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Clumped isotopes in near-surface atmospheric CO_2 over land, coast and ocean in Taiwan and its vicinity

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S1. Error and reproducibility

The reproducibility of Δ_{47} for air CO_2 was checked using three aliquots of air taken out from a compressed air cylinder (40 L cylinder at a pressure of ~2000 psi). The [CO_2] inside the cylinder was 387.7 ppm. CO_2 was extracted following standard cryogenic technique with GC cleaning discussed in the main text. The standard deviations for three measurements were 0.07, 0.08, and 0.01‰ for $\delta^{13}C$, $\delta^{18}O$, and Δ_{47}, respectively (Table S1). The accuracy of Δ_{47} for air CO_2 could not be checked due to lack of air standards. We checked accuracy with AS-2 CO_2 by equilibrating it with waters at different $\delta^{18}O$, viz., -106‰, -25‰, and +22 ‰ at 15 ^oC and 25 ^oC. The results are summarized in Table S2.

S2. Local meteorological parameters

Table S3 shows Δ_{47} values along with the local meteorological parameters for the sub-urban and coastal stations. This is to check the effect of wind speed and direction on the Δ_{47} values of air CO_2. Meteorological parameters are taken from the nearest weather stations, Nankang (station code: C0A9G0; 25°03′27″ N, 121°35′41″ E, 42 m a.s.l.) and Keelung (station code: 466940; 25°08′05″ N, 121°43′56″ E, 26.7 m a.s.l.). Most of the time of the post summer and winter, Academia Sinica campus observes easterly and north-easterly winds, except in some days on which south-easterly and southerly winds are also observed. In the coastal station the winds are mainly northerly and north-easterly during the sampling period.

S3. Alteration in Δ_{47} due to contribution from fossil fuel combustion

We estimated the contribution in Δ_{47} of air CO_2 from the fossil fuel combusted CO_2 in the urban and sub-urban station, i.e., Roosevelt Road and Academia Sinica Campus (Section 4.4 in main text). Table S4 shows the average Δ_{47} values observed at the two sites and compared to the expected Δ_{47} values considering air CO_2 is a mixture of two components, viz., background CO_2 and vehicle emitted CO_2. The observed Δ_{47} value at the urban street is similar to that obtained from the mixing of the two components while it significantly lower in the sub-urban site.

Table S1. Reproducibility of stable isotope analysis including Δ_{47} from three aliquots of air CO_2 extracted from a compressed air cylinder.

Sl.No.	$\delta^{13}C$(‰) (VPDB)	$\delta^{18}O$ (‰) (VSMOW)	δ^{47}(‰)	Std. Err.	Δ_{47}(‰) (ARF)	Std. Err
1	-8.37	25.51	13.03	0.02	0.8737	0.007
2	-8.44	25.71	13.18	0.02	0.8557	0.014
3	-8.54	25.56	12.85	0.02	0.8489	0.012
Average	-8.45	25.60	13.02		0.859	
Std. dev.	0.07	0.08	0.14		0.010	
Std. Err.	0.04	0.05	0.07		0.006	

Table S2. Clump and bulk isotopes and temperature estimated from Δ_{47} values for AS-2 cylinder CO_2 equilibrated at 25±2 ^{o}C and 15±2 ^{o}C with waters of different $\delta^{18}O$ values.

Sl. No.	$\delta^{13}C$(‰) (VPDB)	$\delta^{18}O$(‰) (VSMOW)	δ^{47}(‰)	Std. Err.	Δ_{47} (ARF)	Std. Err	Δ_{47} Temp. (^{o}C)
At 25±2 ^{o}C, $\delta^{18}O_{water}$ ~ 0‰							
1	-32.59	41.26	-12.35	0.02	0.923	0.016	25
2	-32.53	41.17	-12.39	0.02	0.926	0.017	25
At 25±2 ^{o}C, $\delta^{18}O_{water}$ ~ -8‰							
3	-32.68	33.93	-2.91	0.02	0.929	0.015	24
4	-32.54	34.11	-2.60	0.01	0.923	0.010	25
At 15±2 ^{o}C, $\delta^{18}O_{water}$ ~ -25‰ and 22‰							
5	-32.39	16.99	-19.12	0.01	0.962	0.012	18
6	-32.40	64.45	24.34	0.01	0.972	0.006	16

Table S3. Δ_{47} values along with the meteorological parameters (averaged over the sample collection duration) for semi-urban (Academia Sinica Campus) and Coastal (Keelung and Fuguei Cape) stations.

Date time	Δ_{47} (‰) (ARF)	Press. (mb)	Temp. (^{o}C)	RH (%)	Wind speed (m/s)	Wind direction (degree)
Academia Sinica Campus						
17/10/2013 10:00	0.893	1017	24	71	1.1	81
17/10/2013 14:30	0.883					
17/10/2013 17:20	0.89					
30/10/2013 10:00	0.878	1014	26	69	1.1	77
30/10/2013 14:30	0.887					
4/11/2013 10:30	0.89	1017	22	90	0.6	86
4/11/2013 14:30	0.881					
4/11/2013 18:30	0.885					
9/11/2013 10:30	0.912	1013	29	67	1.0	117
9/11/2013 14:00	0.914					
9/11/2013 18:30	0.918					
19/11/2013 10:00	0.923	1020	19	50	0.9	89
19/11/2013 14:00	0.912					
19/11/2013 18:00	0.888					
27/01/2014 10:30	0.894	1018	19	60	1.6	82
27/01/2014 15:20	0.91					
27/01/2014 18:00	0.896					
3/02/2014 11:00	0.954	1007	23	69	1.5	195
3/02/2014 14:30	NA					
3/02/2014 19:30	0.962					
17/02/2014 10:30	0.875	1015	22	68	0.5	131
17/02/2014 14:30	0.892					
17/02/2014 18:30	0.889					
19/02/2014 10:00	0.892	1017	13	89	0.4	113
19/02/2014 18:00	0.892					
20/02/2014 14:30	0.863	1024	13	57	0.8	39
20/02/2014 18:00	0.86					
22/02/2014 12:15	0.869	1020	19	72	0.8	70
22/02/2014 17:00	0.85					
24/02/2014 17:30	0.859	1016	24	53	1.2	203
Keelung coast						
3/10/2013 11:30	0.896	1011	24	70	7.7	13
3/10/2013 12:30	0.917					
13/11/2013 11:00	0.946	1014	19	91	5.3	51
21/11/2013 12:30	0.890	1017	21	72	1.8	60

28/11/2013 12:00	0.908	1022	14	66	7.2	12
Fuguei Cape coast						
13/11/2013 13:30	0.916	1014	19	91	5.3	51
21/11/2013 15:30	0.880	1017	21	72	1.8	60
28/11/2013 15:00	0.886	1022	14	66	7.2	12

Table S4. Average Δ_{47} value in air CO_2 at Roosevelt Road (urban) and Academia Sinica Campus (sub-urban) and that expected assuming mixtures of background and anthropogenic CO_2.

Sampling location	Average Δ_{47} (ARF)	CO_2 Conc. (ppmv)	Expected Δ_{47} (ARF)*	Difference Δ_{47}†
Roosevelt Road	0.807	500	0.798	0.009
Academia Sinica Campus	0.897	411	0.923	0.026

*Linear summation of the equilibrium Δ_{47} values of background air (395 ppmv) and car exhaust.

†Difference between the expected and observed Δ_{47} values assuming air CO_2 as a mixture of background and car exhaust CO_2. Δ_{47} value of car exhaust CO_2 was taken to be 0.273‰ (see Table 2 in the main text).