

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
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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 km³/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 μm cellulose acetate membranes. Then, about 50 ml of the dissolved load (an operational definition of the fraction in water that pass through 0.45 μm pore-size filter) were acidified to $\text{pH} < 2$ with concentrated 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.

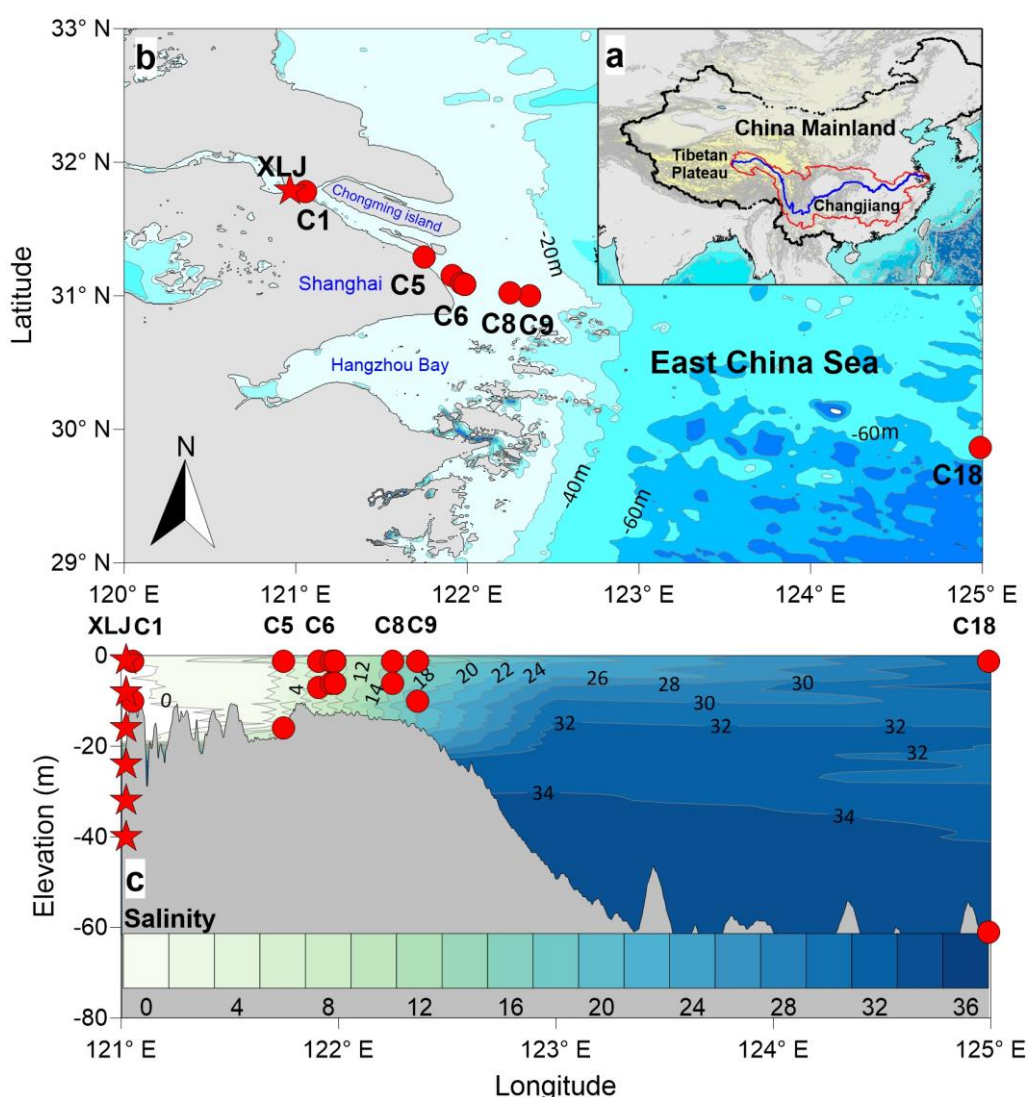


Figure S-1 Maps showing (a) the Changjiang drainage basin, (b) sampling sites (red dots) along an estuarine transect, (c) salinity variation and sampling strategy along the depth profiles. The blue colour associated with isobath in (b) refers to water depth below the modern sea-level. The XLJ SPM samples (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 HNO₃ 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 HNO₃. The dried samples were re-digested in 2 ml 30 % HNO₃ with a temperature of 190 °C. Finally, the solution was diluted to ~100 g with 2 % HNO₃ 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 HNO₃. The NIST L-SVEC standard was measured before and after each sample to monitor instrument drift. The ~5 ppb Li solution generally yielded a ⁷Li signal exceeding 4 V, with an acid blank of generally 30 - 40 mV, systematically subtracted. The Li isotopic ratios are reported in δ notation, representing ⁷Li/⁶Li 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 (~ 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 ~ 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 ± 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 δ^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 δ^7Li would therefore be significantly altered. The dissolved δ^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 ~ 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).

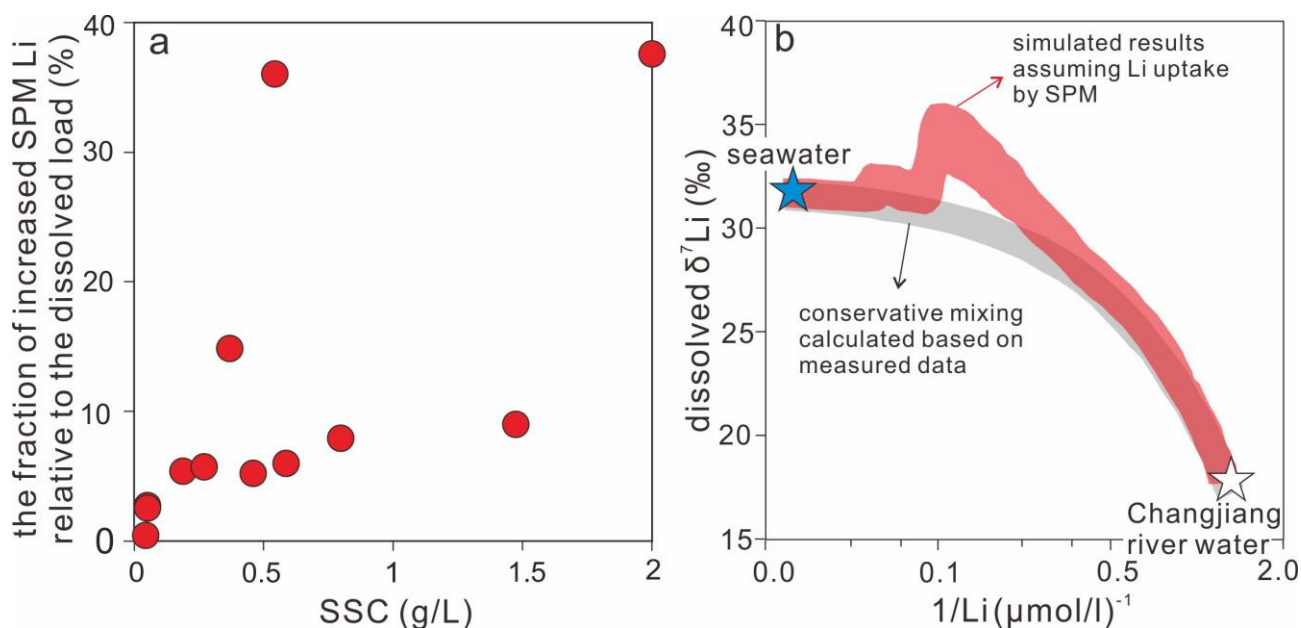


Figure S-2 (a) The fraction of increased SPM Li relative to the dissolved load as a function of suspended sediment concentration (SSC), and (b) the comparison between measured and simulated dissolved $\delta^7\text{Li}$ as a function of inverse Li concentration.

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 ^6Li 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 Li^+ and other alkali elements (Na^+ and 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.

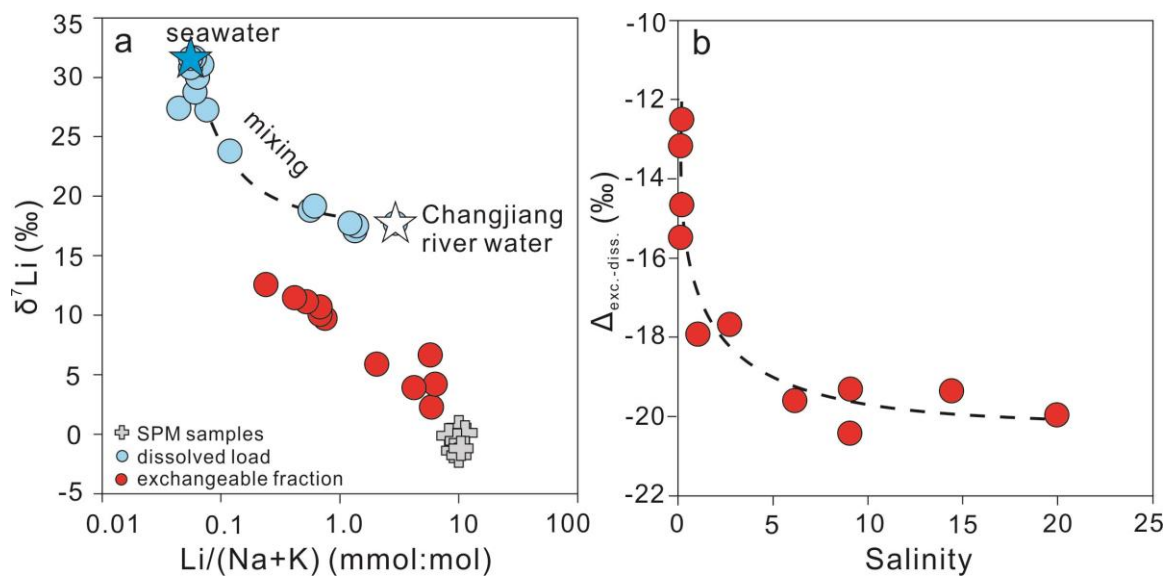


Figure S-3 (a) $\delta^7\text{Li}$ variation as a function of $\text{Li}/(\text{Na}+\text{K})$ ratios for the SPM exchangeable fractions (in red) compared to bulk SPM (in grey) and to water (in blue), and (b) non-linear variation of isotopic difference between the exchangeable fraction and dissolved 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 ⁷ 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 ⁷ Li ‰	Li μg/g	Na μg/mg	K μg/mg	δ ⁷ Li ‰	Li μg/g	Al %	Na %	K %	δ ⁷ 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

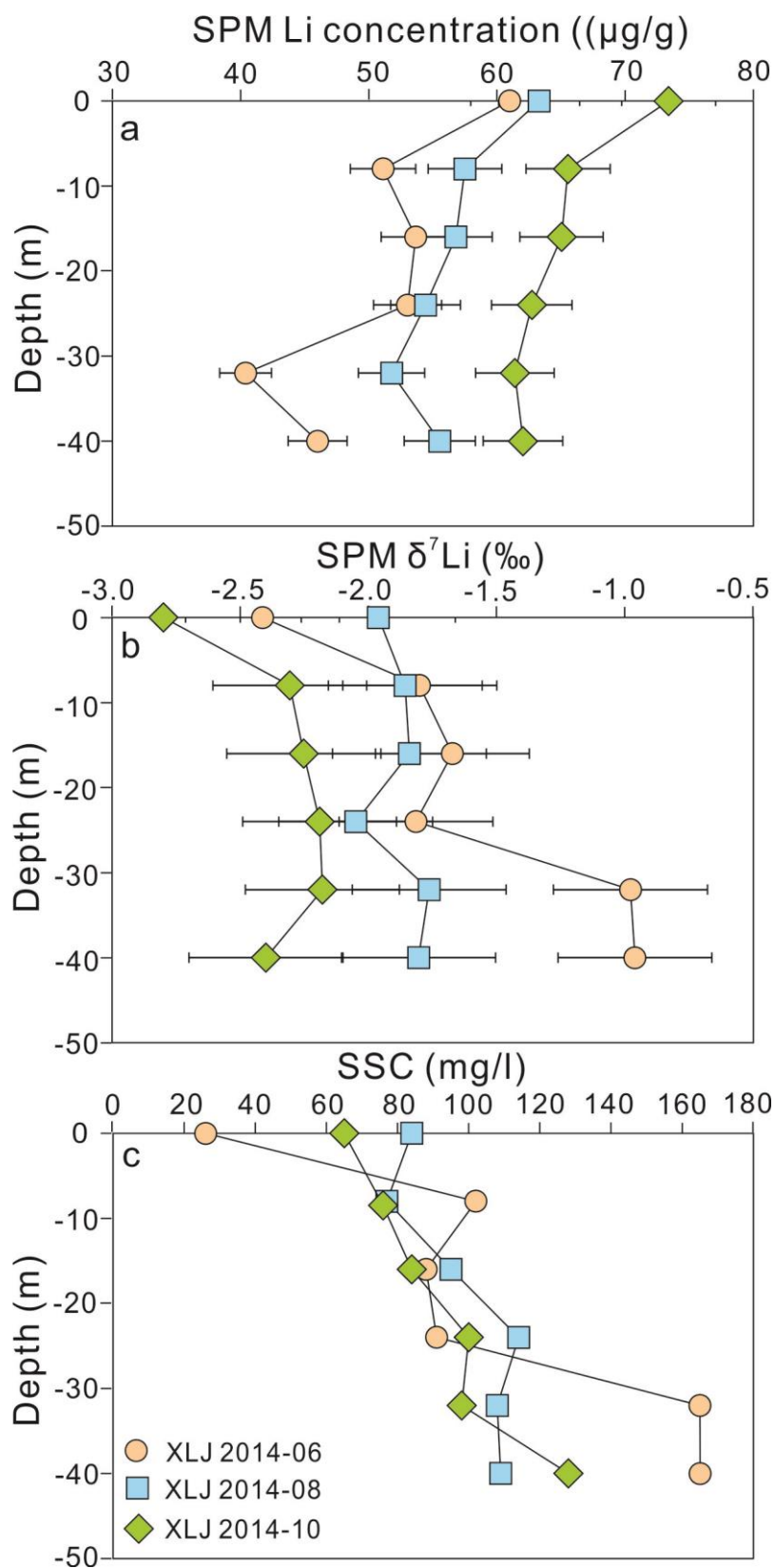


Figure S-4 (a) Seasonal and depth variations of SPM Li concentration, (b) SPM $\delta^7\text{Li}$ values, and (c) suspended sediment concentration (SSC) at Xuliujing (XLJ) gauging station. The analytical uncertainties for Li concentrations and $\delta^7\text{Li}$ are 10 % and 0.6 ‰ (2SD), respectively.

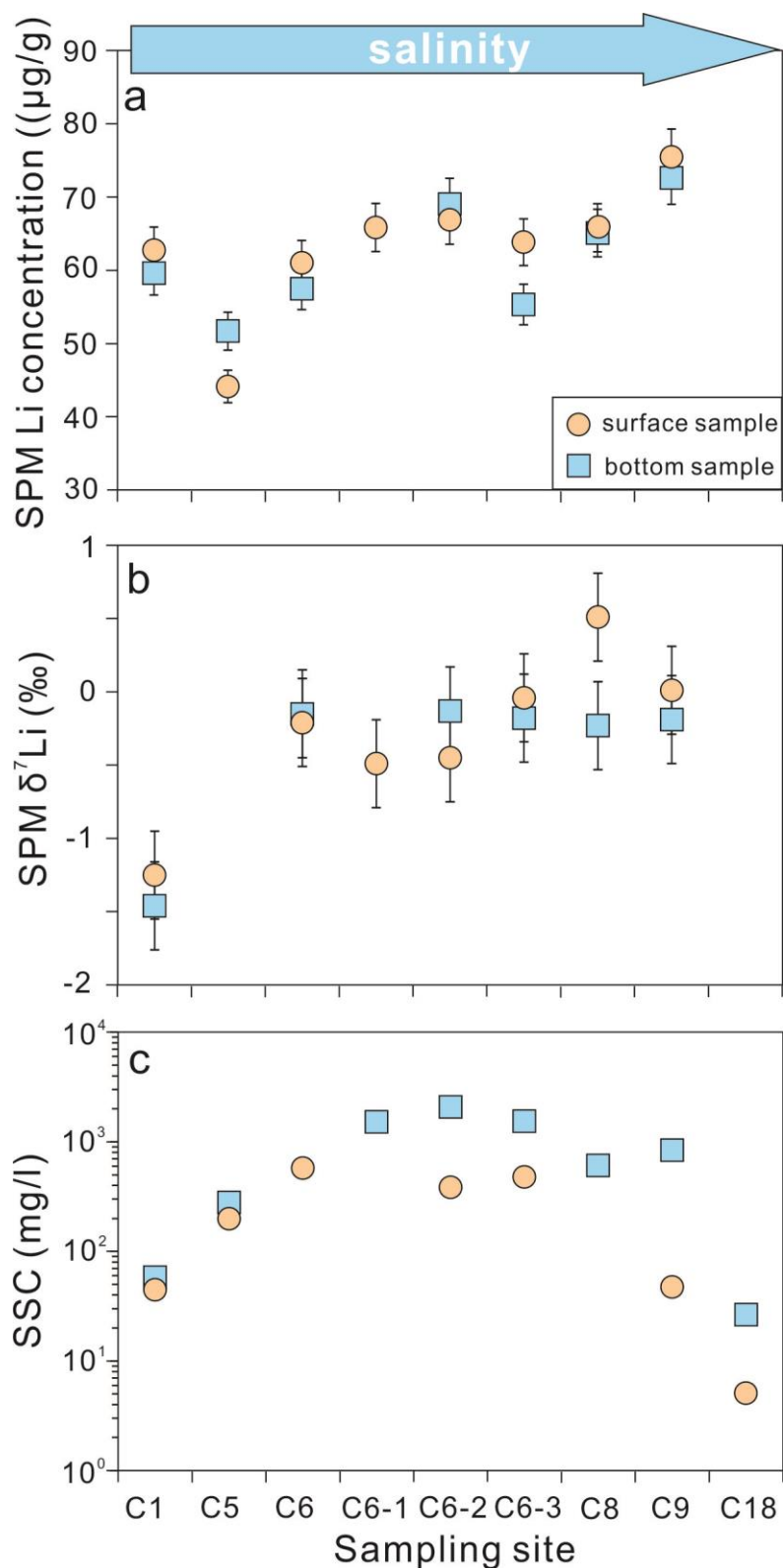


Figure S-5 (a) Variations of SPM Li concentration, (b) SPM $\delta^7\text{Li}$ values, and (c) suspended sediment concentration (SSC) along the 2D transect of ~400 km in the mixing zone of the Changjiang Estuary. The analytical uncertainties for Li concentrations and $\delta^7\text{Li}$ are 10 % and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

Supplementary Information References

- Choi, H.B., Ryu, J.S., Shin, W.J., Vigier, N. (2019) The impact of anthropogenic inputs on lithium content in river and tap water. *Nature Communications* 10, 5371.
- Gu, H.Q., Moore, W.S., Zhang, L., Du, J.Z., Zhang, J. (2012) Using radium isotopes to estimate the residence time and the contribution of submarine groundwater discharge (SGD) in the Changjiang effluent plume, East China Sea. *Continental Shelf Research* 35, 95-107.
- Hindshaw, R.S., Tosca, R., Gout, T.L., Farnan, I., Tosca, N.J., Tipper, E.T. (2019) Experimental constraints on Li isotope fractionation during clay formation. *Geochimica et Cosmochimica Acta* 250, 219-237.
- Huh, Y., Chan, L.H., Zhang, L., Edmond, J.M. (1998) Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget. *Geochimica et Cosmochimica Acta* 62, 2039-2051.
- Jeandel, C., Oelkers, E.H. (2015) The influence of terrigenous particulate material dissolution on ocean chemistry and global element cycles. *Chemical Geology* 395, 50-66.
- Jones, M.T., Pearce, C.R., Jeandel, C., Gislason, S.R., Eiriksdottir, E.S., Mavromatis, V., Oelkers, E.H. (2012) Riverine particulate material dissolution as a significant flux of strontium to the oceans. *Earth and Planetary Science Letters* 355, 51-59.
- Jones, M.T., Gislason, S.R., Burton, K.W., Pearce, C.R., Mavromatis, V., Pogge von Strandmann, P.A.E., Oelkers, E.H. (2014) Quantifying the impact of riverine particulate dissolution in seawater on ocean chemistry. *Earth and Planetary Science Letters* 395, 91-100.
- Li, W.S., Liu, X.M. (2020) Experimental investigation of lithium isotope fractionation during kaolinite adsorption: Implications for chemical weathering. *Geochimica et Cosmochimica Acta* 284, 156-172.
- Liu, W., Liu, W., Li, X., Liu, Y., Ogunmoroti, A.E., Li, M., Bi, M., Cui, Z. (2021) Dynamic material flow analysis of critical metals for lithium-ion battery system in China from 2000–2018. *Resources, Conservation and Recycling* 164, 105122.
- Milliman, J.D., Farnsworth, K.L. (2011) *River Discharge to the Coastal Ocean: A Global Synthesis* Cambridge University Press, New York.
- Misra, S., Froelich, P.N. (2012) Lithium isotope history of Cenozoic seawater: changes in silicate weathering and reverse weathering. *Science* 335, 818-823.
- Morin, G.P., Vigier, N., Verney-Carron, A. (2015) Enhanced dissolution of basaltic glass in brackish waters: Impact on biogeochemical cycles. *Earth and Planetary Science Letters* 417, 1-8.
- Shi, J.Z. (2010) Tidal resuspension and transport processes of fine sediment within the river plume in the partially-mixed Changjiang River estuary, China: A personal perspective. *Geomorphology* 121, 133-151.
- Vigier, N., Decarreau, A., Millot, R., Carignan, J., Petit, S., France-Lanord, C. (2008) Quantifying Li isotope fractionation during smectite formation and implications for the Li cycle. *Geochimica et Cosmochimica Acta* 72, 780-792.
- Wang, Q.L., Chetelat, B., Zhao, Z.Q., Ding, H., Li, S.L., Wang, B.L., Li, J., Liu, X.L. (2015) Behavior of lithium isotopes in the Changjiang River system: Sources effects and response to weathering and erosion. *Geochimica et Cosmochimica Acta* 151, 117-132.
- Xu, K.H., Milliman, J.D. (2009) Seasonal variations of sediment discharge from the Yangtze River before and after impoundment of the Three Gorges Dam. *Geomorphology* 104, 276-283.
- Yang, S.Y., Jung, H.S., Choi, M.S., Li, C.X. (2002) The rare earth element compositions of the Changjiang (Yangtze) and Huanghe (Yellow) river sediments. *Earth and Planetary Science Letters* 201, 407-419.

