

Supplementary Material

Spatiotemporal variability of oxygen isotope anomaly in near surface air CO₂ over urban, semi-urban and ocean areas in and around Taiwan

S1. Notations

The isotopic composition of a gas is defined as

$$\delta_i = R_i/R_{\text{std}} - 1, \quad (\text{S1})$$

where $R_i = (^{13}\text{C}/^{12}\text{C})$, $(^{17}\text{O}/^{16}\text{O})$, or $(^{18}\text{O}/^{16}\text{O})$ for CO₂ in this study, and R_{std} is the same ratio in a standard sample. The unit ‰ reads per mil or parts per thousand. Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are reported with respect to V-PDB and V-SMOW, respectively.

In typical biogenic/atmospheric processes, the partitioning between species oxygen isotope ratios follow a mass-dependent relation, i.e.,

$$\ln(1+\delta^{17}\text{O}) = \lambda \times \ln(1+\delta^{18}\text{O}). \quad (\text{S2})$$

The factor λ in our work is taken to be 0.516 (λ_0) but may vary between 0.500 and 0.532 depending on fractionation processes. The $\Delta^{17}\text{O}$ value is defined to quantify the deviation from the mass-dependent fractionation line:

$$\Delta^{17}\text{O} = \ln(1+\delta^{17}\text{O}) - 0.516 \times \ln(1+\delta^{18}\text{O}). \quad (\text{S3})$$

S2. The selection of λ

The definition of λ and the selection of the reference do not change the interpretation, as long as the same scales are used consistently. The factor λ is chosen to be 0.516, following the fractionation that occurs in transpiration globally between 60°S-75°N (Landais *et al.*, 2006) at averaged relative humidity of 75% (Dai, 2006). The selected λ is close to the fractionation of evaporative and diffusional processes (Barkan and Luz, 2007; Luz and Barkan, 2010). With this definition, the formulation of the partitioning of triple oxygen isotopes between meteoric, vapor, soil, stem, and leaf waters and CO₂ can be simplified to prescribing meteoric water only. Given that the triple isotope variation in these processes follows a similar λ , the so-called oxygen anomaly remains unchanged during its transfer across reservoirs.

S3. Analytical method

The CO₂-O₂ oxygen isotope exchange method developed by Mahata *et al.* (2013) was followed with a slight modification to measure the $\Delta^{17}\text{O}$ value of CO₂ samples. Isotopic analyses were done using a FINNIGAN MAT 253 mass spectrometer in the dual inlet mode at Research Center for Environmental Changes, Academia Sinica, Taiwan. The O₂ is measured for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ before and after the exchange reaction. First, the sample CO₂ gas is measured in the mass spectrometer for δ^{45} and δ^{46} relative to an aliquot of working reference (WR-CO₂; WES in Mahata *et al.*, 2012) gas. Following analysis the gas is frozen back in the sample tube, transferred to a reaction chamber and exchanged with an equal amount of tank O₂ for approximately 2 hours. The O₂ used for exchange is taken from a large reservoir (3-liter at ~1-bar) and expanded in the reaction chamber and a sample bottle simultaneously. The reaction chamber and the sample

bottle are kept in contact for at least 10 min for full equilibration and then isolated. The sample in the bottle is analyzed for ^{17}O and ^{18}O relative to a laboratory working reference WR-O₂ (AP-4 in Mahata *et al.*, 2012) gas to obtain the pre-exchange δ -values. After the reaction, the exchanged O₂ is separated from CO₂, taken in a molecular sieve and measured relative to the same WR-O₂ gas to obtain the post-exchange δ -values. The removal of CO₂ is done by passing the mixture through a coiled U-trap submerged in LN₂. During the transfer, the line pressure is kept below ~ 5 mbar, to ensure that part of O₂ is not trapped along with CO₂ at LN₂ temperature. Mass spectrometer cross-contamination for O₂ isotope analysis is checked and is found beyond detection limit, consistent with a previous study (Assonov and Brenninkmeijer, 2003).

The analytical precision obtained for the $\Delta^{17}\text{O}$ value of CO₂ is better than 0.01‰ (1- σ standard deviation; see Table S1-S3). Table S1 shows the analytical reproducibility of $\Delta^{17}\text{O}$ value in CO₂ from a commercial CO₂ tank (AS-1). The overall precision is 0.01‰. The precision, however, is better when a sample is analyzed batch-wise in which three aliquots were run at the same time taking advantage of the system design having three exchange chambers. Better precision in a single batch is obtained because the exchange reaction in each reaction chamber proceed nearly identically. The three chamber design is optimized to obtain high precision for CO₂ diurnal variation study (see Table 2 of Mahata *et al.*, 2016).

A more rigorous precision test is summarized in in Liang and Mahata (2015), where aliquots of the same gas were taken from a tank of compressed air with CO₂ concentration of 387.7 ppmv. The compressed air tank is a commercially available cylinder of 47 L with air pressurized to

~4000 psi using a compressor which has an inbuilt water removal system (MingShen Enterprise Co., Ltd., Taiwan). Besides that, no additional moisture trap was used.

For checking reproducibility we also compared samples collected in duplicates (Table S2). In this case two sample flasks were connected in series. We see that the difference between duplicates is slightly larger for $\delta^{13}\text{C}$ values relative to the $\delta^{18}\text{O}$ values. For $\Delta^{17}\text{O}$ values the difference is only ~0.005‰. The larger deviation in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is likely due to the fact that we did not wait long enough for the two flasks to equilibrate. Due to mass dependent nature of oxygen isotope fractionation during collection reproducibility is not impaired for $\Delta^{17}\text{O}$ values.

The accuracy in determination of $\Delta^{17}\text{O}$ value is established using samples of CO_2 with known $\Delta^{17}\text{O}$ values made by converting O_2 with known $\Delta^{17}\text{O}$ values using the graphite/platinum technique (Mahata *et al.*, 2012; Barkan and Luz, 1996) (Table S3). During the conversion, there is exchange of oxygen isotopes of CO_2 and O_2 with that of hot quartz. A deviation of ~0.2‰ in $\delta^{18}\text{O}$ value in sample #5 is observed. As a result, $\delta^{17}\text{O}$ value is also modified. However, we note that the exchange with hot quartz possibly follows a slope of 0.523 (by analogy of $\text{CeO}_2\text{-O}_2$ exchange; see Hofmann and Pack, 2010). If we attribute the change in $\delta^{18}\text{O}$ value to quartz exchange, following our definition of $\Delta^{17}\text{O}$ (equation S3), 0.2‰ deviation in $\delta^{18}\text{O}$ value would change the $\Delta^{17}\text{O}$ value by $(0.523-0.516)\times 0.2\text{‰} = 0.0014\text{‰}$, well within our current analytical precision. Moreover, if the exchange with quartz is present in a larger degree (say 1% in $\delta^{18}\text{O}$ value), we should be able to get measurable shift in the $\Delta^{17}\text{O}$ value for those samples which have large $\Delta^{17}\text{O}$ difference from that of quartz. Assuming that our quartz tube has $\Delta^{17}\text{O}$ value of -

0.25‰ (similar to CeO₂; Hofmann and Pack, 2010) oxygen samples #6 and #7 with $\Delta^{17}\text{O}$ value of 1.809‰ would result in CO₂ having ~0.007‰ less in $\Delta^{17}\text{O}$ value, i.e. a value of 1.802‰. So the quartz exchange effect, if present, is beyond the current nominal precision, and we do not consider or attempt to calibrate for it. In addition, a few aliquots of AS-1 CO₂ were sent to UCSD for calibration, using the fluorination system in Thiemens' laboratory and there is good agreement between our assigned value and what they determined.

Table S1: Reproducibility of $\Delta^{17}\text{O}$ values ($\lambda=0.516$) in CO_2 samples from a commercial CO_2 tank (AS-1). AS-1 CO_2 is a pure CO_2 cylinder, with $\delta^{13}\text{C} = -39.92\text{‰}$ (V-PDB) and $\delta^{18}\text{O} = 11.53\text{‰}$ (V-SMOW). The $\Delta^{17}\text{O}$ value of AS-1 CO_2 was also determined independently using fluorination at UCSD (see Table S3). Our current design is to handle three samples at a time in one batch.

Sample	Batch	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Avg	Stdev
1	#1	-39.92	11.53	0.133	0.141	0.007
2				0.145		
3				0.146		
4	#2			N/A	0.139	0.011
5				0.147		
6				0.131		
7	#3			0.127	0.135	0.017
8				0.124		
9				0.155		
10	#4			0.142	0.141	0.006
11				0.135		
12				0.146		
13	#5			0.133	0.128	0.007
14				0.120		
15				0.132		
16	#6			0.121	0.130	0.008
17				0.131		
18				0.137		
Average				0.136		
Stdev				0.010		

Table S2: Isotopic ratios of CO₂ samples collected in duplicates on the 4th of June, 2014 in the campus of Academia Sinica. The average differences in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between flask pairs are: 0.12 and 0.07 ‰ respectively. In contrast, absolute difference in $\Delta^{17}\text{O}$ values of flask pairs is ~0.005‰.

	[CO ₂] (ppmv)	$\delta^{13}\text{C}$ (‰) V-PDB	$\delta^{18}\text{O}$ (‰) V-SMOW	$\Delta^{17}\text{O}$ (‰)	Diff. (‰)
Pair #1	423.5	-9.36	40.77	0.374	0.004
		-9.23	40.88	0.378	
Pair #2	420.2	-9.13	41.18	0.372	0.008
		-9.20	41.15	0.380	
Pair #3	417.3	-9.09	41.16	0.406	0.003
		-9.25	41.09	0.409	
				Average	0.005

Table S3: Determination of accuracy in the $\Delta^{17}\text{O}$ values of CO_2 in the present experimental setup. Calibration is done using tanks of O_2 and CO_2 from OZTECH (OZTECH Trading Corporation, Safford, AZ, USA). Samples #1-7 are CO_2 made in the laboratory following the graphite method described in the text. Nominal $\Delta^{17}\text{O}$ (CO_2) is either assumed to be the same as initial O_2 used for converting to CO_2 (samples #1-7) or measured at UCSD (AS-1 CO_2 and NBS-18). Measured $\Delta^{17}\text{O}$ (CO_2) values refer to the final values after correction (see Mahata *et al.*, 2013 for details). Diff. refers to the difference of the measured $\Delta^{17}\text{O}$ value from the nominal value.

Sample	Nominal $\Delta^{17}\text{O}(\text{CO}_2)$ V-SMOW ‰	Graphite conversion			Measured $\Delta^{17}\text{O}(\text{CO}_2)$ ‰	Diff. ‰
		$\delta^{17}\text{O}(\text{O}_2)$ V-SMOW ‰	$\delta^{18}\text{O}(\text{O}_2)$ V-SMOW ‰	$\delta^{18}\text{O}(\text{CO}_2)$ V-SMOW ‰		
1	-0.254	7.708	15.491	15.455	-0.260	-0.006
2	-0.254	7.708	15.491	15.455	-0.257	-0.003
3	-0.254	7.708	15.491	15.455	-0.256	-0.002
4	-0.169	7.762	15.430	15.416	-0.160	0.009
5	0.124	8.044	15.404	15.590	0.132	0.008
6	1.809	12.523	20.827	20.824	1.796	0.013
7	1.809	12.523	20.827	20.824	1.805	0.004
AS-1	0.15 ± 0.03^a	N/A	N/A	N/A	0.136 ± 0.010	-0.01
NBS-18	0.10 ± 0.03^b	N/A	N/A	N/A	0.090^b	-0.01

^aThe AS-1 value was measured at UCSD, using fluorination method to convert CO_2 to O_2 for direct oxygen isotope analysis.

^bThe NBS-18 nominal value is taken from Farquhar *et al.* (1998). Following the same acid digestion method, our measured value is 0.090‰ ($n=1$).

Note: For absolute calibration of oxygen isotopes we did not measure V-SMOW but we do measure air O_2 . $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ values of several samples ($n=5$) of air O_2 measured by us are $23.95 \pm 0.06\text{‰}$, $12.07 \pm 0.03\text{‰}$, and $-0.213 \pm 0.013\text{‰}$, respectively. For comparison, Barkan and Luz (2011) report 23.881‰ , 12.026‰ , and -0.223‰ . Our calibration CO_2 standard is from OZTECH, in good agreement with an independent check using NBS-19 CO_2 ; the scale differences in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between OZTECH CO_2 and NBS-19 CO_2 are about 0.05‰ .

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