Supplementary information for

The Li isotopic composition of soil porewater responses to evapotranspiration

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Model

The model simulates evolution of porewater δ^7Li in response to evapotranspiration. According to the exponential decrease of evaporable water content in loess (Fig. 1B), a first order kinetics is used to calculate the changing volume of water (v, m^3) in soil:

$$\frac{dv}{dt} = -\varepsilon v \qquad (S1)$$

where t (s) is time and ε (s^{-1}) is the rate constant of evaporation. Integration of Eq. (1) can give changes of water volume with an initial volume of v_0:

$$v = v_0 e^{-\varepsilon t} \qquad (S2)$$

The amount of ^{6}Li in porewater, i.e., cv, where c (mol m^{-3}) is ^{6}Li concentration, changes due to the dissolution of silicate minerals and uptake by clays:

$$\frac{dcv}{dt} = R\frac{v}{p}c_R - KFR\frac{v}{p}c \qquad (S3)$$

The first term on the right side of Eq. (S3) is the releasing rate of ^{6}Li by silicate dissolution, and the second term is the uptake rate of ^{6}Li by clays. The releasing rate of ^{6}Li (mol s^{-1}) is a product of the concentration of ^{6}Li in silicate (c_R, mol m^{-3}) and silicate dissolution rate $R \times v/p$ (m^3 s^{-1}), where R is rate constant of silicate dissolution (s^{-1}) that include possible changes in fraction of reactive surface area (grainsize) and surface-specific rate constant, p (m^3 m^{-3}) is porosity, and v/p is the volume of minerals immersed in porewater. The uptake rate of ^{6}Li is proportional to the concentration of ^{6}Li in porewater, the partition coefficient of ^{6}Li between fluid and clay (K, non-dimensional), and the rate of clay formation ($F \times R \times v/p$), where F (m^3 m^{-3}) is the fraction of clay formed by silicate dissolution.

Replacing v by Eq. (S2) enables integration of Eq. (S3), which result in the following analytical solution for the evolving porewater Li concentration with no initial concentration of Li:

$$c = \frac{c_R R_p \left[1 - e^{-\left(K_f R_p - \varepsilon\right)t}\right]}{K_f R_p - \varepsilon} \qquad (S4)$$

where R_p (R/p, s^{-1}) is the porosity normalized rate constant of silicate dissolution, and K_f ($K \times F$, non-dimensional) is water-clay ^{6}Li partition coefficient normalized by fraction of clay formation by silicate dissolution.

The ^{6}Li concentration of porewater in absence of clay Li uptake ($c_{K=0}$) can be calculated from Eq. (S4) with $K_f = 0$:

$$c_{K=0} = \frac{c_R R_p \left(e^{\varepsilon t} - 1\right)}{\varepsilon} \qquad (S5)$$

Thus, dividing c by $c_{K=0}$ from Eq. (S4) and Eq. (S5) would give the fraction of ^{6}Li which remains in porewater:

$$f = \frac{\varepsilon c_R R_p \left[1 - e^{-\left(K_f R_p - \varepsilon\right)t}\right]}{c_R R_p \left(e^{\varepsilon t} - 1\right)\left(K_f R_p - \varepsilon\right)} \qquad (S6)$$

The ^{7}Li/^{6}Li ratio of porewater (γ) can be coupled to the evolution of ^{6}Li concentration in Eq. (S3) to illustrate the evolution of ^{7}Li concentration:

$$\frac{dcv\gamma}{dt} = R_p v c_R \gamma_R - K_f R_p v c \gamma \alpha \qquad (S7)$$

where α is the isotopic fractionation between clay and fluid, γ_R is the $^7Li/^6Li$ ratio of dissolving silicates.

It is convenient to convert the above equations by non-dimensional parameters of reaction time (T), fluid ^6Li concentration (C), isotopic ratio (r), water volume (V), and normalized rate constant of evaporation (E):

$$T = tK_f R_p \qquad \text{(S8)}$$

$$C = \frac{cK_f}{c_R} \qquad \text{(S9)}$$

$$r = \frac{\gamma}{\gamma_R} \qquad \text{(S10)}$$

$$V = \frac{v}{v_0} \qquad \text{(S11)}$$

$$E = \frac{\varepsilon}{K_f R_p} \qquad \text{(S12)}$$

where C_R is ^6Li concentration of dissolving silicates. Thus, Eq. (S2), (S4), (S6) and (S7) can be converted to:

$$V = e^{-ET} \qquad \text{(S13)}$$

$$C = \frac{e^{(E-1)T} - 1}{E - 1} \qquad \text{(S14)}$$

$$f = \frac{[e^{(E-1)T} - 1]E}{(E-1)(e^{ET} - 1)} \qquad \text{(S15)}$$

$$\frac{dCVr}{dT} = V(1 - Cr\alpha) \qquad \text{(S16)}$$

By treating CVr as one single variable, Eq. (16) can be solved, which leads to the following expression for the normalized isotopic ratio (r):

$$r = \frac{(E-1)\left[e^{(E-\alpha)T}-1\right]}{(E-\alpha)\left[e^{(E-1)T}-1\right]} \qquad (S17)$$

Samples, leaching experiment, and measurements

Eolian loess deposited during the last glacial (L_1 layer) with low degree of pedogenic alteration and during the last interglacial periods (S_1 layer) with higher pedogenesis are sampled at five sites on the CLP. The sample of L_1 layer taken from Caoxian site on the northwest of the CLP shows the least pedogenic alteration, and thus is used by leaching experiment to constrain the endmember composition associated with the weathering of evaporite, carbonate, and silicate.

About 0.5 g of loess was immersed in 50 ml Milli-Q water in a pre-cleaned polyethylene container for 30 min. The dissolved solution is then separated from the residue by centrifuging followed by filtering. The residual solid was treated by 50 ml of 3% high purity acetic acid for 48 h in a glass beaker, and was ultrasonically shaken for 20 min every 12 h in order to dissolve all calcite and dolomite in the loess sample. The dissolved solution is separated by centrifugation and filtration. The residual solid was washed by Milli-Q for three times to eliminate the interference of acetic acid, and was then treated by 0.01M HCl for 2 h to mimic the incipient weathering of silicate under field conditions. Results of the leaching experiment, which were used as the evaporite, carbonate and silicate weathering endmembers are shown in Table S1.

Samples of stream water were collected on the CLP during the summer monsoon season of 2019. At each site, ~1 liter of stream water was filtered using Teflon filtration units (0.22 μm) and stored in two 500 ml pre-cleaned Nalgene® bottles with one being acidified by 200 μl concentrated HNO_3.

Major anions, cations and Li concentrations of the stream water and leaching solution were measured by ion chromatography, ICP-OES and quadrupole ICP-MS, respectively. For Li isotope measurements, samples containing ~50 ng Li were dried in a Teflon beaker before being treated with 200 μl 7N HNO_3 and 200 μl H_2O_2 to remove dissolved organic matter. The residue was then re-dissolved in 4 ml 0.1 N distilled HCl and heated at 100 °C for at least 2 h. Li was separated from the matrix by a one-stage cation exchange column chemistry (AG50W X-12 resin) modified from a previous study Dellinger et al. (2015). Na/Li ratios of the column elution were monitored to ensure acceptable separation of Na and Li with $^{23}Na/^{7}Li$ signal ratio measured on MC-ICP-MS below 10. The Li isotopic ratio of the purified samples was measured by a Neptune Plus MC-ICP-MS using the sample standard bracketing method. The Li isotopic ratio is reported in $\delta^{7}Li$ relative to L-SVEC. Repeat analyses of the IAPSO seawater give $\delta^{7}Li$ of 30.73 ± 0.14‰ (mean ± 2 standard error, n = 14), which is close to recently published values of 30.78±0.14‰ and 30.89±0.18‰ (He et al., 2021; Zhang et al., 2021).

X-Ray diffraction (XRD) was used to qualitatively identify the clay mineral composition of the loess samples. The samples were first decarbonated by acetic acid of 1 mol/L, followed by sedimentation and centrifugation to separate the clay-sized particles. Air-dried slices were made for the XRD test using a Rigaku D/max-rA diffractometer with Cu-K$_\alpha$ radiation. The scan range of the goniometer is 3° to 36° (2θ) with step length is 0.01°. Details on the XRD measurement and the 4 loess sections used in this study can be found in Zhao et al. (2005). The X-Ray diffractograms of the 8 samples are shown in Fig. 1C.

Endmember calculation

Endmember calculation uses the concentration of NO_3^-, Cl^-, SO_4^{2-}, Na^+, Mg^{2+} of stream water. It is assumed that NO_3^- in stream water is solely derived from anthropogenic pollution

(e.g., agriculture input) with $Cl^-/Na^+ = 4\pm1$, $NO_3^-/Na^+ = 7\pm3$, and $SO_4^{2-}/Na^+ = 1$ according to Zhang et al. (2015). The ions contributed by anthropogenic pollution to the stream water can then be calculated by following equations:

$$[NO_3^-]_{anth} = [NO_3^-]_{stream} \qquad (S18)$$

$$[Na^+]_{anth} = [NO_3^-]_{anth} \times \left(\frac{[Na^+]}{[NO_3^-]}\right)_{anth} \qquad (S19)$$

$$[Cl^-]_{anth} = [Na^+]_{anth} \times \left(\frac{[Cl^-]}{[Na^+]}\right)_{anth} \qquad (S20)$$

$$[SO_4^{2-}]_{anth} = [Na^+]_{anth} \times \left(\frac{[SO_4^{2-}]}{[Na^+]}\right)_{anth} \qquad (S21)$$

The remaining Cl^- and SO_4^{2-} after anthropogenic correction are from rain and evaporite which can be solved by equations of two unknowns once the composition of rain and evaporite are fixed. The rain endmember is assumed to have the same composition as seawater ($Cl^-/Na^+=1.17$, $SO_4^{2-}/Na^+=0.06$) and the evaporite endmember is represented by the result of the loess leaching experiment ($Cl^-/Na^+=0.32\pm0.02$, $SO_4^{2-}/Na^+=0.35\pm0.02$, 2 standard error of measurement error). These two endmembers have distinct Cl^-/SO_4^{2-} which allows accurate calculation of endmember mixing for the stream waters used in this study.

$$[Cl^-]_{stream} - [Cl^-]_{anth} = [Cl^-]_{rain} + [Cl^-]_{evap} \qquad (S22)$$

$$[SO_4^{2-}]_{stream} - [SO_4^{2-}]_{anth} = [Cl^-]_{rain} \times \left(\frac{[SO_4^{2-}]}{[Cl^-]}\right)_{rain} + [Cl^-]_{evap} \times \left(\frac{[SO_4^{2-}]}{[Cl^-]}\right)_{rain} \qquad (S23)$$

$[Cl^-]_{rain}$ and $[Cl^-]_{evap}$ can be solved by Eqs. (S22) and (S23). Thus, the content of Na^+ and Mg^{2+} in these two endmembers can be calculated according to the Cl^-/Na^+ and Mg^{2+}/Na^+ of the endmembers.

$$[Na^+]_{rain} = [Cl^-]_{rain} \times \left(\frac{[Na^+]}{[Cl^-]}\right)_{rain} \qquad (S24)$$

$$[Na^+]_{evap} = [Cl^-]_{evap} \times \left(\frac{[Na^+]}{[Cl^-]}\right)_{evap} \qquad (S25)$$

$$[Mg^{2+}]_{rain} = [Na^+]_{rain} \times \left(\frac{[Mg^{2+}]}{[Na^+]}\right)_{rain} \qquad (S26)$$

$$[Mg^{2+}]_{evap} = [Na^+]_{evap} \times \left(\frac{[Mg^{2+}]}{[Na^+]}\right)_{evap} \qquad (S27)$$

Carbonate dominants weathering source of Mg ions in stream water (Li and Li, 2014) while Na released from carbonate weathering can be quantified by the Mg^{2+}/Na^+ of carbonate component of the loess leaching experiment. Thus,

$$[Mg^{2+}]_{carb} = [Mg^{2+}]_{stream} - [Mg^{2+}]_{rain} - [Mg^{2+}]_{evap} \qquad (S28)$$

$$[Na^+]_{carb} = [Mg^{2+}]_{carb} \times \left(\frac{[Na^+]}{[Mg^{2+}]}\right)_{carb} \qquad (S29)$$

This may overestimate the Mg^{2+} and Na^+ from the carbonate contribution. However, since the final results of carbonate contribution to Li and Na budget are quite low (Fig. 3), this approximation won't influence our conclusion. After the correction of anthropogenic, rain, evaporite and carbonate input, the remaining Na^+ is ascribed to contribution of silicate weathering.

$$[Na^+]_{sili} = [Na^+]_{stream} - [Na^+]_{anth} - [Na^+]_{rain} - [Na^+]_{evap} - [Na^+]_{carb} \quad \text{(S30)}$$

Na is a conservative element in stream water which can hardly be adsorbed or enter any secondary precipitates. Thus, the initial Li^+ concentration of the stream water without any removing of Li into secondary precipitates can be given based on the Na contribution and Li/Na ratio of each endmember. Similarly, the initial δ^7Li of stream water before any precipitation happens can be calculated based on the Li contribution and δ^7Li of each endmember. The two equations are expressed as follows:

$$[Li^+]_{initial} = \Sigma_i \left[[Na^+]_i \times \left(\frac{[Li^+]}{[Na^+]} \right)_i \right] \quad \text{(S31)}$$

$$\delta^7Li_{initial} = \frac{\Sigma_i \left[[Na^+]_i \times \left(\frac{[Li^+]}{[Na^+]} \right)_i \times \delta^7Li_i \right]}{[Li^+]_{initial}} \quad \text{(S32)}$$

where i represents either of the 5 endmembers (anthropogenic pollution, rain, evaporite, carbonate and silicate). The result of Eq. (S31) can then be used to calculate the f value which represents the ratio of Li remains in stream water, and the result of Eq. (S32) can be used to constrain the apparent isotope fractionation:

$$f = \frac{[Li]_{stream}}{[Li]_{initial}} \quad \text{(S33)}$$

$$r = \frac{\delta^7Li_{stream}/1000 + 1}{\delta^7Li_{initial}/1000 + 1} \quad \text{(S34)}$$

Monte Carlo simulations

Monte Carlo simulation is applied to estimate the propagated errors in the calculation. In each simulation, the input values, such as the endmember ion ratios and lithium isotopic ratios, are randomly shifted by a value following a Gaussian distribution with given standard deviation σ. For measurement of a single sample representing an endmember (e.g., leaching experiment of Caoxian loess for evaporite, carbonate and silicate), σ stands for the measurement error (2SD=5% for ion content and 2SD=0.52‰ for lithium isotopes). For average results of several samples representing an endmember (e.g., evaporite of Yellow River), σ stands for the standard deviation of those samples. As the calculated results change in every simulation, the whole algorithm was repeated for 100 times to get average value and the propagated standard deviation of the results. The detailed endmember values and their standard deviations are shown in Table S1.

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TABLES

Table S1. Endmember values and their standard deviations (2SD) used in the endmember mixing model

Endmember		Mg/Na	Cl/Na	NO_3/Na	SO_4/Na	1000*Li/Na	δ^7Li/‰	Data Source
Rain		0.112	1.17	0	0.06	0.054	9.3±0.5	Gou et al., 2019; Turner et al., 1981
Anthropogenic		0	4±1	7±3	1	0.014+0.001	23.8±0.5	Gou et al., 2019; Zhang et al., 2015
Evaporite	CLP	0.05±0.004	0.32±0.02	0	0.35±0.02	0.103±0.007	14.8±0.5	leaching experiment
	Yellow River	0	0.77±0.15	0	0.64±0.15	0.252±0.14	23.6±4.8	Gou et al., 2019
Carbonate		25.6±1.8	0	0	0	19.32±1.41	4.4±0.5	leaching experiment
Silicate		7.1±0.5	0	0	0	52.95±3.74	1.4±0.5	leaching experiment

Table S2. Sample information and testing results of all the sampling sites in this study

Sample Name	Latitude/°N	Longitude/°E	Concentration (umol/L)										δ^7Li	2SE
			Ca	K	Mg	Na	Sr	F	Cl	NO_3	SO_4	Li		
20190807-1	34.836140	111.155696	924	50	1403	2502	12	12	55	0	7	2.30	23.10	0.14
20190807-3	35.937766	110.756548	3047	271	1728	4659	14	5	419	17	108	3.73	17.05	0.53
20190808-1	36.121007	110.688269	1138	117	626	1267	6	9	76	2	17	1.62	23.13	0.05
20190808-3	36.080030	110.230421	1292	130	895	1418	7	11	72	2	7	1.60	27.59	0.04
20190808-4	36.045072	110.143154	1097	57	1102	1541	8	14	32	1	10	1.90	22.11	0.17
20190808-5	36.023364	110.147966	1262	35	769	756	6	11	52	3	10	1.13	22.84	0.15
20190808-6	35.710569	109.424710	1348	68	950	1696	8	7	745	6	103	2.08	20.29	0.44
20190809-1	36.622006	109.419401	883	67	1041	2465	9	7	229	3	60	2.67	22.66	0.05
20190809-2	36.694322	109.422173	1009	90	1336	4611	11	9	231	3	61	2.76	22.91	0.19
20190809-3	36.791824	109.890846	1339	63	863	1814	10	9	209	2	34	3.41	15.04	0.55

20190809-4	36.846407	110.009821	1237	81	1168	2773	11	7	254	2	38	3.09	15.77	0.64
20190809-6	36.927438	110.175012	1011	115	1160	4061	11	11	277	4	39	3.02	23.54	0.05
20190809-7	37.187493	110.129156	833	85	1603	4946	11	8	139	2	58	2.84	21.85	0.20
20190809-8	37.419463	110.144037	1196	83	2366	5689	18	6	530	3	104	3.50	21.04	0.10
20190809-9	37.508907	110.220537	988	61	1185	4013	11	9	308	1	55	2.73	21.06	0.37
20190810-4	38.041787	109.363503	1301	53	1071	3516	10	9	104	1	74	1.42	28.50	0.04
20190810-5	37.835355	109.223078	835	66	1785	6129	14	7	244	1	76	2.38	26.11	0.49
20190811-3	36.864132	107.237387	19267	382	30430	143932	339	4	20235	51	1030	37.42	18.62	0.16
20190811-4	36.775609	107.179976	7962	314	28908	61462	179	25	8373	105	1066	7.64	22.41	0.16
20190811-5	36.714926	107.185894	5831	217	23353	44802	170	20	6203	52	907	7.07	27.57	0.05
20190811-6	36.641002	107.221692	2667	129	6937	12310	53	10	1773	15	277	5.25	22.33	0.11
20190811-7	36.578984	107.277533	1710	131	6879	15028	60	12	1855	6	356	6.25	23.23	0.14
20190811-8	36.441128	107.441810	1074	75	4978	11253	35	8	1366	6	218	5.29	27.31	0.14
20190811-9	36.235776	107.606541	3281	198	9578	22431	74	15	2863	26	443	6.39	22.41	0.06
20190812-1	35.768010	107.789424	757	93	1340	3709	11	10	178	1	32	3.96	21.33	0.13
20190812-2	35.680876	107.502420	1080	55	2125	5294	24	8	428	3	108	4.89	23.75	0.10
20190812-3	35.722346	107.349337	383	36	514	1964	4	16	58	0	28	2.60	22.11	0.05
20190812-4	35.710092	107.143584	679	131	1902	7234	19	7	558	0	129	4.74	21.40	0.40
20190812-5	35.674309	107.092054	687	50	2177	6003	23	6	268	0	89	3.79	24.15	0.14
20190812-6	35.619019	106.889413	250	24	841	3425	6	6	60	0	21	2.84	21.78	0.07
20190812-7	35.485906	106.913291	366	71	1282	5067	8	9	128	0	61	3.73	26.72	0.04
20190812-8	35.488584	106.883880	310	51	1673	4598	9	7	139	1	58	3.74	25.84	0.05
20190812-9	35.499771	106.841050	1316	75	1129	1401	19	7	56	3	44	1.20	25.53	0.04
20190813-4	35.154415	106.794178	1373	31	904	822	7	12	18	1	13	1.07	22.41	0.04
20190813-5	35.124701	106.790524	1397	64	899	567	6	10	24	3	17	1.47	19.37	0.09
20190813-6	35.124701	106.790524	1798	24	786	385	6	12	18	0	6	1.30	18.70	0.58
20190813-7	35.022014	106.781489	1315	42	973	358	4	14	32	1	8	1.15	17.05	0.10
20190813-8	34.974321	106.779637	1066	50	1023	653	6	10	19	2	13	1.73	17.82	0.41
20190813-9	34.887404	106.837948	934	53	416	367	4	13	30	3	15	0.49	21.74	0.50

20190814-1	34.378676	107.049914	1266	108	1000	2593	9	4	15	3	11	2.09	22.31	0.05
20190814-4	34.309371	108.099221	1365	164	1147	3082	7	11	18	8	11	2.63	22.34	0.04
20190814-5	34.338256	108.109578	2047	64	1695	2921	11	9	176	5	26	2.50	20.55	0.51
20190814-6	34.337634	108.115576	893	77	1290	2972	9	6	253	15	41	2.63	23.26	0.12
20190815-1	35.545473	109.300906	933	176	1886	8378	14	6	635	1	139	4.10	23.19	0.04
20190815-2	34.547079	109.305005	1099	128	968	3758	10	6	268	5	57	2.44	19.54	0.36
20190815-3	34.424047	109.519657	973	31	488	690	4	3	24	6	12	0.80	22.05	0.19
20190815-4	34.610877	110.283662	1247	94	1000	2924	10	8	223	4	50	2.22	18.40	0.14