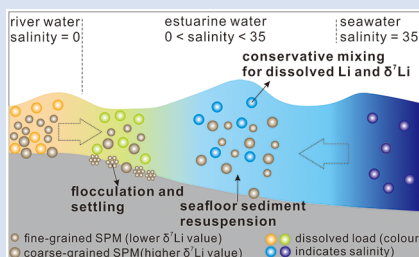
## Decoupling of dissolved and particulate Li isotopes during estuarine processes

C. Yang<sup>1,2</sup>, N. Vigier<sup>2</sup>, E. Lian<sup>1</sup>, Z. Lai<sup>1</sup>, S. Yang<sup>1\*</sup>



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### Abstract



Lithium isotopes in marine authigenic or detrital sedimentary archives have been recently used to trace continental weathering over geologic timescales. However, interpretations are predominantly based on the assumption that riverine Li isotopic signals can be propagated through estuaries without modification. Here, we verify this hypothesis by investigating the behaviour of Li isotopes in the Changjiang (Yangtze) River estuary. We observe a conservative mixing of dissolved Li and its isotopes between the Changjiang River water and seawater. The dissolved  $\delta^7\text{Li}$  yields a non-linear increase with salinity, and a significant increase occurs during the initial water mixing. Through the studied transect, estuarine flocculation and resuspension processes cause the homogenisation of offshore particulate  $\delta^7\text{Li}$  values, which are

close to the average composition of upper continental crust. This study provides clear and direct evidence that the riverine dissolved Li isotopic signal is not modified during estuarine processes in large rivers, but caution should be exercised when using detrital  $\delta^7\text{Li}$  in marginal seas to investigate past continental weathering.

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### Introduction

As critical interfaces between continents and oceans, estuaries typically feature gradients of ionic strength and suspended particle concentration, providing an ideal environment for studying land–sea and water–sediment interactions. Over the last decades, numerous studies have demonstrated that riverine elemental fluxes and isotope compositions (*e.g.*, Si, Sr, and Nd) can be modified by physical, chemical, and/or biological processes during their transport through estuaries (Lacan and Jeandel, 2005; Jones *et al.*, 2012, 2014; Zhang *et al.*, 2020). For instance, the dissolution of basaltic particles and Ca–Na exchange on clay minerals in saline water were considered to play non-negligible roles in global climate stabilisation (Gislason *et al.*, 2006; Tipper *et al.*, 2021). Investigating elemental and isotopic alteration of particles and water in estuaries is thus essential for a better understanding of oceanic elemental cycles, and of the carbon cycle in particular.

River Li isotopes ( $\delta^7\text{Li}$ ) are thought to be a powerful proxy of continental weathering (Huh *et al.*, 1998; Wang *et al.*, 2015; Dellinger *et al.*, 2017). During weathering processes, the light  $^6\text{Li}$  isotope is preferentially incorporated into the solids, causing the dissolved phase to be isotopically heavy. To date, Li isotopes registered in bulk carbonate or detrital sedimentary archives have been widely applied to assess changes of continental weathering regimes during mass extinctions and long or short term global warming/cooling events (Misra and

Froelich, 2012; Pogge von Strandmann *et al.*, 2013; Bastian *et al.*, 2017; Yang *et al.*, 2021). All these studies implicitly or explicitly assume that riverine Li fluxes to the ocean and their isotopic signals behave conservatively in estuaries. However, thus far, this assumption has not been verified over large scales. Indeed, few case studies have highlighted either the conservative or non-conservative behaviour of Li isotopes in small estuaries (Pogge von Strandmann *et al.*, 2008; Murphy *et al.*, 2014). For instance, Pogge von Strandmann *et al.* (2008) observed an increase of particulate  $\delta^7\text{Li}$  values (from  $\sim 0$  ‰ to  $\sim 5$  ‰) along a transect in the Borgarfjörður estuary (Iceland) related to ongoing weathering of suspended particles.

Major rivers in Asia, such as the Changjiang (Yangtze) River (Fig. S-1a), drain large continental basins and deliver huge amounts of detrital particles, dissolved elements, and nutrients to the marginal seas and oceans. Detailed investigations of elemental geochemical behaviours in these estuaries provide constraints on the application of Li isotopes as a robust weathering proxy. We present Li isotopic data for the dissolved load, suspended particulate matter (SPM), and their exchangeable phase (see Supplementary Information) in the Changjiang River estuary (Fig. S-1). Our primary goal is to investigate the dissolved and particulate Li isotopic compositions during the mixing processes, and to evaluate the propagation and alteration of terrestrial Li isotopic signals in a large, turbid, and highly dynamic river estuary.

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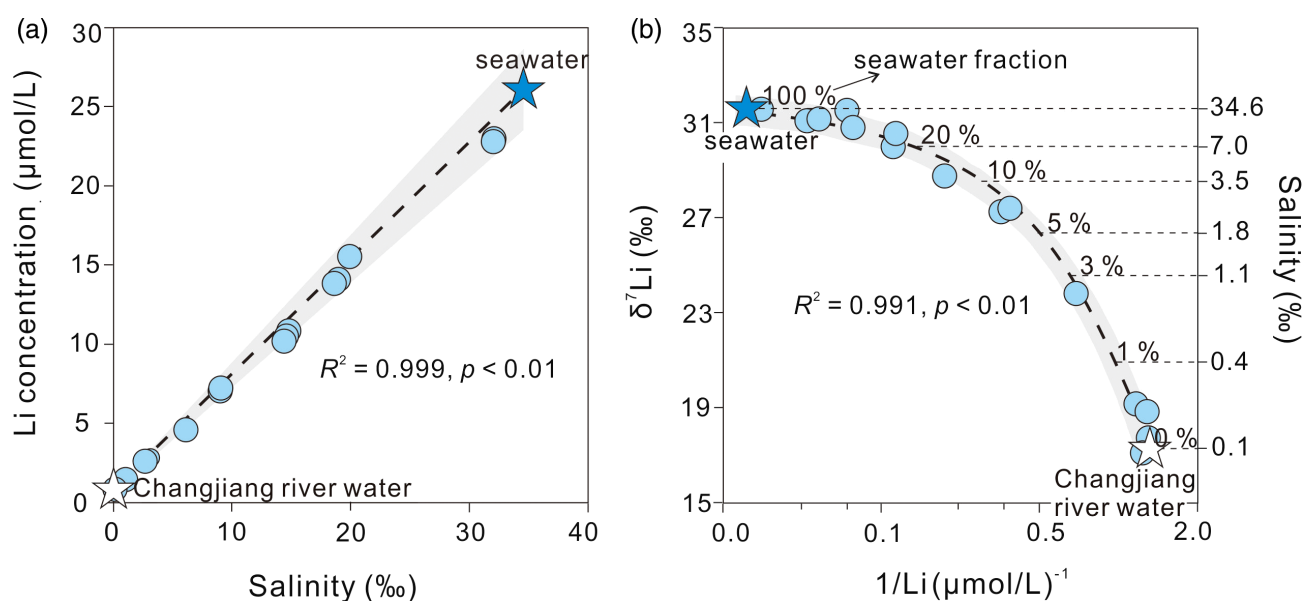
## Evidence for Conservative Mixing of Dissolved Li and $\delta^7\text{Li}$

As shown in Figure 1a, the dissolved Li concentrations are linearly correlated with salinity, suggesting that the Li-poor Changjiang River water and Li-rich seawater are the only two major contributors of dissolved Li in the mixing zone. This salinity–Li relationship is consistent with observations made in the St. Lawrence estuary and the Gulf of Papua (Stoffyn-Egli, 1982; Brunskill *et al.*, 2003). However, the use of Li concentrations alone does not permit identification of all the processes potentially occurring in the mixing zone. Indeed, as indicated by experimental investigations and by previous studies of Icelandic estuaries, isotopic exchanges may modify riverine dissolved isotopic compositions without significantly affecting elemental concentrations (Jones *et al.*, 2012, 2014). When we report the dissolved  $\delta^7\text{Li}$  as a function of the inverse of the Li concentration (Fig. 1b), all the samples are distributed along the theoretical mixing line between the Changjiang River water and seawater. These results *a priori* support the conservative behaviour of the dissolved Li and its isotopes along the studied transect.

The relatively high seawater Li concentration may mask some of the Li release during SPM dissolution (Morin *et al.*, 2015) or Li uptake by SPM (Pogge von Strandmann *et al.*, 2008). The dissolution rates of quartz, albite, and clays, which are major constituent minerals of Changjiang SPM, are relatively slow, because they have undergone intermediate to strong chemical weathering in the catchment. For instance, less than 0.1 % of kaolinite and illite would be expected to dissolve in seawater annually (Jeandel and Oelkers, 2015). As a first approximation, we can assume that 0.1 % of the SPM Li could be released by dissolution in the Changjiang Estuary, although the average residence time of the Changjiang diluted water plume is only 5.4 d (Gu *et al.*, 2012). A mass balance model suggests that, in that case, the dissolved  $\delta^7\text{Li}$  would decrease by  $\sim 0.2$  ‰ (see Supplementary Information), which is within

analytical uncertainties. For the possible influences of Li uptake, modelling results suggest that the dissolved  $\delta^7\text{Li}$  values would be significantly altered in the maximum turbidity zone where suspended sediment concentration can reach  $\sim 2$  g/L (for detailed calculations, see Supplementary Information and Fig. S-2). This is apparently inconsistent with the conservative behaviour of dissolved Li and  $\delta^7\text{Li}$  observed in this study (Fig. 1). Thus, we suggest that the influence of sediment–water interactions on dissolved Li is insignificant in the Changjiang Estuary. Additionally, submarine groundwater discharge (SGD,  $0.2\text{--}1.0 \times 10^9 \text{ m}^3 \text{ d}^{-1}$ ) was estimated to be 6–30 % of the river discharge during the flooding season in the Changjiang Estuary (Gu *et al.*, 2012). Although no Li data were reported for this discharge, our results imply that the SGD plays a small role in the isotope compositions of the Li flux to the East China Sea. A similar conclusion has been drawn by Bagard *et al.* (2015) for assessing the modern Li isotopic budget of the ocean, based on investigation of the Li flux and  $\delta^7\text{Li}$  of groundwater in the Ganges–Brahmaputra downstream basin.

The conservative mixing of dissolved Li and Li isotopes observed in the Changjiang Estuary exhibits a nonlinear  $\delta^7\text{Li}$  variation as a function of salinity. Indeed, the dissolved  $\delta^7\text{Li}$  values increase significantly in the head of the estuary, during the initial mixing between river water and seawater (Fig. 1b). This is because seawater is enriched in Li and isotopically heavy compared to river water. We calculate that the addition of 1 % seawater to the Changjiang River water causes the  $\delta^7\text{Li}$  value to increase by  $\sim 3$  ‰ (Supplementary Information). When salinity exceeds 7 ‰, the dissolved  $\delta^7\text{Li}$  value remains more or less constant (between  $\sim 30$  ‰ and 31.6 ‰). Due to differences in catchment lithologies, climate regimes, and other environmental parameters, the dissolved Li concentrations and  $\delta^7\text{Li}$  values of river waters worldwide yield significant spatial and seasonal variations. Nevertheless, as discussed above, physical mixing of different water masses cannot modify the conservative behaviours of dissolved Li and Li isotopes in estuaries. Therefore, the fast response and significant variation of riverine  $\delta^7\text{Li}$  to a small volume of seawater addition observed in this study



**Figure 1** (a) Variations of dissolved Li concentration as a function of salinity, and (b) variations of dissolved  $\delta^7\text{Li}$  as a function of the inverse of the molar Li concentration ( $1/\text{Li}$ ). The x-axis in (b) is logarithmic. The dashed lines and shaded areas represent calculated conservative mixing between seawater (dark blue star) and Changjiang River water (white star). The mass balance model is provided in the Supplementary Information. The shaded areas are estimated using the Monte Carlo method, given that analytical uncertainties in Li concentrations and  $\delta^7\text{Li}$  are 10 % and 0.6 ‰, respectively. The analytical uncertainty for each  $\delta^7\text{Li}$  value is smaller than the symbol size.

is expected to be universal. Indeed, in most large rivers, dissolved Li concentrations are two orders of magnitude lower than that of seawater, and  $\delta^7\text{Li}$  values are 5–10 ‰ less (Huh *et al.*, 1998). Caution must therefore be paid to this effect when sampling rivers at their mouths for quantifying their contribution of Li and  $\delta^7\text{Li}$  flux to the ocean.

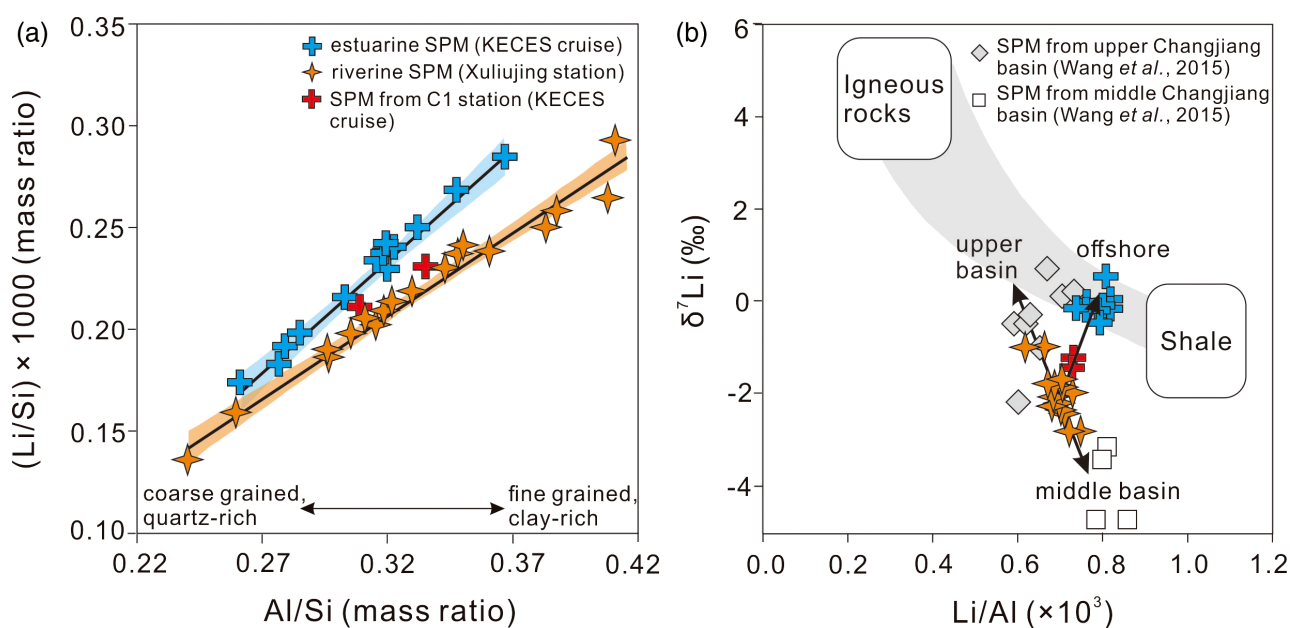
## Particulate Li and $\delta^7\text{Li}$ Behaviour in the Estuary

At the XLJ gauging station, SPM Li concentrations,  $\delta^7\text{Li}$  values, and suspended sediment concentrations (SSC) exhibit seasonal and depth variations (see Fig. S-4). In contrast, depth profiles performed along the estuarine transect exhibit negligible or small variations, and a noticeable increase can be observed as one moves offshore (Fig. S-5). Generally, depending on the grain size, density, and shape of detrital minerals, hydrodynamic sorting in riverbeds and floodplains may cause mineralogical and geochemical fractionation during SPM transport (Guo *et al.*, 2018). The sediment Al/Si ratio allows us to constrain the effects of hydrological sorting on isotope proxies (Dellinger *et al.*, 2014). As shown in Figure 2a, Li/Si ratios positively correlate with Al/Si ratios for both riverine SPM (orange symbols) and estuarine SPM (blue symbols), suggesting a dominant control on Li concentrations by Al-rich materials (*e.g.*, clays) present in the SPM (Vigier *et al.*, 2008; Dellinger *et al.*, 2014). Nevertheless, the river and estuary data follow significantly different slopes (Fig. 2a). This cannot be attributed to adsorption in the estuary as exchangeable Li accounts for less than 1 % of the SPM Li and thus has a negligible influence on particulate Li (see Supplementary Information). As indicated by previous studies, this difference in slope can be caused either by ongoing weathering (Lupker *et al.*, 2012) or by a change of sediment source (Yang *et al.*, 2019). In the former case, the steeper slope defined by the estuarine SPM data may indicate clay formation in the estuarine environment. However, the formation of clay minerals along the sampling transect is not supported by XRD results

(Table S-3). On the other hand,  $\delta^7\text{Li}$  values of SPM samples show no shift toward seawater (Fig. S-3a), in contrast to the altered  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios observed in Icelandic estuaries, for instance (Jones *et al.*, 2014). This discrepancy may be explained by the low chemical reactivity of Changjiang-derived SPM, which mainly come from highly weathered and recycled continental sediments and shales. All these observations suggest that SPM Li is not controlled by a chemical process (*e.g.*, water-sediment interactions) in the Changjiang Estuary, and a physical process could be the dominant factor, as discussed below.

More information can be inferred from the  $\delta^7\text{Li}$  vs. Li/Al diagram (Dellinger *et al.*, 2017). As shown in Figure 2b, all the river SPM samples are isotopically fractionated compared to their likely parent lithologies because they contain weathering products formed within the basin (Yang *et al.*, 2021). SPM collected in the lower reaches logically represents an average composition of fine particulates from the whole basin. Accordingly,  $\delta^7\text{Li}$  and Li/Al variations of SPM collected at the XLJ station are best explained by a simple binary mixing between sediments collected in the upper Changjiang basin and those from the middle basin (Fig. 2b). In contrast,  $\delta^7\text{Li}$  and Li/Al ratios of SPM collected along the estuarine transect show a distinct trend. From the C1 site to offshore sites, these values progressively increase towards the binary mixing trend defined between un-weathered shale and igneous rocks (Dellinger *et al.*, 2014). Quartz, feldspar, illite, and kaolinite are four major minerals (*i.e.* each accounting for >10 %) of terrigenous sediments from the Changjiang River (Yang *et al.*, 2002). According to the XRD results, quartz contents in the estuarine SPM increase from ~26 % to ~41 % in the offshore direction, while illite and kaolinite contents both decrease by ~10 % (Table S-3). Thus, the trend observed for estuarine SPM in Figure 2b can be explained by a physical loss of clay minerals and/or a gain of Si-rich primary minerals.

Flocculation and resuspension of fine sediments are two fundamental processes occurring in river estuaries. When encountering alkaline seawater, river-borne clay minerals, especially kaolinite, can be easily aggregated and deposited rapidly



**Figure 2** (a) Variations of Li/Si ratios as a function of Al/Si ratios for riverine (orange, including the most inland site C1 in red) and estuarine SPM (blue), and (b)  $\delta^7\text{Li}$  versus Li/Al ratios for the same samples. The linear correlations between Li/Si and Al/Si are displayed with 95 % confidence intervals (shaded areas). The igneous rocks and shale endmembers in (b) are modified after Dellinger *et al.* (2014), and the shaded area reflects their mixing. Changjiang River SPM data are from Wang *et al.* (2015).

onto the seafloor. Milliman *et al.* (1985) once estimated that nearly 40 % of the sediment load can be trapped in the Changjiang Estuary during flood season. Seafloor sediments can be resuspended by strong tidal and wind-driven currents, as supported by the several orders of magnitude higher SPM concentration observed at sites C6–C8 than at landward or seaward sites (see Fig. S-5c). Therefore, the offshore transport of SPM in the Changjiang Estuary may result in the preferential flocculation and deposition of clay minerals during the flooding season, while primary minerals or other fine-grained particles tend to be resuspended and carried seaward by currents. Consequently, these physical processes result in a visible increase of SPM  $\delta^7\text{Li}$  values (by  $\sim 1.2\%$ ) from the most inland site (C1) to the most offshore sites.

## Implications for Li Isotopes as Tracers of Continental Weathering

Previous studies suggest that both the dissolved and particulate  $\delta^7\text{Li}$  values related to clay formation are powerful tracers of weathering processes. Our results demonstrate that their behaviours are visibly decoupled in the estuary. During estuarine flocculation and resuspension of river-borne fine particles, the SPM  $\delta^7\text{Li}$  values progressively approach the upper continental crust value. This process is distinct from the general control of hydrodynamic sorting on elemental geochemical compositions during source-to-sink river sediment transport (Lupker *et al.*, 2012; Dellinger *et al.*, 2014). Although the effects of ongoing weathering are negligible in Changjiang-like estuaries, an increase of particulate  $\delta^7\text{Li}$  values would be expected in rivers draining basaltic terrains (Pogge von Strandmann *et al.*, 2008). Consequently, the utility of detrital  $\delta^7\text{Li}$  values for tracing past continental weathering in coastal and marginal seas seems to be more complicated than for the isotopic values of the dissolved phase (Yang *et al.*, 2021). Caution should therefore be exercised when using  $\delta^7\text{Li}$  values, and other similar sediment geochemical proxies, measured in bulk sediments from marginal seas to reconstruct past continental weathering.

Our data along a salinity transect provide the first and clear evidence of the conservative behaviour of dissolved Li and Li isotopes during estuarine mixing in a large, particle-rich river. Differing from the case study on Li isotopes in a small Icelandic estuary (Borgarfjörður) draining dominantly basaltic terrains (Pogge von Strandmann *et al.*, 2008), the large Changjiang basin contains various rock types, including intensely weathered shales and Ca-Mg-depleted sediments. This strongly supports the notion that information on continental weathering carried by the dissolved loads (*i.e.*  $\delta^7\text{Li}$ ) of large rivers can be propagated to the ocean without significant modification. Scavenging processes thus have negligible influence on aqueous Li behaviour, at least in Changjiang-like basins and estuaries, which verifies the assumption of conservative behaviour when using Li isotopes in marine authigenic archives to reconstruct past continental weathering variations and related carbon cycles (Misra and Froelich, 2012). Additionally, it is noteworthy that  $\delta^7\text{Li}$  values of estuarine waters significantly increase with seawater addition at low salinities. This highlights the need for precise salinity assessments when sampling estuarine waters for quantifying global Li and  $\delta^7\text{Li}$  budgets and continental fluxes to the ocean.

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## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2133>.



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## Decoupling of dissolved and particulate Li isotopes during estuarine processes

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### Supplementary Information

The Supplementary Information includes:

- Materials and Methods
- Estimation of Dissolved Li and  $\delta^7\text{Li}$  Values Assuming Conservative Mixing
- The Potential Influences of SPM Li Release and Uptake on Dissolved Li Isotopes
- Isotopic Exchange Between Water and Particles
- Tables S-1 to S-4
- Figures S-1 to S-5
- Supplementary Information References

### Materials and Methods

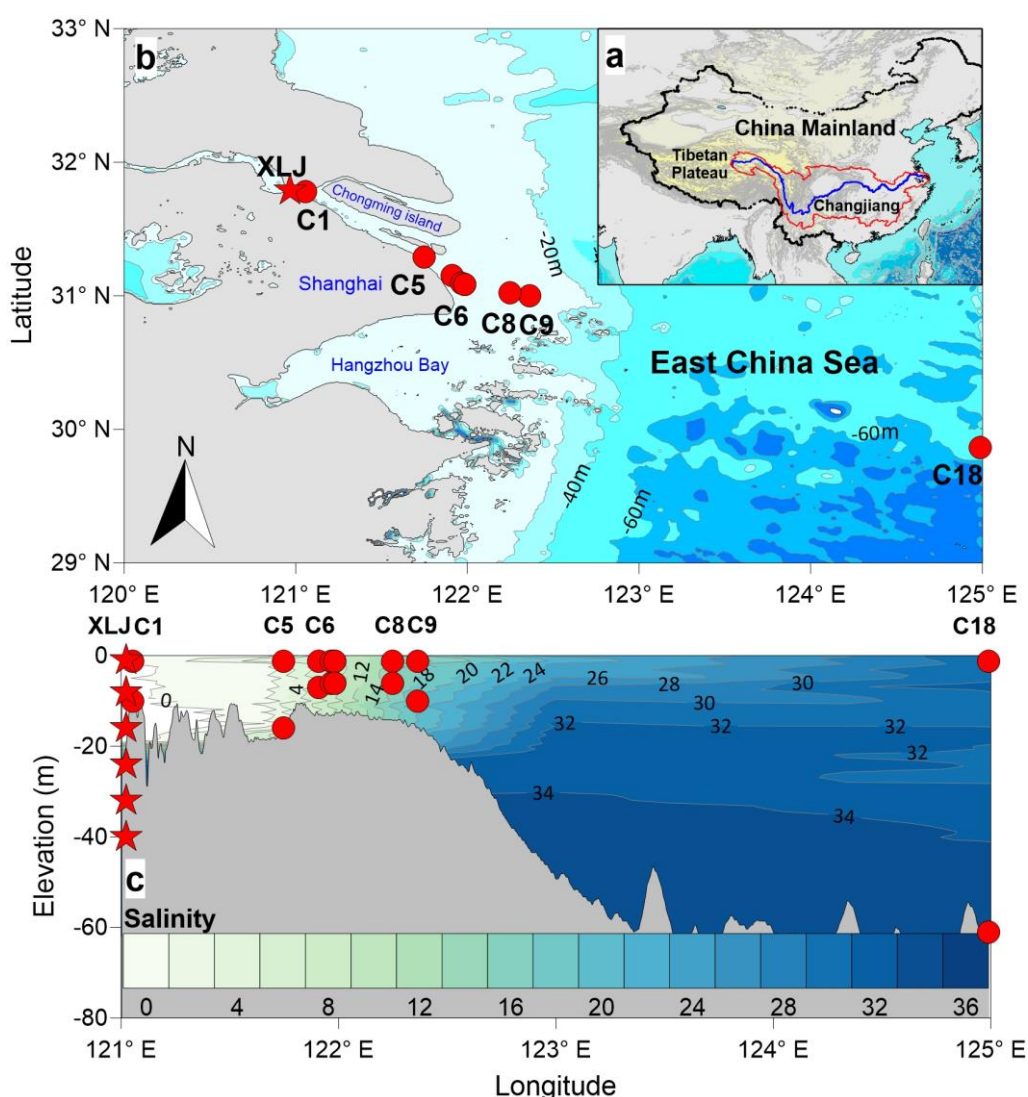
#### Sample collection

The Changjiang (Yangtze) River is one of the largest rivers in the world (Fig. S-1a), which historically delivered ~470 Mt/yr of sediment and ~900 km<sup>3</sup>/yr of water into the East China Sea (Milliman and Farnsworth, 2011). Generally, the sediment flux and water discharge vary seasonally with the change of monsoon climate, yielding higher values in flood season and lower in dry season. The flood season (May–October) accounts for >70 % of sediment flux and ~60 % of water discharge (Xu and Milliman, 2009). The Changjiang Estuary is generally river-dominated, with the width increasing seaward from 5.8 km at Xuliujing station to nearly 90 km at the river mouth bar. The tide within the Changjiang Estuary is semidiurnal, and the average tidal range is about 2.7 m near the river mouth, with the maximum reaching 4.6 m. Consequently, the strong river-sea interaction can resuspend the fine-grained seafloor sediments, and develop a turbidity maximum zone in the river mouth bar (Shi, 2010).

During the KECES (Key Elements Cycling in the Changjiang-Estuary-Shelf Transect) cruise organised by the State Key Laboratory of Marine Geology in September 2019, we performed systematic observations and sampled along a 2D transect of ~400 km in the mixing zone of the Changjiang Estuary (Fig. S-1b). Water and suspended particulate matter (SPM) samples were collected over several depth profiles from salinity 0.1 to salinity 34.6 (Fig. S-1c). The water samples were first collected using a 60 L bottle, and filtered on-site immediately through 0.45  $\mu\text{m}$  cellulose acetate membranes. Then, about 50 ml of the dissolved load (an operational definition of the fraction in water that pass through 0.45  $\mu\text{m}$  pore-size filter) were acidified to  $\text{pH} < 2$  with concentrated  $\text{HNO}_3$ , and stored in pre-cleaned

centrifuge tubes. These acidified water samples were used for measurement of elemental concentrations and Li isotopes. After the filtering, the cellulose acetate membranes were stored in refrigerator with a temperature of 4 °C. Additionally, SPM samples were also collected along depth profiles at the Xuliujing (XLJ in Fig. S-1b), just upstream of the estuarine mixing zone and also the last hydrological station in the Changjiang mainstream.

In the laboratory, the SPM samples were dried to constant weight at 40 °C in a hot-air convection oven. The SPM exchangeable phase was extracted for estuarine samples, following the established procedures by Vigier *et al.* (2008). Briefly, 10 ml of 1 N ammonium chloride was added to the pre-cleaned tube, mixing with about 0.1 g SPM samples. The tube was placed on a rotary shaker to ensure sufficient saturation. After 1 h shaking, the slurry was then centrifuged at 4000 rpm and finally the supernatant was decanted. After two-times extraction, the residue was washed with the ultrapure Milli-Q water and dried for measurement of elemental concentrations and Li isotope compositions.



**Figure S-1** Maps showing (a) the Changjiang drainage basin, (b) sampling sites (red dots) along an estuarine transect, (c) salinity variation and sampling strategy along the depth profiles. The blue colour associated with isobath in (b) refers to water depth below the modern sea-level. The XLJ SPM samples (red stars) were collected repeatedly along a depth profile in June, August and October 2014 at Xuliujing gauging station.



### Salinity, Temperature, pH and SPM concentration analyses

With the sampling, the salinity, temperature and pH were measured on-site. Temperature data were obtained using a conductivity-temperature-depth (CTD) profiler (Sea-Bird 911plus). The salinity was measured using a portable multifunction water quality meter (Multi-350i, WTW Company, Germany). The pH measurement was carried out by pH-meter (PHS-3C), with analytical uncertainty of 0.01. The suspended sediment concentration (SSC) was determined by weighting the difference of dried membranes before and after water filtration of a given volume.

### Mineralogical analyses

The major mineral compositions of SPM samples were measured by X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer at the State Key Laboratory of Marine Geology, Tongji University. About 1.5 g SPM samples were ground to <200 mesh in an agate mortar, and the powder was then pressed into metal sample holder for XRD measurement. Mineral contents were estimated using Siroquant software, with uncertainty of ~5 %.

### Elemental concentration analyses

About 50 mg powder samples were ignited in muffle furnace at 600 °C in order to remove organic matter before acid digestion. Afterwards, these powder samples were dissolved with a mixture of 1:1 concentrated HNO<sub>3</sub> and HF in a tightly closed Teflon vessel for at least 48 h at a temperature of 190 °C. After drying, samples were re-dissolved in HNO<sub>3</sub>. The dried samples were re-digested in 2 ml 30 % HNO<sub>3</sub> with a temperature of 190 °C. Finally, the solution was diluted to ~100 g with 2 % HNO<sub>3</sub> for elemental measurement. The dissolved load was measured directly, as they have been acidified during sampling. The concentrations of major elements were measured by Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES, IRIS Advantage). The Li concentration was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7900). The accuracy and precision were determined by repeat analyses of the sediment geostandard GSD-9, with accuracy better than 5 % (Table S-4). All the work was done at the State Key Laboratory of Marine Geology, Tongji University.

### Li isotope composition analyses

The measurement of Li isotopes was performed using a Thermo Scientific™ Neptune Plus multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Ecole Normale Supérieure de Lyon (National Facilities). The Li purification was conducted in a clean laboratory at Laboratory of Oceanography of Villefranche-sur-Mer (LOV), Sorbonne University, following the method of chromatographic separation described in Vigier *et al.* (2008). Before isotopic analyses, the purified Li solution was converted into nitric form, and diluted to ~5 ppb Li in 0.05 N HNO<sub>3</sub>. The NIST L-SVEC standard was measured before and after each sample to monitor instrument drift. The ~5 ppb Li solution generally yielded a <sup>7</sup>Li signal exceeding 4 V, with an acid blank of generally 30 - 40 mV, systematically subtracted. The Li isotopic ratios are reported in  $\delta$  notation, representing <sup>7</sup>Li/<sup>6</sup>Li ratios of samples deviated from the ratio of L-SVEC standard. The long-term external uncertainty (two standard deviations, 2SD) monitored by measuring Li7-N pure solution is 0.6 ‰. The repeated measurements of BE-N basaltic standard yield mean  $\delta^7\text{Li}$  value of  $+5.0 \pm 0.4$  ‰ (2SD), which is well in the range of other published values (GeoReM database: <http://georem.mpch-mainz.gwdg.de/>).

## Estimation of Dissolved Li and $\delta^7\text{Li}$ Values Assuming Conservative Mixing

Water samples collected at site C1 (see Fig. S-1b) have a salinity of 0.0, and are thus used as the Changjiang river water end-member. The corresponding dissolved Li concentration and isotope composition are 0.8  $\mu\text{mol/l}$  and 17.5 ‰, respectively. This is slightly different from values of river water (*i.e.* 0.5  $\mu\text{mol/l}$  and 20.3 ‰) collected in August 2006 in the lower Changjiang reaches (Wang *et al.*, 2015), which is possibly caused by seasonal variations and/or by an increasing contribution from urban waste water. As found for the Han River crossing Seoul city in South Korea (Choi *et al.*, 2019), riverine dissolved Li can be impacted by anthropogenic activities. The use of lithium-ion battery also increased dramatically over recent years in China (Liu *et al.*, 2021), which may have somewhat underestimated influence on the dissolved Li compositions in the Changjiang River. The water sample collected at site C18 with the

highest salinity (*i.e.* 34.6, Fig. S-1c) has dissolved Li concentration and  $\delta^7\text{Li}$  values of 26.1  $\mu\text{mol/l}$  and 31.6 ‰, diagnostic of seawater end member with the homogeneous ocean value (Misra and Froelich, 2012). This observation is due to much longer residence time of Li in the ocean ( $>1$  Myr) than the oceanic water mixing time ( $\sim 1.5$  kyr).

The conservative mixing of dissolved Li ( $[\text{Li}]_{diss.}$  and  $\delta^7\text{Li}_{diss.}$ ) between the Changjiang river water (r) and seawater (s) can be represented by the following equations:

$$[\text{Li}]_{diss.} = [\text{Li}]_r \times f_r + [\text{Li}]_s \times (1 - f_r) \quad \text{Eq. S-1}$$

$$\delta^7\text{Li}_{diss.} \times [\text{Li}]_{diss.} = \delta^7\text{Li}_r \times [\text{Li}]_r \times f_r + \delta^7\text{Li}_s \times [\text{Li}]_s \times (1 - f_r) \quad \text{Eq. S-2}$$

The fraction of river water ( $f_r$ ) can be calculated from salinity (Sal) as:

$$\text{Sal}_{diss.} = \text{Sal}_r \times f_r + \text{Sal}_s \times (1 - f_r) \quad \text{Eq. S-3}$$

The analytical uncertainties of Li concentration and  $\delta^7\text{Li}$  values in this study are 10 % and 0.6 ‰ (2SD), respectively. Using a Monte-Carlo method, we first randomly generated values for water salinity and Li concentrations,  $\delta^7\text{Li}$  values of river water and seawater end members. The fraction of river water in the dissolved load is calculated based on the generated water salinity. Then, the theoretical dissolved Li concentrations and  $\delta^7\text{Li}$  values can be calculated. This operation was run  $10^5$  times.

## The Potential Influences of SPM Li Release and Uptake on Dissolved Li Isotopes

The potential influence of possible SPM dissolution on the dissolved Li behaviour can be estimated using a simple mass balance model as following equations:

$$\text{Li}_{simu.} = \text{Li}_{spm} \times f_{rea} \times \text{SSC} + \text{Li}_{diss.} \quad \text{Eq. S-4}$$

$$\delta^7\text{Li}_{simu.} = (\delta^7\text{Li}_{spm} \times \text{Li}_{spm} \times f_{rea} \times \text{SSC} + \delta^7\text{Li}_{diss.} \times \text{Li}_{diss.}) / \text{Li}_{simu.} \quad \text{Eq. S-5}$$

where  $\text{Li}_{simu.}$  and  $\delta^7\text{Li}_{simu.}$  represent simulated dissolved Li concentrations and Li isotope compositions, and  $f_{rea}$  is the fraction of Li release from SPM dissolution relative to SPM Li. The Changjiang SPM is mostly derived from sedimentary rocks and shales widely distributed in the large catchment, which have experienced intermediate to strong chemical weathering. A low chemical reactivity of SPM can therefore be expected when they interact with seawater. Quartz, feldspar, illite and kaolinite are four major minerals (*i.e.* each content  $>10$  %) of fine terrigenous sediments from the Changjiang River (Yang *et al.*, 2002). The dissolution rates of these minerals are relatively low. For instance, less than 0.1 % of kaolinite and illite would be expected to dissolve in seawater annually (Jeandel and Oelkers, 2015). As a first approximation, we can assume 0.1 % of SPM Li ( $f_{rea}$ ) could be released by dissolution in the Changjiang Estuary, and then the mass balance model suggests that, in that case, the dissolved  $\delta^7\text{Li}$  would decrease by  $\sim 0.2$  ‰. This small variation in dissolved  $\delta^7\text{Li}$  is within our analytical uncertainties, which implies that potential Li releases from SPM dissolution could not significantly influence the dissolved Li behaviours during estuarine mixing processes.

A second simulation has been done in order to quantify the effect of Li uptake by SPM during their transport in the estuary. Indeed, compared to the samples collected at Xuliujing gauging station, the estuarine SPM display slightly

higher Li concentrations by  $10 \pm 5.6\%$ . Although SPM exchangeable fraction has been removed and clay formation in estuarine environment is not supported by the XRD results, dissolved Li uptake by clay minerals as amorphous authigenic aluminosilicates may partially account for the observed increase in SPM Li concentrations. Thus, the fraction of Li uptake from water ( $f_{Li}$ ) can be estimated following:

$$[Li]_{diff} = [Li]_m - (Li/Al)_r \times Al_m \quad \text{Eq. S-6}$$

$$f_{Li} = ([Li]_{diff} \times SSC) / ([Li]_{diss.} + [Li]_{diff} \times SSC) \quad \text{Eq. S-7}$$

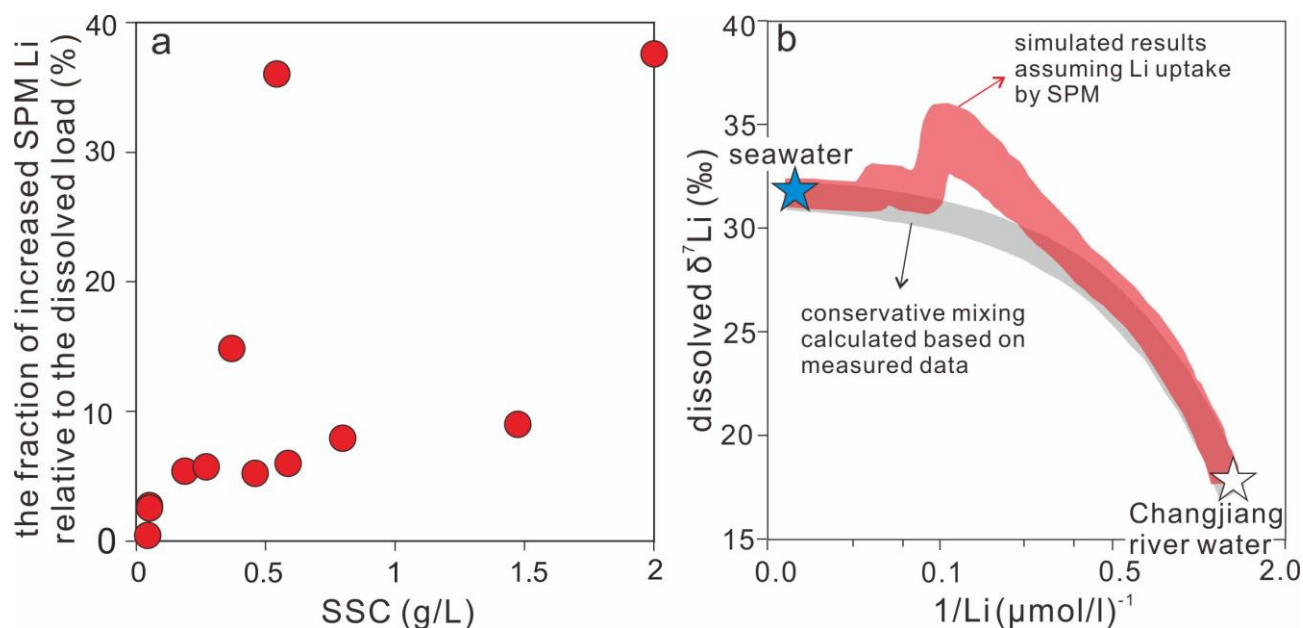
Where  $[Li]_m$  and  $Al_m$  respectively represent Li and Al concentrations of estuarine SPM, and  $(Li/Al)_r$  represents average Li/Al ratio of SPM collected at Xuliujing station, and  $[Li]_{diff}$  is the difference in Li concentration between estuarine SPM and river end-member.

The potential influence of Li uptake on the dissolved Li isotope compositions can then be estimated following equation:

$$\delta^7Li = \delta^7Li_{diss.} - 1000 \times \ln(\alpha_{sec-diss}) \times f_{Li} \quad \text{Eq. S-8}$$

Where  $\alpha_{sec-diss}$  is Li isotopic fractionation factor. We set  $\alpha_{sec-diss}$  value as  $0.984 \pm 0.004$  which is estimated from Li isotope fractionation between exchangeable fraction and dissolved load (Fig. S-3b). This range is also consistent with the value reported by Wang *et al.* (2015) for the Changjiang basin.

Assuming the increase of estuarine SPM Li is primarily caused by Li uptake from water, the calculated Li uptake by SPM is less than 10% of dissolved Li flux at most sampling stations. This is consistent with previous studies that isotopic exchange and particle dissolution may not alter dissolved elemental concentration significantly (Jones *et al.*, 2012, 2014; Morin *et al.*, 2015). We also notice that this fraction is positively related to SSC to some extent. As shown in Figure S-2b, a visible  $\delta^7Li$  difference can be observed between the measured data and simulated results. With the increase of sediment/water ratio, more Li can be incorporated into clay minerals, and the dissolved  $\delta^7Li$  would therefore be significantly altered. The dissolved  $\delta^7Li$  difference between simulated and measured results reach a maximum (*i.e.*  $\sim 5.5\%$ ) at the maximum turbidity zone, where suspended sediment concentration can be up to  $\sim 2$  g/L (Fig. S-2b). Therefore, the simulated results indirectly confirm a negligible effect of SPM Li uptake on altering the dissolved Li behaviour in the Changjiang Estuary, otherwise, dissolved Li behaviour would not be conservative (Fig. 1).

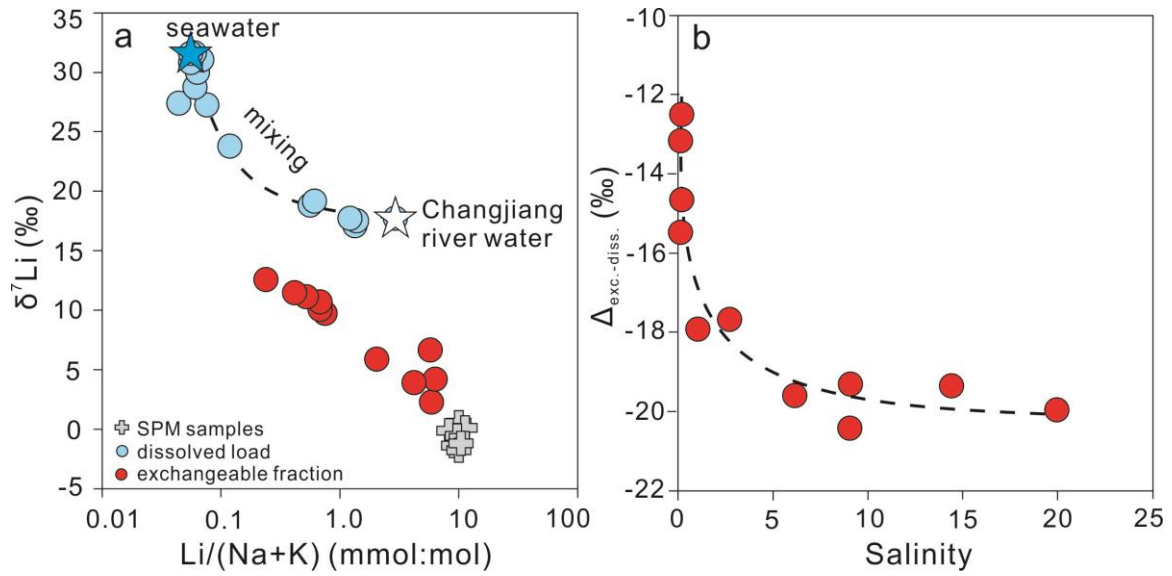


**Figure S-2 (a)** The fraction of increased SPM Li relative to the dissolved load as a function of suspended sediment concentration (SSC), and **(b)** the comparison between measured and simulated dissolved  $\delta^7\text{Li}$  as a function of inverse Li concentration.

## Isotopic Exchange Between Water and Particles

Li as an alkali element bears a large difference in concentration between river water and seawater (Huh *et al.*, 1998; Misra and Froelich, 2012), similar as Na. It is therefore important to explore the potential of its isotopes to trace exchange processes in the estuarine mixing zone. The SPM exchangeable Li concentration is expressed as mass per milligram of SPM. The values range from 0.4 to 0.7 ng/mg (Table S-2), which is much low compared to the SPM Li concentration (44 – 76  $\mu\text{g/mg}$ ). Exchangeable Li thus accounts for less than 1 % of the SPM Li. As shown in Figure S-3,  $\delta^7\text{Li}$  values of the exchangeable fractions vary negatively as a function of  $\text{Li}/(\text{Na}+\text{K})$  ratios, and are always significantly lower (by -12 ‰ to -20 ‰) than  $\delta^7\text{Li}$  values of water sampled at the same site. The trend between  $\delta^7\text{Li}$  and  $\text{Li}/(\text{Na}+\text{K})$  displayed by SPM exchangeable fraction cannot be explained by a binary mixing between SPM and the ambient water (Fig. S-3a). In fact, along with the salinity increase, the difference in  $\delta^7\text{Li}$  between the exchangeable fraction and dissolved load ( $\Delta_{\text{exc.-diss.}}$ ) decreases sharply and then stabilises (Fig. S-3b).

When entering saline water, exchangeable Li concentration increases rapidly (Table S-2), and preferentially uptakes the light  $^6\text{Li}$  isotope. This is consistent with kinetic effects as the adsorption process starts to operate. Subsequently, when salinity gets higher, an equilibrium of isotopic exchange is reached between the dissolved Li and the SPM exchangeable fractions. The competition between  $\text{Li}^+$  and other alkali elements ( $\text{Na}^+$  and  $\text{K}^+$ ) likely plays a key role during this process, because elemental exchanges mostly depend on water ionic strength (Hindshaw *et al.*, 2019; Li and Liu, 2020). This would deserve to be explored experimentally in the future. Although our results evidence an increasing isotope exchange along the salinity gradient in the estuarine zone, this effect plays a minor role on the particulate and dissolved Li flux to the ocean, and therefore on their related isotopic signals.



**Figure S-3** (a)  $\delta^7\text{Li}$  variation as a function of  $\text{Li}/(\text{Na}+\text{K})$  ratios for the SPM exchangeable fractions (in red) compared to bulk SPM (in grey) and to water (in blue), and (b) non-linear variation of isotopic difference between the exchangeable fraction and dissolved load ( $\Delta_{\text{exc.-diss.}}$ ) as a function of water salinity.

## Supplementary Tables

**Table S-1** Elemental and Li isotope compositions of suspended particulate matter (SPM) from the Xuliujing gauging station.

Sample ID	Sampling Date	Longitude °E	Latitude °N	Depth m	SSC mg/l	Li µg/g	Al %	Na %	K %	δ <sup>7</sup> Li ‰
S370	2014-06	120.9647	31.7919	0	26	61.0	8.6	0.7	2.1	-2.4
S371	2014-06	120.9647	31.7919	8	102	51.1	7.4	0.9	2.0	-1.8
S372	2014-06	120.9647	31.7919	16	88	53.6	7.6	0.9	2.0	-1.7
S373	2014-06	120.9647	31.7919	24	91	53.0	7.6	0.9	2.0	-1.8
S374	2014-06	120.9647	31.7919	32	165	40.4	6.5	1.1	1.8	-1.0
S375	2014-06	120.9647	31.7919	40	165	46.0	6.9	1.0	1.9	-1.0
S424	2014-08	120.9647	31.7919	0	84	63.3	8.7	0.7	2.2	-2.0
S425	2014-08	120.9647	31.7919	8	77	57.5	8.1	0.8	2.1	-1.9
S426	2014-08	120.9647	31.7919	16	95	56.8	8.0	0.8	2.1	-1.8
S427	2014-08	120.9647	31.7919	24	114	54.4	8.0	0.8	2.1	-2.0
S428	2014-08	120.9647	31.7919	32	108	51.8	7.7	0.9	2.1	-1.8
S429	2014-08	120.9647	31.7919	40	109	55.5	7.9	0.8	2.2	-1.8
S472	2014-10	120.9647	31.7919	0	65	73.4	9.8	0.5	2.3	-2.8
S473	2014-10	120.9647	31.7919	8	75	65.5	9.3	0.7	2.2	-2.3
S474	2014-10	120.9647	31.7919	16	84	65.0	9.5	0.7	2.3	-2.3
S475	2014-10	120.9647	31.7919	24	100	62.7	9.1	0.6	2.2	-2.2
S476	2014-10	120.9647	31.7919	32	98	61.4	8.8	0.7	2.1	-2.2
S477	2014-10	120.9647	31.7919	40	128	62.0	8.6	0.7	2.2	-2.4

**Table S-2** Hydrological parameters, elemental and Li isotope compositions of the dissolved load, suspended particulate matter (SPM) and its exchangeable phase in the Changjiang (Yangtze River) Estuary.

Sample ID	Longitude	Latitude	Depth	Salinity	pH	T	SSC	Dissolved load				SPM exchangeable fraction				SPM				
	°E	°N	m			°C	mg/l	Li μmol/L	K mmol/L	Na mmol/L	δ <sup>7</sup> Li ‰	Li μg/g	Na μg/mg	K μg/mg	δ <sup>7</sup> Li ‰	Li μg/g	Al %	Na %	K %	δ <sup>7</sup> Li ‰
C1S	121.0561	31.7805	-1	0.0	7.8	28.9	44.7	0.79	0.03	0.24	17.7	0.45	0.13	0.21	2.2	62.8	8.57	0.61	2.50	-1.3
C1B	121.0561	31.7805	-10	0.0	7.8	28.9	58.4	0.81	0.06	0.54	17.1	0.43	0.21	0.22	3.9	59.6	8.17	0.67	2.47	-1.5
C5S	121.7494	31.2883	-1	0.0	7.8	28.9	198.9	0.78	0.06	0.58	17.7	0.38	0.09	0.19		44.2	6.13	0.76	1.93	
C5B	121.7494	31.2883	-16	0.0	7.8	29.1	279.8	0.78	0.06	0.56	17.6	0.47	0.25	0.22		51.7	7.26	0.79	2.23	
C6S	121.9116	31.1529	-1	0.2	8.0		575.1	0.77	0.09	1.29	18.8	0.44	0.08	0.25	4.2	61.0	8.01	0.76	2.39	-0.2
C6B	121.9116	31.1529	-7	0.2	7.9			0.85	0.09	1.31	19.2	0.42	0.13	0.19	6.7	57.5	7.69	0.84	2.34	-0.2
C6-1S	121.9674	31.0939	-1	1.0	7.8	28.1		1.44	0.32	11.9	23.8	0.38	0.43	0.29	5.9	65.8	8.28	0.73	2.53	-0.5
C6-1B	121.9674	31.0939	-6	3.2	7.8	27.7	1517.2	2.80	0.82	36.2	27.2									
C6-2S	121.9860	31.0852	-1	2.7	7.8	27.8	384.1	2.60	1.28	57.4	27.4	0.64	2.50	0.54	9.7	66.9	8.43	0.68	2.55	-0.5
C6-2B	121.9860	31.0852	-6	6.2	7.8	27.4	2078.5	4.57	1.59	73.9	28.7	0.64	2.04	0.64	9.1	69.1	8.62	0.66	2.62	-0.1
C6-3S	121.9850	31.0843	-1	9.1	7.8	26.9	478.9	7.04	2.38	113.1	30.5	0.58	2.51	0.50	10.1	63.8	8.35	0.71	2.55	0.0
C6-3B	121.9850	31.0843	-6	9.1	7.8	26.9	1541.3	7.19	2.34	111.9	30.0	0.47	1.99	0.48	10.7	55.3	7.49	0.85	2.31	-0.2
C8S	122.2495	31.0217	-1	14.4	7.8	27.5		10.2	3.69	180.6	30.8	0.64	4.65	0.62	11.4	65.8	8.14	0.67	2.54	0.5
C8B	122.2495	31.0217	-6	14.8	7.8	27.5	609.2	10.8	3.80	185.4	31.5	0.65	8.50	0.76	12.5	65.1	8.24	0.70	2.53	-0.2
C9S	122.3643	31.0019	-1	18.6	7.8	27.1	47.3	13.8	4.38	209.4	31.1	1.06	47.3	1.93	18.6	75.5	9.21	0.58	2.90	0.0
C9B	122.3643	31.0019	-10	20.0	7.8	26.8	837.7	15.5	4.62	221.1	31.0	0.67	3.86	0.61	11.1	72.6	8.87	0.60	2.72	-0.2
C18S	124.9874	29.8646	-1	32.1	8.2	29.4	5.1	22.9	8.35	404.8	31.6									
C18B	124.9874	29.8646	-62	34.6	7.9	21.9	26.5	26.1	8.90	428.8	31.6									



**Table S-3** Mineral composition of SPM samples collected in the Changjiang Estuary.

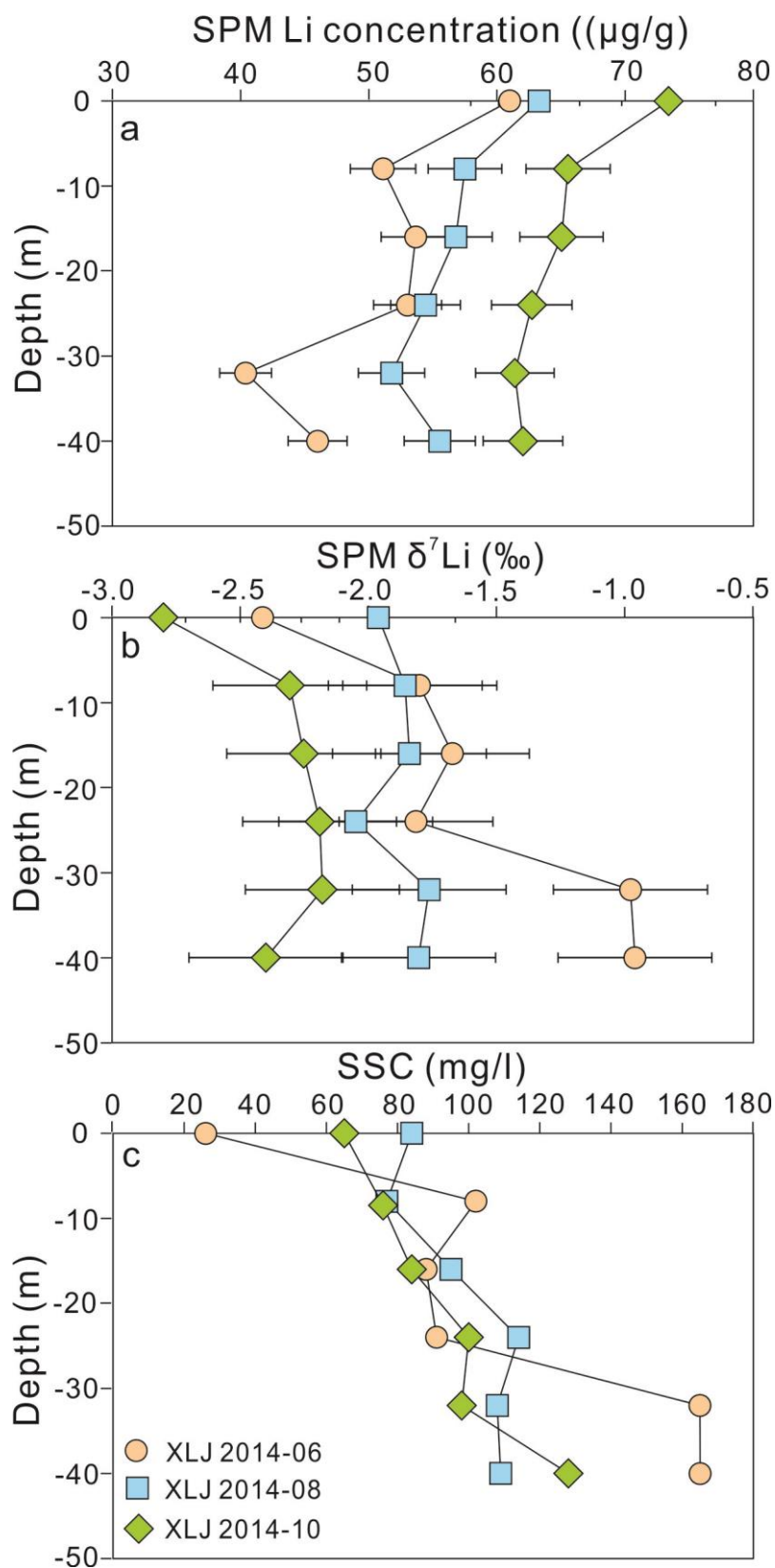
Sample ID	Quartz %	Albite %	K-feldspar %	Illite %	Chlorite %	Kaolinite %	Calcite %	Dolomite %
C1S	25	6	3	39	6	16	4	2
C1B	27	8	5	34	6	13	4	3
C5S	43	15	3	20	9	3	5	3
C5B	44	13	3	21	9	2	5	4
C6S	41	11	4	24	9	3	5	4
C6B	42	12	4	23	9	2	5	3
C6-1S	40	11	4	25	10	3	5	2
C6-2S	35	8	4	32	10	4	5	2
C6-2B	39	9	4	27	9	3	6	3
C6-3S	41	11	4	24	10	3	6	2
C6-3B	45	14	5	21	8	2	5	2
C8S	40	11	4	25	9	3	6	2
C8B	40	10	5	26	8	4	6	2

**Table S-4** Elemental compositions and Li isotope compositions of standard materials GSD-9 and BE-N.

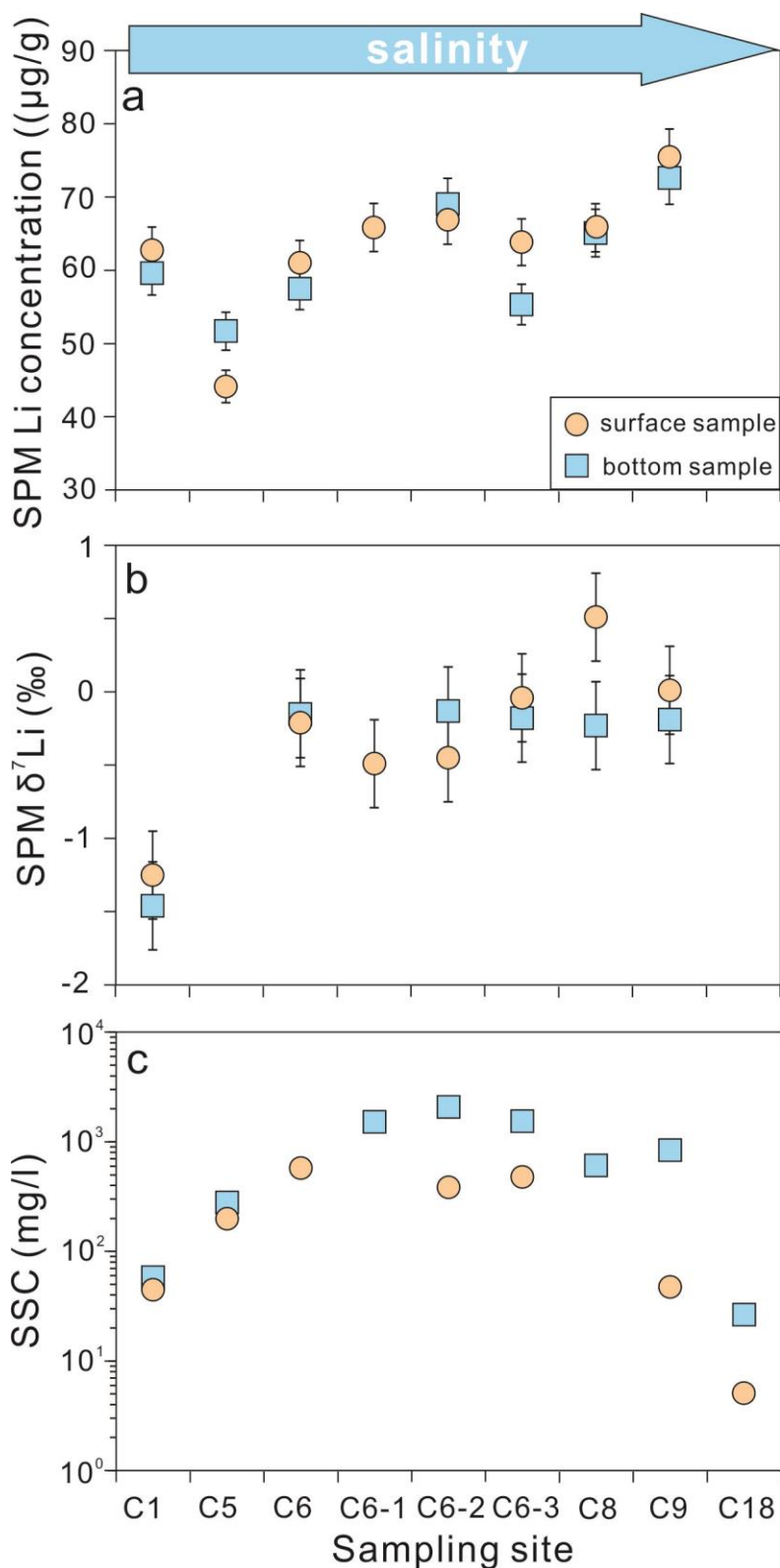
Sample ID	Al %	K %	Na %	Li %	$\delta^7\text{Li}$ ‰
GSD-9	5.58	1.73	1.08	29.5	
GSD-9	5.42	1.71	1.07	28.7	
GSD-9	5.36	1.69	1.06	29.8	
GSD-9	5.18	1.65	1.04	29.0	
GSD-9	5.21	1.65	1.04	29.9	
GSD-9	5.13	1.66	1.03	29.8	
GSD-9	5.28	1.68	1.06	29.5	
BE-N					5.4
BE-N					4.9
BE-N					4.4
BE-N					4.2
BE-N					5.2
BE-N					5.7
BE-N					5.2
Average	5.31	1.68	1.05	29.5	5.0



## Supplementary Figures



**Figure S-4** (a) Seasonal and depth variations of SPM Li concentration, (b) SPM  $\delta^7\text{Li}$  values, and (c) suspended sediment concentration (SSC) at Xuliujing (XLJ) gauging station. The analytical uncertainties for Li concentrations and  $\delta^7\text{Li}$  are 10 % and 0.6 ‰ (2SD), respectively.



**Figure S-5** (a) Variations of SPM Li concentration, (b) SPM  $\delta^7\text{Li}$  values, and (c) suspended sediment concentration (SSC) along the 2D transect of ~400 km in the mixing zone of the Changjiang Estuary. The analytical uncertainties for Li concentrations and  $\delta^7\text{Li}$  are 10 % and 0.6 ‰ (2SD), respectively. The sampling depth refer to Figure S-1c or Table S-2.

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