

1 **Clumped isotopes in near surface atmospheric CO₂ over land, coast and ocean in**
2 **Taiwan and its vicinity**

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25 **Abstract**

26 Molecules containing two rare isotopes (e.g., $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ in CO_2), called clumped isotopes, in
27 atmospheric CO_2 are powerful tools to provide an alternative way to independently constrain
28 the sources of CO_2 in the atmosphere because of their unique physical and chemical
29 properties. We presented clumped isotope data (Δ_{47}) in near surface atmospheric CO_2 from
30 urban, sub-urban, ocean, coast, high mountain (~3.2 km a.s.l.) and forest in Taiwan and its
31 vicinity. The primary goal of the study was to use the unique Δ_{47} signature in air CO_2 to show
32 the extents of its deviations from thermodynamic equilibrium due to different processes such
33 as photosynthesis, respiration, local anthropogenic emissions, which the commonly used
34 tracers such as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ cannot provide. We also explored the potential of Δ_{47} to
35 identify/quantify the contribution of CO_2 from various sources. Atmospheric CO_2 over ocean
36 was found to be in thermodynamic equilibrium with the surrounding surface sea water.
37 Respired CO_2 was also in close thermodynamic equilibrium at ambient air temperature. In
38 contrast, photosynthetic activity result in significant deviation in Δ_{47} values from that
39 expected thermodynamically. The disequilibrium could be a consequence of kinetic effects
40 associated with the diffusion of CO_2 in and out of the leaf stomata. We observed that $\delta^{18}\text{O}$
41 and Δ_{47} do not vary similarly when photosynthesis was involved unlike simple water- CO_2
42 exchange. Additionally we obtained Δ_{47} values of car exhaust CO_2 that were significantly
43 lower than the atmospheric CO_2 but higher than that expected at the combustion temperature.
44 In urban and sub-urban regions, the Δ_{47} values were found to be lower than the
45 thermodynamic equilibrium values at the ambient temperature, suggesting contributions from
46 local combustion emissions.

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52 **Keywords:** clumped isotopes; atmospheric CO_2 ; thermodynamic equilibrium; anthropogenic;
53 car exhaust

54 **1. Introduction**

55 The budget of atmospheric CO₂ is widely studied using the temporal and spatial variations in
56 concentration and conventional isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of CO₂ (Francey and
57 Tans, 1987; Francey et al., 1995; Yakir and Wang, 1996; Ciais et al., 1995a,b, 1997; Peylin et
58 al., 1999; Cuntz et al., 2003; Drake et al., 2011; Welp et al., 2011; Affek and Yakir., 2014).
59 $\delta^{13}\text{C}$ is useful to differentiate the exchange of CO₂ with the ocean and land-biospheres. This
60 is due to the fact that the photosynthetic discrimination against ^{13}C during exchange with land
61 plants is higher than that associated with the chemical dissolution of CO₂ in the ocean (e.g.,
62 Tans et al., 1993; Ciais et al., 1995a; Francey et al., 1995; Ito, 2003; Bowling et al., 2014).
63 The major limitation of $\delta^{13}\text{C}$ is that it cannot distinguish CO₂ produced by high temperature
64 combustion or low temperature respiration (Affek and Eiler, 2006; Laskar et al., 2016a).
65 $\delta^{18}\text{O}$ in atmospheric CO₂ is mainly controlled by various water reservoirs (ocean, leaf and
66 soil). In urban locations, a significant fraction of CO₂ may have combustion origin possessing
67 $\delta^{18}\text{O}$ signature of atmospheric O₂ (Kroopnick and Craig, 1972; Ciais et al., 1997; Yakir and
68 Wang, 1996). $\delta^{18}\text{O}$ is used for partitioning net CO₂ terrestrial fluxes between soil respiration
69 and that exchange with plant leaves, the exchange rate is enhanced by the presence of
70 carbonic anhydrase in plants and soils (Francey and Tans, 1987; Farquhar and Lloyd, 1993;
71 Yakir and Wang, 1996; Ciais et al., 1997; Peylin et al., 1999; Murayama et al., 2010; Welp et
72 al., 2011). This is because $\delta^{18}\text{O}$ of CO₂ fluxes originated from soil respiration are different
73 from that exchanged with leaf water. $\delta^{18}\text{O}$ in soil water reflect the $\delta^{18}\text{O}$ value of local
74 meteoric water while leaf water is relatively enriched due to transpiration. The $\delta^{18}\text{O}$ values
75 from these processes and interactions are different and hence the tracer is widely used for
76 constraining the gross production of CO₂ (Francey and Tans, 1987; Ciais et al., 1997; Gillon
77 and Yakir, 2001; Cuntz et al., 2003; Welp et al., 2011). However, due to rapid exchange of
78 oxygen isotopes between CO₂ and different water reservoirs with diverse $\delta^{18}\text{O}$ and processes
79 such as evapotranspiration complicate its interpretation (Riley et al., 2003).

80 The doubly substituted isotopologues or clumped isotopes such as $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ in CO₂, denoted
81 by Δ_{47} , provides an additional and independent constraint to study the atmospheric CO₂
82 budget. Δ_{47} in air CO₂ can help to identify the mechanisms for CO₂ production and
83 consumption. Unlike conventional isotopes, clumped isotope studies for the atmospheric CO₂
84 are very limited mainly because of challenges to apply it to the atmospheric study (Eiler and
85 Schauble, 2004; Affek et al., 2007; Yeung et al., 2009). The available data are not sufficient

86 to address some key issues such as quantification of CO₂ from different sources and to what
87 extent the air CO₂ is in thermodynamic equilibrium with leaf and surface waters, especially in
88 regions with strong anthropogenic activities such as urban areas. Also the effect of
89 photosynthesis on the Δ_{47} of air CO₂ has not been studied rigorously. $\delta^{18}\text{O}$ and Δ_{47} were
90 reported to have similar time-scales for the isotope exchange between CO₂ and water (Affek,
91 2013; Clog et al., 2015), but no comparative study on their behavior in presence of other
92 processes such as photosynthesis and respiration was done. A combined assessment from all
93 the three aforementioned isotopic tracers can better constrain the budget of CO₂ and
94 associated processes than $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ alone.

95

96 Theoretically it is shown that in thermodynamic equilibrium, Δ_{47} values of CO₂ are
97 temperature dependent (Eiler and Schauble, 2004; Wang et al., 2004), verified over a wide
98 range from 10 to 1000 °C (Dennis et al., 2011). Processes that involve CO₂ and liquid water
99 as medium, such as isotopic exchange with ocean water are expected to have Δ_{47} values close
100 to the thermodynamic equilibrium. Δ_{47} values in ambient air CO₂ should reflect a balance of
101 CO₂ fluxes between biosphere-atmosphere exchange, ocean-atmosphere exchange, and
102 emissions from combustion sources. Photosynthesis involves gas phase diffusion of CO₂ into
103 leaves, fixes ~1/3 of the CO₂, and returns the rest back to the atmosphere. CO₂ molecules
104 inside a leaf are generally expected to be in thermodynamic equilibrium with leaf water
105 because of presence of enzymatic carbonic anhydrase that greatly enhances the isotopic
106 exchange (Cernusak et al., 2004). Δ_{47} values of soil respired CO₂ is also not well constrained,
107 though it is believed to be in thermodynamic equilibrium with the soil water (Eiler and
108 Schauble, 2004).

109 Here, we present clumped and conventional isotope data in near surface air CO₂ covering a
110 wide variety of processes and interactions. Air samplings were made in South China Sea, two
111 coastal stations in northern Taiwan, an urban traffic street, a sub-urban location, a forest site,
112 a greenhouse, top of a high mountain and car exhausts. The study was designed and aimed to
113 show the extents of the deviations of near surface atmospheric CO₂ from thermodynamic
114 equilibrium with local surface water. Possible influences from other processes such as
115 anthropogenic emission, respiration, and photosynthesis on clumped isotopes were explored.

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118 **2. Materials and methods**

119 Stable isotopic compositions of CO₂ including mass 47 were measured using a Finnigan
120 MAT 253 gas source stable isotope ratio mass spectrometer configured to measure ion beams
121 corresponding to M/Z 44 through 49. The instrument registers the major ion beams (44, 45
122 and 46) through resistors 10⁸, 3×10¹⁰, and 10¹¹ Ohm, respectively, and minor ion beams (47,
123 48 and 49) through 10¹² Ohm. All the measurements were carried out at Research Center for
124 Environmental Changes, Academia Sinica, Taiwan.

125
126 Air samples were collected in 2 L flasks and compressed to 2 atmospheric pressure using a
127 membrane pump. The flasks, equipped with two stopcocks, were first flushed with the
128 ambient air for ~10 mins before starting the sample collection. We then closed the
129 downstream end stopcock, allowed the pressure to build to 2 atm and then isolated by closing
130 the other stopcock. The air pumping for flushing and sampling was carried out through a
131 column packed with magnesium perchlorates to remove moisture. The moisture content was
132 reduced from the ambient value of 70-90 % to less than 1 % relative humidity, checked using
133 a LI-COR infrared gas analyzer (model 840A, LI-COR, USA). See, for example, Liang and
134 Mahata (2015) for more details of air sampling.

135
136 To show how photosynthesis and respiration affect the abundances of CO₂ isotopologues and
137 to demonstrate what different information the Δ₄₇ can give from the other isotopologues, we
138 performed analyses for CO₂ collected in a controlled greenhouse with cemented floor located
139 in the top (3rd) floor of the Greenhouse Building, Academia Sinica. The size of the
140 greenhouse was about 8m long, 5m wide and 5m high. It was closed at least one day before
141 each experiment and the ventilation was kept off. More than 70 % of the ground area inside
142 the greenhouse was occupied with *Cinnamomum cassia* plants, each of ~2 m height kept in
143 pots. Samples were collected at intervals of less than half an hour to a few hours on three
144 sunny days and one cloudy day to investigate the influence of photosynthesis and respiration
145 on the isotopologues of CO₂. Inside the room relative humidity was ~50-70 % for the three
146 sunny days and was above 90 % for the cloudy day.

147
148 Forest air CO₂ was collected from a dense natural forest at the west end of the Academia
149 Sinica Campus. The vegetation mainly consists of medium to big size trees with canopy
150 heights varying between 10 to 20 m. The samples were collected ~100 m inside the forest on
151 a small plateau at a height of ~30 m from the ground in the slope of a hill; the dense

152 vegetation allowed little sunlight penetrating to the surface. The relative humidity at the site
153 was 80-90 % during the sampling days and wind speed was nearly zero due to presence of
154 hills on three sides of the sampling spot. Marine air was collected during a cruise in the South
155 China Sea (for the cruise track see Figure 1) at a height of ~10 m a.s.l. and from two coastal
156 stations: Keelung (25°09'6" N, 121°46'22" E) and Fuguei Cape (25°18' N, 121°32' E) (Figure
157 1) at a height of ~5 m and ~20 m a.s.l. respectively. Sea surface temperatures were measured
158 at the time of sampling. Urban air was collected at a bus stop on Roosevelt Road, a busy
159 street in Taipei. Sub-urban air was collected from an open roof (~30 m above ground) of
160 Institute of Earth Science Building, Academia Sinica (AS; 25°2'41" N, 121°36'52" E);
161 grassland air was collected from a grass field in front of the Department of Atmospheric
162 Science, National Taiwan University Campus (NTU; 25° 1' N, 121°30' E), Taipei. In
163 addition, we collected air from the summit of the Hehuan mountain (24°8'15" N, 121°16'32"
164 E, 3.2 km a.s.l.) (Figure 1) on 9th October, 2013. All air samplings were made when there was
165 no rain to avoid direct interaction with the rainwater. Car exhausts were collected from a
166 Mazda 3000cc TRIBUTE and a Mitsubishi 2400cc New Outlander, using evacuated 2L glass
167 flasks from ~20 cm inside the exhaust pipes through a column of magnesium perchlorate.
168
169 CO₂ was extracted from air using a glass vacuum line connected to a turbo molecular pump
170 by cryogenic technique. The vacuum line as well as the sample flask connection assembly
171 including its head space was pumped to high vacuum before starting the CO₂ extraction. Air
172 in the flask was pumped through a series of five coiled traps, with the first two immersed in
173 dry ice-acetone slush (-77 °C) for trace moisture removal followed by three in liquid nitrogen
174 (-196 °C). CO₂ was collected from the traps immersed in liquid nitrogen by repeated freeze-
175 thaw technique at liquid nitrogen and dry ice temperatures for further removal of traces of
176 water (see Mahata et al., 2012 and Liang and Mahata, 2015 for details). The air was pumped
177 for 40-45 minutes at a controlled rate of ~90 mL/min using a mass flow controller; the
178 pressure on the post mass flow controller was ~10 mm of Hg. No measurable isotopic
179 fractionation caused by mass flow controller at this flow rate was observed, checked using
180 several aliquots of air from a high volume compressed air cylinder (~40 L at 2000 psi). For
181 car exhaust, an aliquot of exhaust air was transferred to a 60 mL bottle and CO₂ was fully

182 extracted cryogenically following the same protocol as discussed above (but with mass flow
183 controller step skipped).

184

185 CO₂ was further purified from other condensable species like N₂O, CH₄, and hydrocarbons
186 by means of gas chromatography (Agilent 6890N, with a 3.0 m × 0.3 cm stainless steel
187 column packed with PorapakQ 80/100 mesh, supplied by Supelco Analytical, Bellefonte, PA,
188 USA) with the column kept at -10 °C. High purity helium (>99.9999 % supplied by Air
189 Products and Chemicals, Inc.) at 20 mL/min was used as carrier gas. CO₂ was eluted first,
190 followed forthwith by N₂O, and CH₄, hydrocarbons and traces of water came out much later.
191 To get an optimized condition for CO₂, we checked the separation of CO₂ from N₂O with
192 varying proportions and at various temperatures (25 °C to -20 °C) and found a temperature of
193 -10 °C at which column separated CO₂ from N₂O perfectly (see Laskar et al., 2016b for
194 details). The column was baked at 200 °C for more than 2 hours prior to use. The conditioned
195 column is good for purifying three samples. At the end of the day, long baking (8-10 hours)
196 was performed. At the initial phase the working gas was taken from a high purity commercial
197 CO₂ called AS-2 (δ¹³C = -32.54 ‰ with respect to VPDB and δ¹⁸O = 36.61 ‰ with respect to
198 VSMOW) procured from a local supplier (Air Products and Chemicals, Inc.). As the
199 difference between the isotopic compositions of samples and AS-2 was high, we later
200 changed the reference to Oztech CO₂ (δ¹³C = -3.59‰ and δ¹⁸O = 24.96 ‰) (Oztech Trading
201 Corporation, USA) from December 2014 onward. No detectable difference in isotopic
202 compositions including Δ₄₇ was observed between the analyses from different working
203 references. All δ¹³C values presented in this work are expressed in VPDB scale and δ¹⁸O in
204 VSMOW scale, unless specified otherwise. Δ₄₇ is calculated following (Affek and Eiler,
205 2006):

$$206 \quad \Delta_{47} = \left[\frac{R^{47}}{2R^{13}R^{18} + 2R^{17}R^{18} + R^{13}(R^{17})^2} - \frac{R^{46}}{2R^{18} + 2R^{13}R^{17} + (R^{17})^2} - \frac{R^{45}}{R^{13} + 2R^{17}} + 1 \right] \times 1000 \quad (1)$$

207 where R^{13} and R^{18} (ratios ¹³C/¹²C and ¹⁸O/¹⁶O) are obtained by measuring the conventional
208 masses 44, 45 and 46 in the same CO₂ sample and R^{17} is calculated assuming a mass
209 dependent relation with R^{18} given by $R^{17} = R^{17}_{VSMOW} \left(\frac{R^{18}}{R^{18}_{VSMOW}} \right)^\lambda$, where exponent
210 $\lambda=0.5164$ is used for all Δ₄₇ calculations (Affek and Eiler, 2006). The value of λ varies
211 between 0.516 and 0.523 (Hoag et al., 2005; Barkan and Luz, 2012; Hoffmann et al., 2012;
212 Thiemens et al., 2014). The variation in Δ₄₇ was less than 0.01 ‰ at 25 °C when the exponent

213 was varied over the aforementioned range. This variation was comparable to the
 214 measurement uncertainty and hence not considered here; all the calculations were based on
 215 $\lambda=0.5164$. Δ_{47} is obtained by measuring CO₂ with respect to which the isotopes among
 216 various CO₂ isotopologues are distributed randomly ($\Delta_{47} \sim 0$ ‰). Practically, this random
 217 distribution is approached by heating CO₂ at 1000 °C for more than two hours (Eiler and
 218 Schauble, 2004; Affek and Eiler, 2006). Measurements were made with a stable ~12 volt
 219 signal at mass 44, with peak centring, background scanning, and pressure-balancing before
 220 each acquisition started. Each sample was analyzed for 10 acquisitions, 10 cycles each at an
 221 integration time of 8 s; the total analysis time was approximately 2.5 h. Masses 48 and 49
 222 were monitored to check isobaric interferences due to contamination of hydrocarbons (Ghosh
 223 et al., 2006). Details about the corrections due to nonlinearity related to Δ_{47} measurements in
 224 the mass spectrometer, reference frame equation for expressing the measured Δ_{47} values in
 225 absolute reference frame (ARF) were discussed in Laskar et al. (2016b). To obtain the
 226 temperature from the Δ_{47} values, we used the following relation (Dennis et al., 2011):

$$227 \quad \Delta_{47} = 0.003 \left(\frac{1000}{T} \right)^4 - 0.0438 \left(\frac{1000}{T} \right)^3 + 0.2553 \left(\frac{1000}{T} \right)^2 - 0.2195 \left(\frac{1000}{T} \right) + 0.0616 \quad (2)$$

228
 229 The reproducibility (1- σ standard deviation) for air CO₂ measurements was established from
 230 three aliquots of CO₂ extracted from a compressed air cylinder with CO₂ concentration
 231 ([CO₂]) of ~388 ppmv. The 1- σ standard deviations were 0.07, 0.08, and 0.01 ‰ for $\delta^{13}\text{C}$,
 232 $\delta^{18}\text{O}$, and Δ_{47} , respectively (Table S1 in Supplement). The long-term reproducibility in Δ_{47}
 233 measurements was found to be 0.014 ‰ (Laskar et al., 2016b) and the accuracy in Δ_{47} values
 234 in terms of temperature, based on CO₂ equilibrated with water at known temperatures were
 235 better than 3 °C (see Table S2 in Supplement).

236 For [CO₂] measurements, flasks of volume 350 cc were used. These small flasks were
 237 connected in series with the larger flasks used for isotopic measurements. [CO₂] was
 238 measured using a LI-COR infrared gas analyzer (model 840A, LI-COR, USA) at 4 Hz,
 239 smoothed with 20-s moving average. The analyzer was calibrated against a working standard
 240 (air compressed in a cylinder) with a nominal [CO₂] of 387.7 ppmv and a CO₂ free N₂
 241 cylinder. The reproducibility of LI-COR was better than 1 ppmv. The working standard was
 242 calibrated using a commercial Picarro analyzer (model G1301, Picarro, USA) by a series of
 243 NOAA/GMD certified tertiary standards with [CO₂] of 369.9, 392.0, 409.2, and 516.3 ppmv,

244 with a precision (1- σ standard deviation) of 0.2 ppmv. The [CO₂] in car exhausts were
245 estimated by gravimetric technique using an MKS Baratron gauge.

246

247 Ambient temperatures were taken from the nearest governmental weather stations (operated
248 by Central Weather Bureau, Taiwan): Nankang (for AS; station code: C0A9G0; 25°03'27"

249 N, 121°35'41" E, 42 m a.s.l.), Taipei (for NTU; station code: C1A730; 25°00' 58" N,

250 121°31' 53" E; 22 m a.s.l.), Hehuan mountain (station code: C0H9C1; 24°08'41" N, 121°15'

251 51" E, 3240 m a.s.l.), and Keelung coast (for the two coastal sites; station code: 466940;

252 25°08'05" N, 121°43'56" E, 26.7 m a.s.l.).

253

254 **3. Results**

255 **3.1 Greenhouse CO₂**

256 Diurnal variation in the concentration and isotopic compositions of CO₂ inside the controlled
257 greenhouse is shown in Figure 2. The lowest CO₂ concentration [CO₂] and highest $\delta^{13}\text{C}$ and
258 $\delta^{18}\text{O}$ values were observed during late morning hours while highest [CO₂] and lowest $\delta^{13}\text{C}$
259 and $\delta^{18}\text{O}$ values were observed during night time and early morning before sunrise (Table 1
260 and Figure 2A-2C), indicating that respiration and photosynthesis played the major role in
261 controlling the variations of the [CO₂] and isotopic compositions. Keeling plot, a graphical
262 approach plotted between isotopic composition and the inverse of the concentration is used to
263 determine the isotopic composition of the source (Pataki et al., 2003). It is valid for a mixing
264 of two components; the intercept of the plot gives the source isotopic composition.
265 Respiration was the main source of CO₂ here added to the background CO₂. Keeling analysis
266 for $\delta^{13}\text{C}$ had an intercept of -26.32 ± 0.40 ‰ (Figure 2D), a value expected for C₃ plant
267 respired CO₂. The Keeling plot for $\delta^{18}\text{O}$ had an intercept of 30.68 ± 0.73 ‰ (Figure 2E), which
268 could be explained by a combined effect of respired CO₂ equilibrated with soil water and
269 kinetic fractionation associated with the diffusion of CO₂ from soil to the air. A Keeling plot
270 for $\delta^{13}\text{C}$ with the early morning and night time greenhouse data, when photosynthesis was
271 absent, was found to have same intercept as observed with all the data, only the correlation
272 was better for the latter ($R^2=0.999$, not shown). The tight correlations among [CO₂], $\delta^{13}\text{C}$ and

273 $\delta^{18}\text{O}$ (Figure 2D-2F) suggest that photosynthesis and respiration were the dominant processes
274 controlling their variations while mixing with ambient air and anthropogenic contribution of
275 CO_2 were insignificant.

276 In contrast, Δ_{47} shows different patterns of diurnal variability due to the effect of
277 photosynthesis and respiration. Figures 3A-3D detail diurnal variations in Δ_{47} in the
278 greenhouse CO_2 in four different days. The first three were bright sunny days with
279 photosynthesis as the dominant process while the last one was a dark cloudy day affected
280 more by respiration. To further reduce photosynthetic activity on the last day, two layers of
281 black cloth that cut down the incident sunlight by ~50% were deployed. The measured Δ_{47}
282 values were also compared with the thermodynamic equilibrium values. The maximum value
283 of Δ_{47} was observed in the morning before ~8 AM and at night and the values were similar to
284 the thermodynamic equilibrium values at the ambient temperatures. This indicates that the
285 respired CO_2 was in close thermodynamic equilibrium with the leaf and soil water. The
286 daytime (from 9 AM to 5 PM) Δ_{47} values, for the three sunny days were higher than the
287 thermodynamic equilibrium values. The Δ_{47} values were observed to decrease steadily in the
288 early morning before ~9 AM and increased afterwards (Figure 3). By comparing the Δ_{47}
289 values acquired in the sunny days with that in the cloudy day, we noticed that when
290 photosynthesis was weak, the Δ_{47} value was close to the thermodynamic equilibrium with soil
291 and leaf water (Figure 4). The correlation between Δ_{47} and $[\text{CO}_2]$, $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ (Figure 3D)
292 was observed only when the photosynthesis was weak. This suggests that Δ_{47} carries
293 information different from concentration and conventional isotopic composition when
294 photosynthesis occurs. See Section 4.1 for detailed discussion.

295

296 **3.2 Car exhaust**

297 The $[\text{CO}_2]$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of car exhaust CO_2 were 39350 ± 50 ppmv, -27.70 ± 0.03 ‰
298 and 25.35 ± 0.07 ‰, respectively (Table 2). $\delta^{13}\text{C}$ value was similar to that reported elsewhere
299 (Newman et al., 2008; Popa et al., 2014), the $\delta^{18}\text{O}$ was slightly higher than the atmospheric
300 O_2 (~23.5 ‰), the source of O_2 for combustion. The average value of Δ_{47} for the exhausts
301 from the two cars was 0.273 ± 0.021 ‰, which gave a temperature of 282 ± 17 °C (Table 2).
302 This temperature is much higher than the fuel combustion temperatures (>800 °C). The
303 possible reason for higher values of $\delta^{18}\text{O}$ and Δ_{47} in the exhaust CO_2 than expected was post

304 combustion partial exchange with water and other gaseous species, released during
305 combustion, inside the catalytic converter and the exhaust pipe (see discussion in Sec. 4.2).

306

307 **3.3 Atmospheric CO₂ over ocean and coasts**

308 Isotopic compositions including Δ_{47} values obtained for CO₂ over ocean and coasts are
309 presented in Table 3. The averaged [CO₂] over ocean between latitudes 18°03' N and 21°17'
310 N was 395±7 ppmv, and the values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were -8.43±0.19 ‰ and 40.72±0.20 ‰,
311 respectively (Table 3). In the coastal stations, the averaged values of [CO₂], $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$
312 were 397±10 ppmv, -8.48±0.11 ‰, and 40.70±0.29 ‰, respectively. Both the [CO₂] and $\delta^{13}\text{C}$
313 values over the ocean and coasts were similar to those observed at Mauna Loa during the
314 sampling period, suggesting little contribution from local/regional anthropogenic sources.
315 The Keeling analysis for $\delta^{13}\text{C}$ gave in intercept of -13.61 ‰ (Figure 5A) for the air CO₂
316 collected over the ocean and coasts. $\delta^{18}\text{O}$ of air CO₂ over the ocean were close to the isotopic
317 equilibrium values with the surface sea water at the sea surface temperatures (see Sec 4.3).
318 The Δ_{47} values varied between 0.880 ‰ and 0.946 ‰ for the marine and coastal CO₂ (Table
319 3, Figures 5B), similar to that predicted at thermodynamic equilibrium at sea surface
320 temperatures (obtained using Eq. (2)). Therefore, both $\delta^{18}\text{O}$ and Δ_{47} values suggest that the
321 air CO₂ over the ocean was in close thermodynamic equilibrium with the underlying sea
322 water.

323

324 **3.4 Atmospheric CO₂ over land**

325 To show how anthropogenic emission affects the isotopic composition especially the Δ_{47}
326 values, we analyzed atmospheric CO₂ samples collected near Roosevelt Road, a busy street in
327 downtown Taipei. The averaged values of [CO₂], $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ obtained were 500±50 ppmv,
328 -11.05±0.90 ‰, and 39.32±0.94 ‰, respectively (Table 4). A significantly higher [CO₂] and
329 lower $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values compared to the marine CO₂ showed signatures of a significant
330 contribution from vehicular emissions. Δ_{47} values near Roosevelt Road were found to be in
331 the range of 0.754‰ to 0.833 ‰, with an average of 0.807±0.028 ‰ (Table 4). The values
332 were lower by ~0.15 ‰ compared to the thermodynamic equilibrium value at 20 °C, the

333 ambient temperature around the sampling time, indicating a significant fraction of CO₂
334 produced at higher temperatures, i.e., of combustion origin.

335 In the sub-urban location (Academia Sinica Campus), [CO₂] averaged over four months was
336 410±10 ppmv (Table 4), which was ~15 ppmv higher than that observed over the South
337 China Sea and that at Mauna Loa Observatory during the time of sampling. The higher [CO₂]
338 suggests contribution from local anthropogenic emissions. δ¹³C values varied between -7.83
339 and -10.30 ‰, with an average of -8.78±0.50 ‰. Keeling analysis for δ¹³C gave an intercept
340 of -26.16±1.58 ‰ (Figure 6), indicating source of CO₂ from C₃ plant respiration and/or
341 combustion. Δ₄₇ values here varied between 0.853 ‰ and 0.972 ‰ (Table 4) with an average
342 of 0.897±0.027 ‰, which were significantly less than the thermodynamic equilibrium values
343 (assuming water bodies had the same temperature as the ambient) (Figure 7).

344 The averaged [CO₂], δ¹³C and δ¹⁸O over the grassland (inside National Taiwan University
345 Campus) were 410±33 ppmv, -8.95±0.70 ‰ and 39.74±1.00 ‰, respectively. The Keeling
346 plot for δ¹³C gave an intercept of -16.98±1.02 ‰ (Figure 6), indicating that a significant
347 fraction of CO₂ originated from C₄ vegetation. This is not surprising as the CO₂ was sampled
348 over a C₄ dominated grassland (area: ~50 m x 50 m). Unlike greenhouse CO₂, no statistically
349 significant correlation between δ¹⁸O and 1/[CO₂] in air CO₂ in these sites was observed (not
350 shown), probably due to influence of multiple sources and processes on oxygen isotopes of
351 atmospheric CO₂. Figure 7C shows the Δ₄₇ values in air CO₂ over the grassland at National
352 Taiwan University Campus. A large variation in Δ₄₇ was observed (0.885 - 0.989 ‰) with an
353 average of 0.937±0.030 ‰. Some of the values were close to the thermodynamic equilibrium
354 while the others deviated significantly.

355 In a small and dense forest near Academia Sinica Campus (Figure 1), average values of
356 [CO₂], δ¹³C and δ¹⁸O in air CO₂ were 438±16 ppmv, -9.99±0.50 ‰ and 40.39±0.63 ‰,
357 respectively (Table 4) during summer (Jul-Aug) of 2015. A significantly higher [CO₂] and
358 lower δ¹³C values than the background indicate strong contribution of CO₂ from local
359 respiration. Δ₄₇ values fall in the range of 0.887 ‰ to 0.920 ‰, with an average of
360 0.895±0.012 ‰ (Table 4). The values were similar to that expected at thermodynamic
361 equilibrium (Figure 7D) except on 11th August, when a significant increase in Δ₄₇ was
362 observed. The deviation was probably due to influence of a super typhoon, which passed over
363 the region on previous days mixing and transporting air masses regionally.

364 Over the top of the Hehuan mountain (~3.2 km a.s.l), [CO₂], δ¹³C, and δ¹⁸O values in air CO₂
365 samples collected on 9th October, 2013 were 364 ppmv, -8.23±0.02 ‰ and 40.59±0.30 ‰,
366 respectively (Table 4). The lower [CO₂] and higher δ¹³C than Mauna Loa suggests
367 photosynthetic uptake, which was also seen at grassland site and inside greenhouse on a few
368 occasions. Here the averaged value of Δ₄₇ was 0.904±0.009 ‰, slightly less than that
369 expected at the ambient temperature (Table 4).

370

371 **4. Discussion**

372 A detailed discussion of the results obtained from different locations is presented below.

373

374 **4.1 Greenhouse air CO₂**

375 To minimize anthropogenic alteration and air mixing/transport and to maximize the
376 variations of CO₂ isotopologues by biological processes, a controlled greenhouse provides an
377 ideal environment. Diurnal variation was observed in [CO₂], δ¹³C, δ¹⁸O (Figure 2), and Δ₄₇
378 (Figure 3) in the greenhouse. Good correlations between [CO₂], δ¹³C and δ¹⁸O suggest
379 common processes affecting all of them, and they were photosynthesis and respiration.
380 Giving July 31st as an example, we estimated the rates of night-time respiration and daytime
381 photosynthetic uptake using the conventional isotopic compositions (analysis of Δ₄₇ is
382 discussed separately below). The dimension of the greenhouse room was 8m, 5m and 5m
383 (length, width and height). The night-time respiration rate was then estimated to be about ~10
384 ppmv per hour (considering change of [CO₂] from 5:30 PM to 9:30 PM; Figure 2A), or
385 ~4×10¹³ molecules cm⁻² s⁻¹. Using simple isotopic mass balance, this increase of [CO₂] could
386 be satisfactorily explained assuming C₃ respiration as the main source of CO₂ (δ¹³C ≈ -26 ‰;
387 intercept in Figure 2D) added to the background (-8.5 ‰). Similarly, the same conclusion
388 could be derived by analyzing δ¹⁸O considering δ¹⁸O of respired and background CO₂ of
389 30.68 ‰ (intercept in Figure 2E) and ~40 ‰ respectively. Thus, we conclude that the main
390 factor that affected the changes in concentration as well as the isotopic compositions in night-
391 time was respiration.

392 The daytime net uptake rate can be estimated by taking the changes from early morning to
393 noon time; the [CO₂] reduced by 110 ppmv, δ¹³C increased by 3.46 ‰, and δ¹⁸O by 2.23 ‰
394 in about six hours. We calculated the number of molecules and their changes inside the
395 greenhouse assuming simple gas laws. The estimated net photosynthetic uptake was ~1×10¹⁴
396 molecules cm⁻² s⁻¹ assuming constant respiration rate that was observed in the night. The
397 photosynthetic discrimination can be calculated using the Rayleigh distillation model

$$398 \quad R = R_o f^{\alpha-1} \quad (3)$$

399 where R_o and R are the initial and modified ¹³C/¹²C or ¹⁸O/¹⁶O ratios (due to photosynthetic
400 activity), respectively, f is the fraction of the material left, and α is the fractionation factor.
401 The estimated discrimination in ¹³C defined by $(\alpha-1)$, following equation (3), was -16.5 ‰,
402 which was slightly higher than that expected for C₃ type vegetation (~ -20 ‰) (Farquhar et
403 al., 1989). For ¹⁸O, in addition to photosynthetic uptake, one has to consider an additional
404 effect due to temperature-dependent water-CO₂ equilibrium fractionation. That is, the process
405 decreases δ¹⁸O by ~0.2 ‰ for an increase of 1 °C in temperature (Brenninkmeijer et al.,
406 1983); from morning to noon time, the temperature effect reduced δ¹⁸O by 4.4 ‰. Adding
407 this factor to the observed change in δ¹⁸O yielded a discrimination factor of -12.0 ‰; the
408 value becomes -7.0 ‰, if this additional temperature-dependence is ignored. The value (-12.0
409 ‰) observed considering the additional exchange with the soil water was slightly higher than
410 that observed previously (-14.4 ‰) (Flanagan et al., 1997). Here the δ¹³C and δ¹⁸O values of
411 the respired components were assumed to be -26 ‰ and 30 ‰ respectively (see Sec. 3.1).

412 We assume that ca. 1/3 of the CO₂ molecules in stomata are fixed photosynthetically and the
413 remaining retro-diffuse back to the atmosphere (Farquhar and Lloyd, 1993) implying that the
414 CO₂-water isotopic exchange rate was ~2×10¹⁴ molecules cm⁻² s⁻¹. Also we assume that the
415 CO₂ molecules that enter into the leaf stomata get isotopically equilibrated with the leaf water
416 before diffusing back to the atmosphere. This implies an approximately 8 hours of oxygen
417 isotope exchange time for CO₂ in the greenhouse room. As a result, we do not expect that
418 CO₂ reached to complete isotopic equilibrium with the substrate water in a few hours inside
419 the room. Δ₄₇ values in the leftover CO₂ could be used to check the disequilibrium. The
420 respired CO₂ were found to be in thermodynamic equilibrium at the ambient temperature,
421 shown by the Δ₄₇ values of CO₂ in the early morning and night-time (Figure 3A-3C) and that
422 collected on a cloudy day with suppressed photosynthetic activity (Figure 3D). The close-
423 thermodynamic equilibrium at reduced photosynthetic condition is also shown in Figure 4A

424 that deviation in Δ_{47} from that expected at ambient temperature is small. On sunny days, the
425 $[\text{CO}_2]$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values change by 50-115 ppm, 2-4 ‰, and 1.1-2.2 ‰, respectively, in
426 a time period of ~5 hours in the morning (Figure 2). Figure 3 shows that the Δ_{47} values
427 retained the thermodynamic equilibrium values in the morning hours (until 9 AM) and then
428 deviate from the thermodynamic equilibrium later of the day. The maximal reduction in the
429 Δ_{47} values during these morning hours was ~0.05 ‰ (Figures 3A-3C) which is significant, as
430 this value is much higher than the uncertainty of the measurements. An increase in Δ_{47} values
431 after ~9 AM was observed. We attribute these changes in the Δ_{47} values of the residual CO_2
432 to photosynthesis as it is seen when photosynthesis is strong. Also we note that there was no
433 significant correlation/anti-correlation between $\delta^{18}\text{O}$ and Δ_{47} when photosynthesis was strong
434 (Figure 3A-3C), but became significant when the photosynthesis was weak (Figure 3D).
435 Therefore, the plant photosynthesis decouples Δ_{47} and $\delta^{18}\text{O}$; in contrast to pure water- CO_2
436 isotopic exchange where the two behave similarly as far as isotopic equilibration is concerned
437 (Affek, 2013; Clog et al. 2015).

438 Strong influence of photosynthesis on Δ_{47} was also reported by Eiler and Schauble (2004).
439 They observed decrease in the Δ_{47} values of the residual CO_2 due to photosynthetic
440 assimilation though the effect observed was different for different species. Here we observed
441 a decrease in Δ_{47} value of the residual CO_2 initially (first 2 hours) due to photosynthesis
442 similar to that observed by Eiler and Schauble (2004) but later it starts increasing in response
443 to the photosynthesis. Photosynthesis as a source of disequilibrium was also shown recently
444 by analyzing the clumped isotopes of O_2 (Yeung et al., 2015). Though enzymatic carbonic
445 anhydrase catalyzes the water- CO_2 isotopic exchange toward equilibrium (Peltier et al., 1995;
446 Cernusak et al., 2004) its activity varies. A large variation in the activity of carbonic
447 anhydrase in different vegetation types (C_3 , C_4) or within the same type was noted previously
448 (see Gillon and Yakir, 2001 and references therein). Therefore, the reaction may be
449 incomplete which is limited by the enzymatic activity inside leaves. Furthermore, a box
450 modeling by Eiler and Schauble (2004) demonstrated that gas diffusion through leaf stomata
451 during photosynthesis fractionates the remaining air CO_2 Δ_{47} value deviating it from the
452 thermodynamic equilibrium set by leaf water. Mixing of more than one component can also
453 cause change in Δ_{47} when $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the components are different (Affek and Eiler,
454 2006; Laskar et al., 2016a), but this can easily be ruled out as it was not observed when
455 photosynthesis was not very strong (Figure 3D). More rigorous investigations with controlled

456 experiments using different plants with diverse carbonic anhydrase activities are needed to
457 resolve the issue.

458 Considering the discrimination for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and variation in the concentration it is possible
459 to model the observed isotopic profile. Rayleigh model (Eq. 3) in terms of δ notation can
460 approximately be written as $\delta = \delta_0 + \epsilon \times \ln(f)$, where δ_0 is the initial δ value, f is the fraction of
461 material left and ϵ is the enrichment factor. Figure 8A shows the concentration profiles for
462 31st Jul, 2015 inside the greenhouse. With the calculated discrimination factors (ϵ) of -16.5 ‰
463 and -12.0 ‰ for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, the modeled isotopic profiles along with actual data are shown in
464 Figure (8B&8C). The model data are generated using Rayleigh fractionation relation.
465 Assuming this relation valid for Δ_{47} , a discrimination factor of 0.065 ‰ due to photosynthesis
466 was observed in the morning hours of 31st July, 2015. Figure (8C) shows the Δ_{47} profile for
467 the same day along with the actual observed values. The observed data match well with the
468 model plots. Unlike δ s, Δ_{47} is not a linear quantity as discussed later, the discrimination factor
469 calculated may slightly change when non-linearity is taken into account. With more data,
470 probably at leaf level will allow to estimate the photosynthetic discrimination for Δ_{47} .

471

472 **4.2 Car exhaust CO₂**

473 Ideally, the Δ_{47} value of car exhaust CO₂ should reflect the temperature of fuel combustion
474 inside the combustion chamber which is >800 °C. However, the temperature estimated from
475 Δ_{47} was found to be 283±18 °C. It is likely that interaction of the sample CO₂ with the
476 exhaust gases and water inside catalytic converter and exhaust pipe modified the Δ_{47} values.
477 Catalytic converter which oxidizes CO and hydrocarbons to CO₂ probably reset the clumped
478 signatures at relatively lower temperature. During combustion water-vapor is also released.
479 We observed that the exhaust gas contained a large amount of water vapor, part of which got
480 condensed on the exhaust pipe and the front part of the magnesium perchlorate column.
481 Partial equilibration with the stream of the exhaust gas and water inside catalytic converter
482 and the exhaust pipe was the likely cause for higher Δ_{47} values than that expected. This was
483 also supported by the higher $\delta^{18}\text{O}$ values than atmospheric O₂, the source of O₂ for water and
484 CO₂ here. Normally isotopes in CO₂ do not exchange with water vapor, but exchange may
485 take place at higher temperature in presence of catalyst. Inside catalytic converter, exchange
486 could take place on the surface of the catalyst at elevated temperatures of 200 – 400 °C

487 (Farrauto and Heck, 1999; Kašpar et al., 2003; Klingstedt et al., 2006). Affek and Eiler (2007)
488 also observed elevated Δ_{47} values for car exhausts and estimated a temperature of CO₂
489 production to be ~200 °C. The temperature estimated here (283 °C) is significantly higher
490 than that observed by Affek and Eiler (2007). Difference could be due to different car models
491 and the variations in the temperatures of the catalytic converters from car to car.

492

493 **4.3 Marine and coastal air CO₂**

494 Carbon Keeling plot for marine and coastal air CO₂ gave an intercept of -13.61 ± 1.14 ‰
495 (Figure 5A), the source signature. The South China Sea is net source of CO₂ to the
496 atmosphere (Zhai et al., 2005). The CO₂ released over ocean is mainly originated from the
497 remineralization of organic matter in the deeper ocean (Francois et al., 1993; Goericke and
498 Fry, 1994). The $\delta^{13}\text{C}$ value of such organic matter ranges between -20 and -30 ‰ in the
499 tropical to subtropical oceans, the intercept observed here (-13.6 ‰) is much higher than this
500 range, though the associated uncertainty is high due to a small span of isotopic values of the
501 samples. A possibility is that the remineralized CO₂ gets equilibrated with the dissolved
502 inorganic carbon before releasing to the atmosphere. Again a complete equilibration of the
503 CO₂ with the dissolved inorganic carbon would lead to a $\delta^{13}\text{C}$ value of released CO₂ to be -9
504 to -10 ‰ (Mook, 1986; Boutton, 1991; Zhang et al., 1995; Affek and Yakir, 2014), the
505 observed value of the intercept (-13.6 ‰) was significantly less than this. Therefore, we
506 conclude that the CO₂ produced in the deeper ocean is partially equilibrated with the
507 dissolved inorganic carbon before releasing to the atmosphere.

508 The $\delta^{18}\text{O}$ values of the surface sea water in the South China Sea region in summer (July-
509 September) and winter (December-February) were about -1.7 ‰ and -0.6 ‰ (Ye et al.,
510 2014). The sea surface temperatures in the summer and winter are about 28 and 24 °C, and
511 the equilibrated $\delta^{18}\text{O}$ values of the atmospheric CO₂ should be 38.9 ‰ and 40.7 ‰,
512 respectively assuming fractionation factors at the respective temperatures (Brenninkmeijer et
513 al., 1983). Our observed values lie in the range of 40.4 ‰ to 41.0 ‰ (Table 3), consistent
514 with the isotopic equilibrium values with the surface water. Therefore, we conclude that
515 oxygen isotopes in near surface air CO₂ over ocean are close to the isotopic equilibrium with
516 the surface sea water. This conclusion was further supported by the observed Δ_{47} values
517 which were found to be close to thermodynamic equilibrium with the underlying sea surface

518 water at the sea surface temperature (Figure 5B). This is due to the same water-CO₂ exchange
519 time for the two species (Affek, 2013; Clog et al., 2015). Comparing this observation with the
520 greenhouse data above, we conclude that $\delta^{18}\text{O}$ and Δ_{47} behave similarly when equilibrium is
521 achieved by simple water-CO₂ exchange but respond differently when photosynthesis is the
522 main governing factor. Though carbonic anhydrase are also present in the surface ocean and
523 marine phytoplankton does photosynthesis, $\delta^{18}\text{O}$ and Δ_{47} in air CO₂ over the ocean show the
524 values at thermodynamic equilibrium unlike greenhouse. The degree of deviation from
525 thermodynamic equilibrium probably increases with the increase in photosynthetic activity.
526 Normally photosynthesis by oceanic plants is much less compared to their terrestrial
527 counterparts, the deviation from thermodynamic equilibrium by the oceanic photosynthesis, if
528 present, is probably not detectable with the present measurement precision. Compared to
529 $\delta^{18}\text{O}$, Δ_{47} is process sensitive and is not affected by the isotopic composition of substrate
530 water. Given that the surface air temperature is better measured, we believe the clumped
531 isotopes potentially provide good tracers for global carbon flux study involving CO₂,
532 complementing the commonly used species like [CO₂], $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$.

533 In the coastal stations, Δ_{47} values were similar to the thermodynamic equilibrium with the sea
534 surface water at the temperature of ~27 °C (Figure 5B). The recorded air temperature during
535 the sampling period over the coasts varied between 14 and 24 °C and was not reflected in the
536 Δ_{47} values. We note that the samples were collected from two open spaces in the coasts where
537 strong north and northeasterly winds overwhelmed, carrying air masses from the oceans
538 towards the sampling locations (See Table S3 in Supplement). Therefore, we expect the
539 major contribution was marine air with little influence from local processes, which could
540 occasionally cause deviation from the thermodynamic equilibrium values.

541

542 **4.4 Urban and sub-urban air CO₂**

543 A significant fraction of anthropogenic CO₂ was present in the air CO₂ over the urban site,
544 indicated by the [CO₂] as well as isotopic compositions including Δ_{47} . Anthropogenic
545 contribution can be estimated following a two component mixing: $\delta = f_{\text{anth}} \times \delta_{\text{anth}} + (1 -$
546 $f_{\text{anth}}) \times \delta_{\text{bgd}}$, where δ 's can be $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ or Δ_{47} and f 's, the corresponding weighting factor,
547 and subscripts 'anth' and 'bgd' refer to anthropogenic and background, respectively. We take
548 the 'anthropogenic' end member as the isotopic compositions of the car exhaust values

549 (Table 2) and ‘background’ end member as that values observed over the ocean (for $\delta^{13}\text{C}$ and
550 $\delta^{18}\text{O}$, Table 3) and thermodynamic equilibrium value at the mean ambient temperature of ~ 20
551 $^{\circ}\text{C}$ in December (0.95‰ for Δ_{47}) at the sampling site, respectively. Assuming that the excess
552 in $[\text{CO}_2]$ above the background was originated from vehicular emissions, the values of the
553 $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Δ_{47} in the urban site obtained using the mixing equation were -12.26‰ ,
554 37.68‰ , and 0.809‰ , respectively, which were similar to those observed (Table 4). Δ_{47} is
555 not a conserved quantity and a linear mixing is not valid when the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the
556 components are widely different (Affek and Eiler, 2006; Laskar et al., 2016a). In the present
557 case, the isotopic compositions of the two components were not drastically different and
558 fraction of anthropogenic CO_2 was much less ($<1/4$) than the background CO_2 , and hence the
559 error due to linear approximation was small (comparable to the uncertainty of measurement).
560 Anthropogenic CO_2 can also be quantified using radiocarbon (^{14}C) as fossil fuels are highly
561 depleted in ^{14}C (Miller et al., 2012); however, it cannot distinguish difference between CO_2
562 from two sources with modern carbon.

563 No systematic diurnal or temporal trend was observed in the Δ_{47} values in the sub-urban CO_2
564 during the sampling period (Figure 7B). However a weak trend was seen in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
565 (not shown) in response to the seasonal variation of the carbon assimilation and oxygen
566 isotopes in the rainwater (Peng et al., 2010; Laskar et al., 2014). This furthermore
567 demonstrates that Δ_{47} behaves differently from $[\text{CO}_2]$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$. Almost all measured
568 Δ_{47} values were lower than that expected at the ambient temperature except two days: 9th
569 November, 2013 and 3rd February, 2014. $\delta^{13}\text{C}$ values were also slightly lower than the
570 background values. The reduced values of Δ_{47} could be due to contribution of CO_2 from
571 combustion processes which produced CO_2 with low Δ_{47} values as discussed in Section 4.2.
572 We estimated the contribution of local anthropogenic emissions in $\delta^{13}\text{C}$ and Δ_{47} using the two
573 components mixing discussed above. The components were the background air CO_2 and car
574 exhausts. The expected $\delta^{13}\text{C}$ and Δ_{47} values of the mixture were -9.1‰ and 0.92‰ ,
575 respectively. The observed Δ_{47} value was significantly different from that estimated from
576 simple two component mixing, though it was not different for $\delta^{13}\text{C}$. After subtracting the
577 local anthropogenic contribution from the observed Δ_{47} values, a difference of $\sim 0.026\text{‰}$
578 between the observed and estimated remains for sub-urban station and it disappeared for
579 urban station (see Table S4 in Supplement). This was not obvious in $\delta^{13}\text{C}$ probably due to
580 larger variation. The lower Δ_{47} values in sub-urban station could possibly be due to kinetic

581 effect during photosynthetic assimilation, partial contribution of marine air, or a combination
582 of them. It could also be due to underestimation of the anthropogenic CO₂ at the sampling
583 spot. The regional background [CO₂] here could be lower than that assumed and the actual
584 anthropogenic fraction of CO₂ could be higher. The marine air in the vicinity of Taiwan,
585 which was at thermodynamic equilibrium with the surface sea water as discussed earlier,
586 might have contributed partially to the air CO₂ at the sampling site. Varying contribution of
587 marine air could explain the lower Δ_{47} values to some extent. The most plausible cause for
588 observed deviation in the Δ_{47} values that cannot be accounted for by anthropogenic and
589 marine alterations was photosynthesis, as discussed earlier for greenhouse CO₂. This is not
590 unreasonable, as the Academia Sinica Campus is surrounded by thick greeneries.

591 On 9th Nov, 2013 and 3rd February, 2014, the Δ_{47} values were close to that expected at
592 thermodynamic equilibrium (Figure 7B). The Δ_{47} values on 9th November were not very
593 different from the values reported for the previous or next days. However, the calculated
594 thermodynamic equilibrium values on that day were relatively low due to high ambient
595 temperatures; air CO₂ probably did not get enough time to equilibrate. On 3rd February,
596 2014, the Δ_{47} values were higher and comparable to the thermodynamic equilibrium values
597 expected at ambient temperatures. A likely explanation is that the air on that day was a
598 mixture of two components at the sampling region. A relatively strong wind from the
599 southern land (Table S3 in Supplement) contributed the air CO₂ and the higher Δ_{47} values
600 were probably due to mixing of the local air with that transported from the south of Taipei.

601

602 **4.5 Grassland, forest and high mountain air CO₂**

603 In the grassland station in Taipei city, the Keelung plot intercept for $\delta^{13}\text{C}$ (-17.0 ± 1.0 ‰)
604 (Figure 5D) indicated some sources of CO₂ with higher $\delta^{13}\text{C}$ values compared to the most
605 expected sources, namely, C₃ vegetation and vehicle emission with a $\delta^{13}\text{C}$ value of ~ -27 ‰.
606 Though the sampling station was located in an urban region, the sampling spot was at least
607 ~ 150 m away from traffic streets, such as Keelung road, along with ~ 60 m wide, ~ 10 m high
608 C₃ trees in between. As a result, anthropogenic signals were not very prominent. The samples
609 were collected just above the surface of the grasses. Tropical warm grasses are mainly C₄
610 type with $\delta^{13}\text{C}$ in the range of -9 to -19 ‰ and a global average of -13 ‰ (Deines, 1980). We
611 measured $\delta^{13}\text{C}$ values of a few grass samples and found values in the range of -15 to -17 ‰.

612 The soil and grass respired CO₂ with higher $\delta^{13}\text{C}$ contributed significantly to the near surface
613 CO₂, resulting in a higher value of intercept (-17 ‰). The concentration was observed to be
614 less than the background level sometimes, probably due to strong CO₂ uptake by plants. The
615 temperature gradually decreased from 26 to 20 °C during the consecutive three days and
616 clumped isotope followed similar trend, reflecting the influence of temperature on CO₂ Δ_{47}
617 and rapid equilibration with the leaf and surface waters. One low value observed on the
618 second day was probably due to plumes of vehicle exhausts, also supported by the elevated
619 level of [CO₂] and depletion in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Table 4). Effect of photosynthesis on the CO₂
620 was also expected specifically due the collection of samples at the grass level. However, in an
621 open system, it is difficult to assess this with limited data points.

622 An elevated CO₂ concentration and low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values indicated significant
623 contribution of respiration and/or anthropogenic CO₂ in the forest station (Table 4) near the
624 Academia Sinica Campus. Though the samples were collected at 10-11 AM under bright
625 sunlight, the vegetation was so dense that little sunlight reached the ground. Probably
626 photosynthetic activity was not very strong at the ground level in the morning hours and the
627 dominant process was respiration. Also poor circulation of air due to presence of high heels
628 on the three sides of the sampling spot made the site nearly isolated from the surroundings.
629 As a result the Δ_{47} values were observed to be similar to the thermodynamic equilibrium
630 expected at the ambient temperatures except on 11th August, 2015 (Figure 7F). This also
631 supports our hypothesis, made in the case of greenhouse CO₂, that respired CO₂ is always in
632 close thermodynamic equilibrium with the substrate water. On 11th August, 2015 a
633 significantly higher Δ_{47} value was observed. The higher value was likely due to the influence
634 of the super Typhoon 'Soudelor' which passed over Taipei during 8-10 August, 2015 causing
635 a decrease in temperature by 3-4 °C and air masses mixing in a larger spatial scale.

636 For high mountain CO₂, the observed Δ_{47} values (Table 4) were lower than that expected at
637 ~10 °C, the ambient temperature at the top of the mountain site during sampling. The Δ_{47}
638 values were similar to that observed in the plain and over the ocean. We note that during the
639 sampling period, the site was affected significantly by winter monsoons. HYSPLIT 24 hours
640 back trajectory showed marine origin of air (not shown) during the sampling time. The air
641 CO₂ on the mountain probably did not get sufficient time to isotopically equilibrate with the
642 local surface and leaf water but showed the signature of the marine CO₂.

643 The deviations in Δ_{47} from the thermodynamic equilibrium values in different atmospheric
644 environments and processes are summarized in Figure 9. It is obvious that the urban and sub-
645 urban CO_2 deviate the most towards lower Δ_{47} values, mainly contributed by CO_2 originated
646 from high temperature combustions, i.e., vehicular emissions. The respired CO_2 are always in
647 close thermodynamic equilibrium at the ambient temperature. On the other hand, CO_2
648 affected by strong photosynthesis show significant increase in the Δ_{47} values compared to the
649 thermodynamic equilibrium values.

650

651 **5. Summary**

652 We presented a compilation of Δ_{47} analyses for car exhaust, greenhouse and air CO_2 over a
653 wide variety of interactions in tropical and sub-tropical regions including marine, coastal,
654 urban, sub-urban, forest, and high mountain environments. Near surface marine air CO_2 is in
655 close thermodynamic equilibrium with the underlying surface water at the sea surface
656 temperature. Car exhaust, urban, sub-urban and greenhouse air CO_2 significantly deviate
657 from the thermodynamic equilibrium values. While respired CO_2 is in thermodynamic
658 equilibrium with leaf and soil surface waters, photosynthesis significantly deviates the Δ_{47}
659 values from the thermodynamic equilibrium or more precisely increases the Δ_{47} values
660 probably due to kinetic effect associated with the diffusion of CO_2 out of leaf stomata. The
661 Δ_{47} values in urban and sub-urban air CO_2 are lower than that expected under thermodynamic
662 equilibrium at the ambient temperature. The deviation is mainly due to contributions from
663 fossil fuel emissions and to some extent due to photosynthesis especially in regions with
664 dense vegetation.

665 We showed that Δ_{47} can serve as an independent tracer for studying photosynthesis. Though
666 the deviation from equilibrium during photosynthesis is also observed in oxygen clumped
667 isotopes CO_2 and O_2 are affected and produced from different processes and sources; the
668 former is affected seriously by water (water- CO_2 isotopic exchange) while the latter is
669 derived from water. We believe the analyses of the clumped isotopes for both CO_2 and O_2 are
670 of great importance in the atmospheric carbon cycling study, providing a new angle for
671 tackling the chemistry chain in photosynthesis. More systematic study in controlled
672 environments including leaf level experiments will help to better understand the role of
673 photosynthesis on Δ_{47} .

674 **Data availability**

675 All the data used in the manuscript are also presented in the form of Tables.

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687

688

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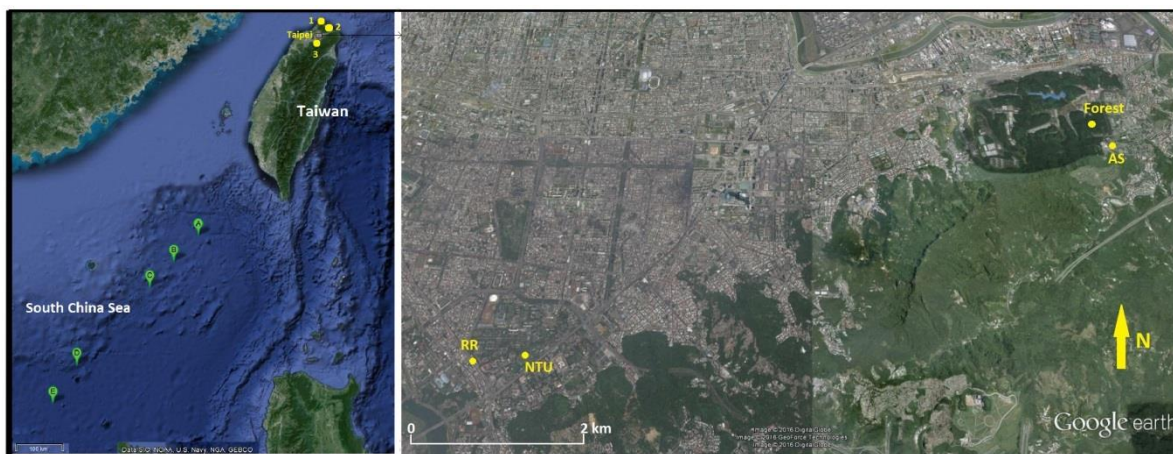
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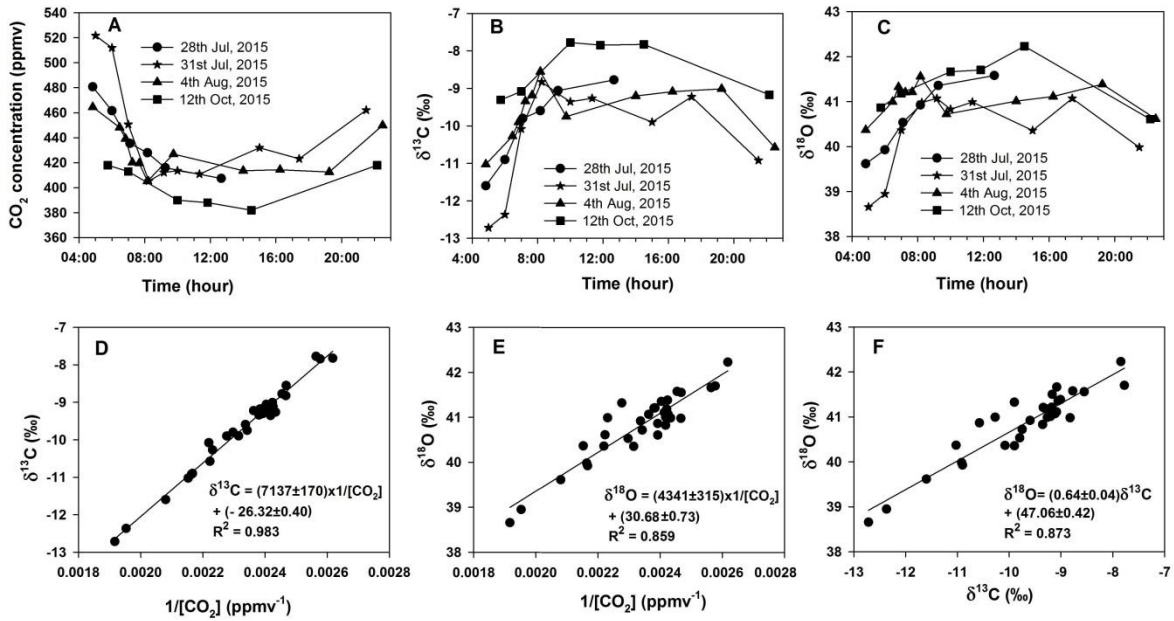
858 **Figures**
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861 Figure 1. Left panel: map of Taiwan and South China Sea with the locations of marine air
862 sampling stations (A to E). The coastal stations 1 and 2 are Fuguei Cape and Keelung and 3 is
863 the high mountain station Hehuan (~3.2 km a.s.l.). Right panel: Part of Taipei city with
864 sampling stations Roosevelt Road (RR), grassland in the National Taiwan University (NTU)
865 Campus, sub-urban site inside the campus of Academia Sinica (AS) and Forest site.

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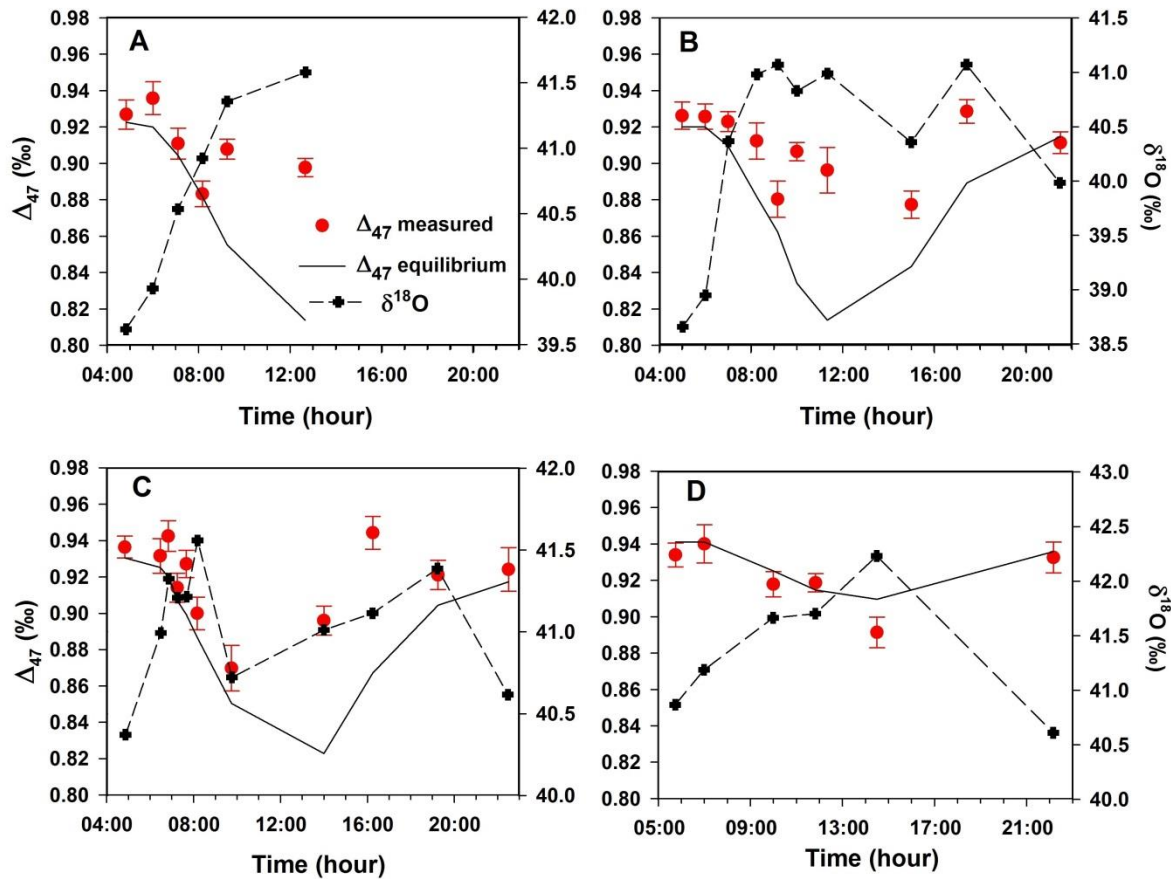


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875 Figure 2. Top panels show the diurnal variation of (A) concentration, (B) δ¹³C, and (C) δ¹⁸O
876 of CO₂ sampled in the greenhouse. Bottom panels are the Keeling plots for (D) δ¹³C and (E)
877 δ¹⁸O and (F) scatter plot of δ¹³C and δ¹⁸O to show their covariance.

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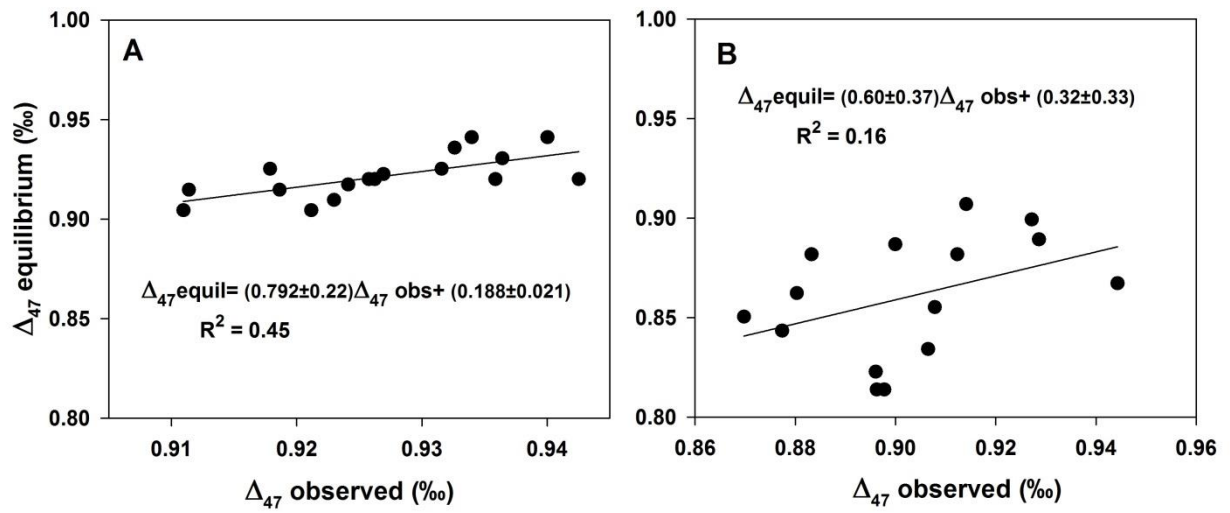
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882 Figure 3. Diurnal variation of the Δ_{47} and $\delta^{18}\text{O}$ values in the greenhouse for samples collected
 883 on four days of 2015: (A) 28th July, (B) 31st July, (C) 4th August, and (D) 12th October. The
 884 first three days (A-C) were bright sunny days and the last one (D) a cloudy day with covered
 885 rooftop (see texts for details). The error bars are 1 standard error associated with the
 886 measurements.

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891 Figure 4. Correlation between the observed and thermodynamic equilibrium Δ_{47} values for
 892 greenhouse CO_2 samples collected when (A) photosynthesis was weak and respiration was
 893 strong and (B) photosynthesis was strong and respiration was weak.

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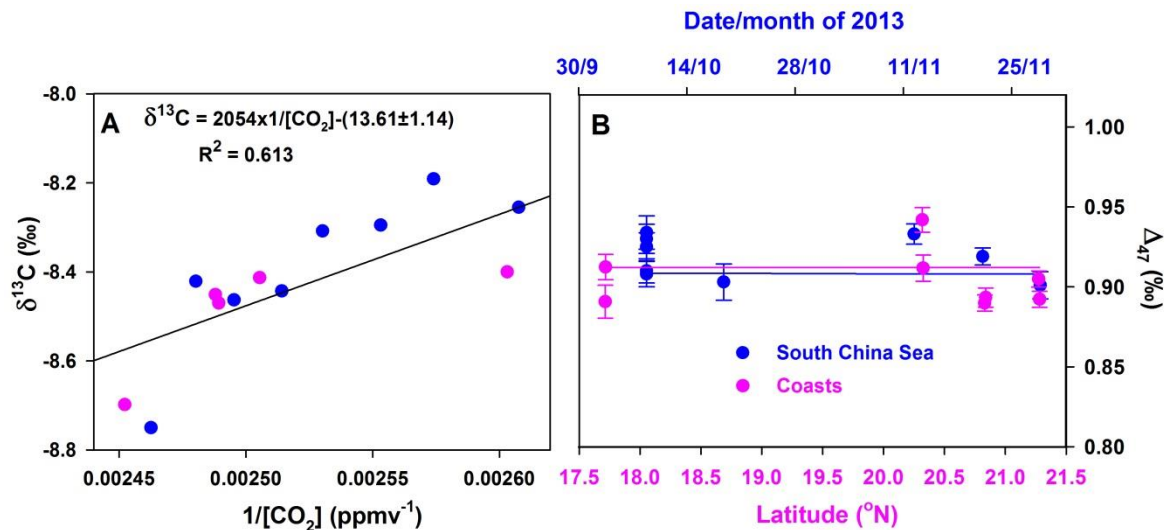
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906 Figure 5. (A) Carbon Keeling plot for air CO₂ collected over South China Sea and coastal

907 stations (Keelung and Fuguei Cape). (B) Δ_{47} values observed over the South China Sea and

908 coastal stations. The error bars are the 1 standard error associated with the measurements.

909 Lines show Δ_{47} values for the CO₂ in thermodynamic equilibrium at ambient temperatures.

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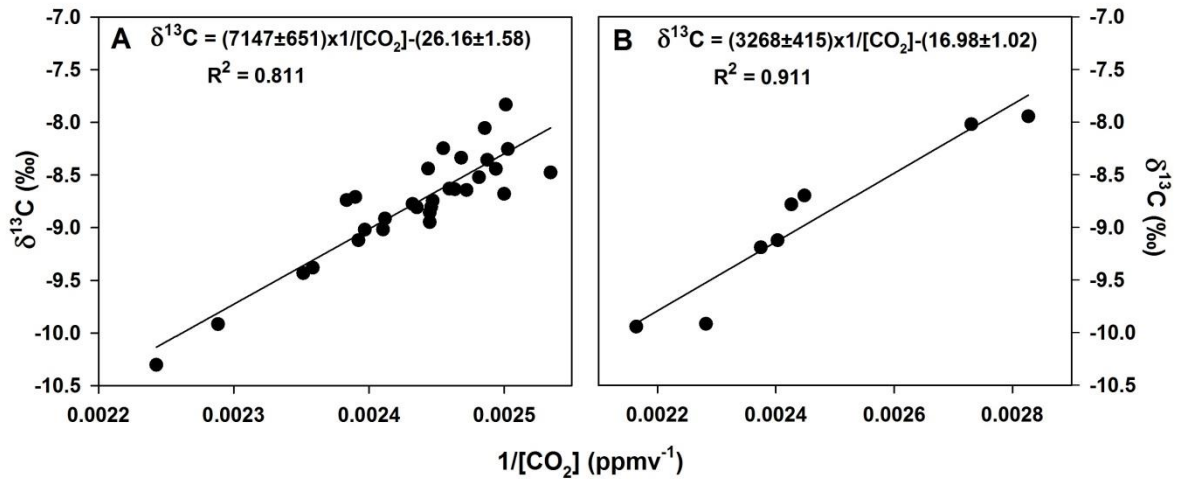
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921 Figure 6. Carbon Keeling plots for air CO₂ collected over (A) sub-urban Academia Sinica

922 Campus and (B) grassland at National Taiwan University Campus.

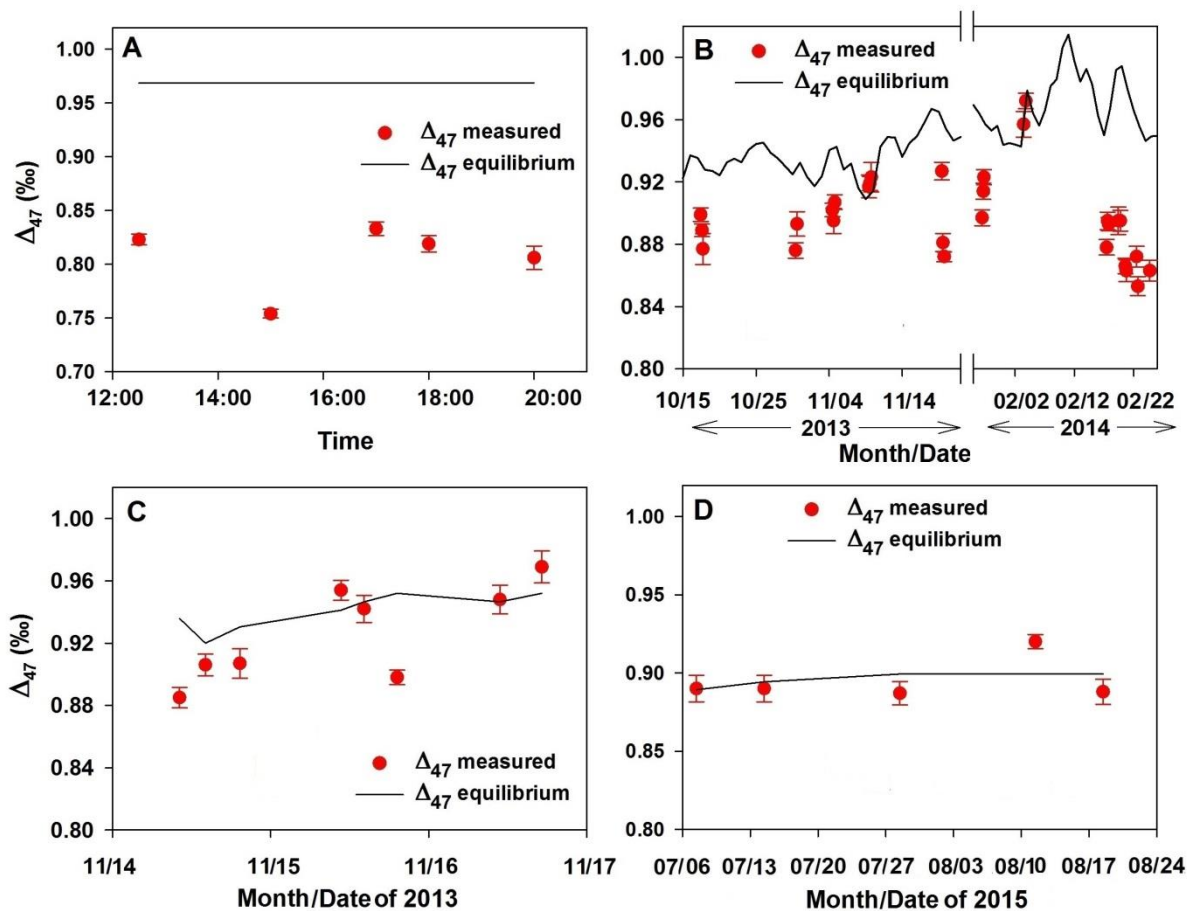
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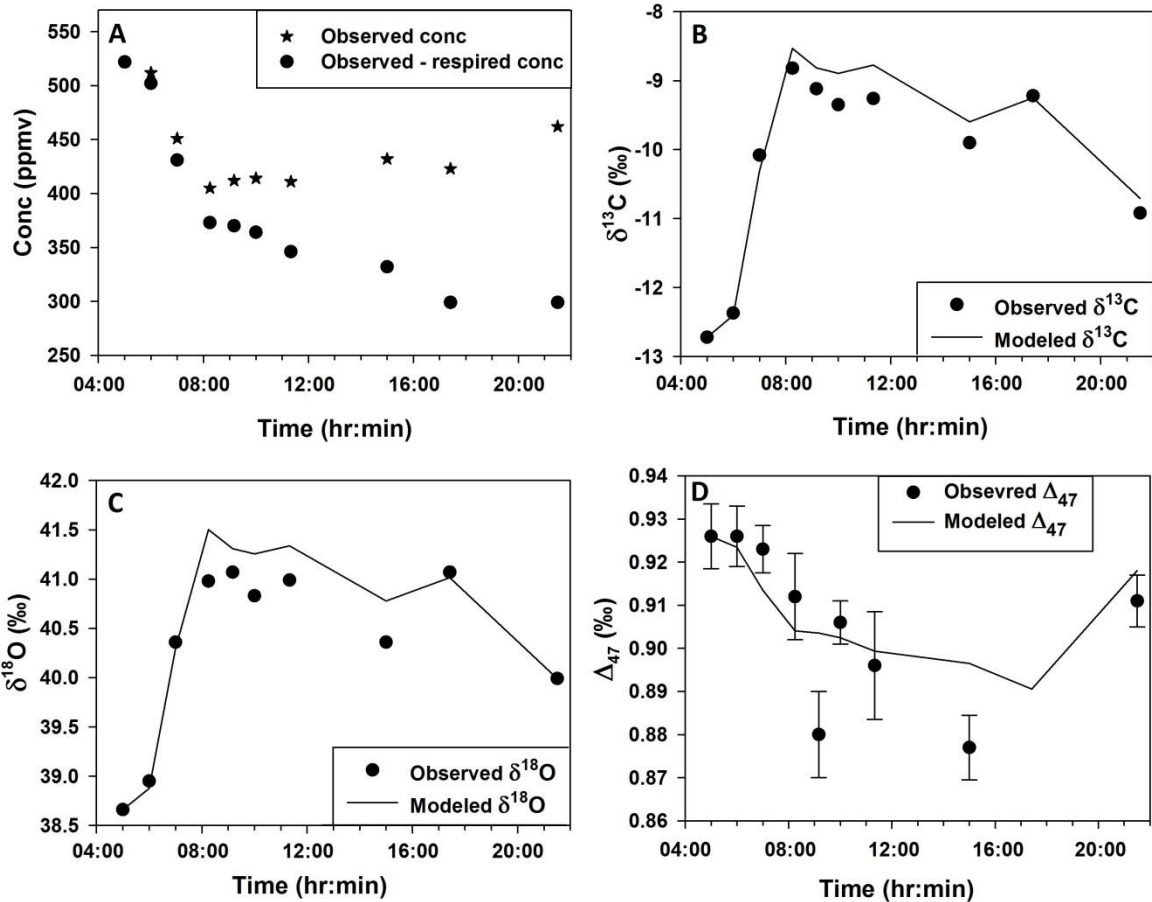
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 929 Figure 7. Δ_{47} values in the near surface atmospheric CO_2 from (A) urban site near Roosevelt
 930 Road on 30th December, 2015, (B) sub-urban station (Academia Sinica Campus), (C)
 931 grassland in the National Taiwan University Campus and (D) forest site near the Academia
 932 Sinica Campus. The error bars are the 1 standard error associated with the measurements.
 933 Lines show Δ_{47} values for the CO_2 at thermodynamic equilibrium at ambient temperatures.
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937 Figure 8: (A) CO₂ concentration inside greenhouse on 31st Aug, 2015: observed
 938 concentration (star) and decrease in concentration by photosynthesis after subtracting the
 939 respiration (solid circle) are also shown. Comparison of observed (B) δ¹³C, (C) δ¹⁸O and (D)
 940 Δ₄₇ values with that modeled using discrimination factors of -16.5 ‰, -12.0 ‰ and 0.065 ‰
 941 for δ¹³C, δ¹⁸O and Δ₄₇ respectively.

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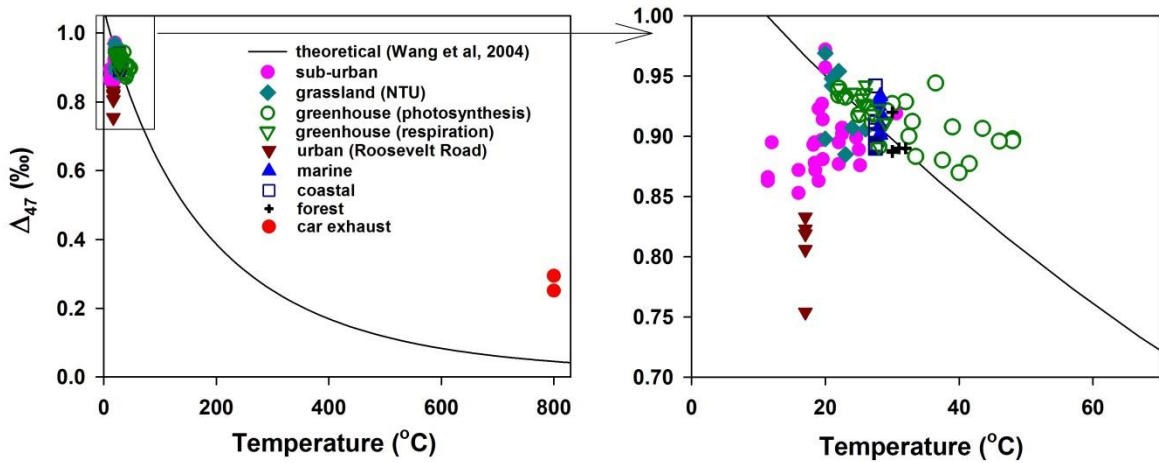
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952 Figure 9. A summary of Δ_{47} values in near surface air CO_2 obtained at different environments
953 and compared with the thermodynamic equilibrium values. Combustion temperature for car
954 exhausts is assumed to be 800 °C (minimum value). Greenhouse CO_2 are divided into two
955 categories: photosynthesis dominated (green open circle) and respiration dominated (green
956 open triangle).

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969 Table 1. Diurnal variation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and clumped isotopes (Δ_{47}) for greenhouse CO_2 . Temperatures estimated using Δ_{47} values and actual air
 970 temperatures inside the greenhouse at the time of sampling are also presented.
 971

Date	Time	Conc. (ppmv)	$\delta^{13}\text{C}$ (‰) (VPDB)	$\delta^{18}\text{O}$ (‰) (VSMOW)	δ^{47} (‰)	Std. err.	Δ_{47} (‰) (ARF)	Std. err.	Δ_{48} (‰)	Estimated temp. (°C)	Air temp. (°C)
7/28/2015	4:50	481	-11.60	39.61	6.99	0.02	0.927	0.016	0.2	24	25.5
	6:00	462	-10.90	39.92	8.16	0.02	0.936	0.018	0.6	21	26
	7:06	435	-9.80	40.54	9.71	0.02	0.911	0.017	0.2	28	29
	8:10	428	-9.60	40.92	10.38	0.02	0.883	0.014	-0.2	33	33.5
	9:15	416	-9.06	41.36	11.30	0.01	0.908	0.011	0.2	24	39
	10:15	422	-9.55	40.82	NA	NA	NA	NA	NA	NA	NA
	12:40	407	-8.77	41.58	11.75	0.01	0.898	0.010	0.2	27	48
7/31/2015	5:00	522	-12.72	38.66	5.10	0.01	0.926	0.015	0.3	24	26
	6:00	512	-12.37	38.95	5.94	0.01	0.926	0.014	0.5	25	26
	7:00	451	-10.08	40.36	9.39	0.02	0.923	0.011	0.4	25	28
	8:15	405	-8.82	40.98	11.25	0.02	0.912	0.020	0.4	28	33
	9:10	412	-9.12	41.07	11.26	0.02	0.880	0.020	0.6	34	37.5
	10:00	414	-9.35	40.83	11.52	0.01	0.906	0.010	0.6	23	43.5
	11:20	411	-9.26	40.99	11.12	0.02	0.896	0.025	0.5	31	48
	15:00	432	-9.90	40.36	9.55	0.02	0.877	0.015	0.5	34	41.5
	17:25	423	-9.22	41.07	12.48	0.02	0.929	0.013	0.7	25	32
	21:30	462	-10.92	39.99	7.90	0.01	0.911	0.012	0.4	28	27
8/4/2015	4:50	465	-11.03	40.37	8.41	0.01	0.936	0.012	0.27	23	24
	5:50	455	-10.82	40.26	NA	NA	NA	NA	NA	NA	NA
	6:28	448	-10.27	41.00	10.01	0.02	0.931	0.017	0.7	24	25.5
	6:50	439	-9.90	41.32	10.10	0.02	0.942	0.009	0.6	22	26

	7:15	420	-9.34	41.22	11.05	0.01	0.914	0.013	0.6	28	28.5
	7:40	419	-9.18	41.22	11.05	0.01	0.927	0.011	0.3	25	30
	8:10	405	-8.55	41.56	12.79	0.02	0.900	0.015	0.6	31	32.5
	9:45	427	-9.75	40.73	10.81	0.02	0.870	0.023	0.3	36	40
	14:00	414	-9.20	41.01	11.02	0.01	0.896	0.011	0.6	31	46
	16:15	414	-9.09	41.11	11.11	0.01	0.944	0.014	0.7	22	36.5
	19:15	413	-9.01	41.38	13.28	0.01	0.921	0.010	0.9	26	29.2
	22:30	450	-10.58	40.61	9.34	0.02	0.924	0.022	0.4	25	26.5
10/12/2015	5:45	418	-9.30	40.87	10.80	0.01	0.934	0.013	0.5	23	22
	7:00	413	-9.08	41.18	10.95	0.02	0.940	0.021	0.4	22	22
	10:00	390	-7.78	41.66	13.00	0.02	0.918	0.014	0.6	26	25
	11:50	388	-7.84	41.71	15.25	0.01	0.919	0.010	0.6	26	27
	14:30	382	-7.82	42.24	14.27	0.02	0.891	0.017	0.4	31	28
	20:10	418	-9.17	40.61	10.85	0.02	0.933	0.017	0.5	23	23

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Table 2. Stable carbon and oxygen isotopic composition and clumped isotopes (Δ_{47}) for car exhaust CO₂. Temperatures estimated using Δ_{47} values and lowest possible combustion temperatures are given.

Car model	Conc. (ppm)	$\delta^{13}\text{C}(\text{‰})$ (VPDB)	$\delta^{18}\text{O}(\text{‰})$ (VSMOW)	$\delta^{47}(\text{‰})$	Std. err.	$\Delta_{47}(\text{‰})$ (ARF)	Std. err.	$\Delta_{48}(\text{‰})$	Estimated temp. (°C)	Combustion temp. (°C)
Mazda 3000cc TRIBUTE	39400	-27.73	25.43	-22.20	0.01	0.251	0.013	-0.4	300	800
Mitsubishi 2400cc New Outlander	39300	-27.67	25.27	-23.08	0.02	0.294	0.007	-0.3	265	800
Average $\pm 1\sigma$	39350 \pm 50	-27.70 \pm 0.03	25.35 \pm 0.07	-22.64 \pm 0.44		0.273 \pm 0.021			283 \pm 18	

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Table 3. Stable isotopic composition including Δ_{47} for air CO₂ collected over South China Sea and two coastal stations (see Figure 1 for sampling locations).
Temperatures estimated using Δ_{47} values and the sea surface temperatures at the time of samplings are also presented.

Marine air CO₂										
South China Sea										
Date time	Conc. (ppm)	$\delta^{13}\text{C}(\text{‰})$ (VPDB)	$\delta^{18}\text{O}(\text{‰})$ (VSMOW)	$\delta^{47}(\text{‰})$	Std. err.	$\Delta_{47}(\text{‰})$ (ARF)	Std. err.	$\Delta_{48}(\text{‰})$	Estimated temp. (°C)	Sea surface temp. (°C)
10/15/2013 8:15 (A)*	403	-8.42	40.85	28.752	0.016	0.901	0.017	1.9	30	28.3
10/15/2013 13:15 (B)	400	-8.46	40.80	28.441	0.012	0.919	0.011	2.6	26	28.3
10/15/2013 18:00 (C)	406	-8.75	40.54	28.133	0.013	0.933	0.013	2.2	24	28.3
10/16/2013 7:00 (D)	391	-8.76	40.53	27.916	0.024	0.903	0.023	3.9	29	28.2
10/16/2013 12:05 (E)	397	-8.44	40.86	28.535	0.015	0.910	0.015	3.3	28	28.2
10/16/2013 14:00 (E)	391	-8.30	40.96	28.922	0.021	0.934	0.021	3.0	23	28.2
10/16/2013 17:20 (E)	395	-8.31	41.02	28.944	0.017	0.908	0.016	1.9	29	28.1
10/16/2013 20:20 (E)	388	-8.19	40.52	28.909	0.018	0.930	0.018	3.8	24	28.1
10/17/2013 8:40 (E)	383	-8.26	40.41	28.194	0.018	0.925	0.018	4.3	25	28.1
Average $\pm 1\sigma$	395 \pm 7	-8.43 \pm 0.19	40.72 \pm 0.20	28.52 \pm 0.36		0.918 \pm 0.012			27 \pm 2	28.2 \pm 0.1
Keelung										
10/03/2013 11:30	380	-8.31	40.31	28.053	0.020	0.896	0.021	3	31	27.5
10/03/2013 12:30	384	-8.40	40.92	29.089	0.017	0.917	0.016	1.9	27	27.5

11/13/2013 11:00	401	-8.45	40.62	29.645	0.015	0.946	0.016	4.0	21	27.5
11/21/2013 12:30		-8.47	40.78	29.866	0.017	0.890	0.010	1.1	32	27.5
11/28/2013 12:00	410	-8.60	40.21	28.992	0.011	0.908	0.010	2.2	28	27.5
Average $\pm 1\sigma$	394 \pm 12	-8.45 \pm 0.09	40.57 \pm 0.26	29.12 \pm 0.63		0.911 \pm 0.020			28 \pm 4	27.5
Fuguei Cape										
11/13/2013 13:30	401	-8.47	40.76	29.56	0.02	0.916	0.016	1.1	27	27.5
11/21/2013 15:30	399	-8.41	40.89	29.37	0.01	0.880	0.012	2.5	34	27.5
11/28/2013 15:00	407	-8.70	41.16	30.11	0.01	0.886	0.010	3.1	33	27.5
Average $\pm 1\sigma$	402 \pm 3	-8.53 \pm 0.12	40.94 \pm 0.16	29.68 \pm 0.29		0.894 \pm 0.015			31 \pm 3	27.5

985 *Sampling Stations (see Figure 1 for locations in South China Sea)

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989 Table 4. Stable isotopic composition including clumped isotopes (Δ_{47}) for air CO₂ collected in urban and sub-urban stations, grassland, forest and high
990 mountain environments. Temperatures estimated using Δ_{47} values and air temperatures are also presented.

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Urban CO₂: Roosevelt Road, Taipei City											
Date	Time	Conc. (ppm)	$\delta^{13}\text{C}(\text{‰})$ (VPDB)	$\delta^{18}\text{O}(\text{‰})$ (VSMOW)	$\delta^{47}(\text{‰})$	Std. err.	$\Delta_{47}(\text{‰})$ (ARF)	Std. err.	$\Delta_{48}(\text{‰})$	Estimated temp. (°C)	Air temp. (°C)
12/30/ 2015	12:30	510	-10.41	40.00	25.26	0.014	0.823	0.010	2.3	46	20
	15:00	478	-11.50	38.49	22.63	0.012	0.754	0.008	0.9	62	19.5
	17:00	461	-9.69	40.70	26.74	0.017	0.833	0.013	0.9	44	17
	18:00	594	-12.30	38.14	21.56	0.014	0.819	0.015	1.5	47	16
	20:00	457	-11.34	39.24	23.61	0.022	0.806	0.022	3.1	50	15
Average $\pm 1\sigma$		500 \pm 50	-11.05 \pm 0.90	39.31 \pm 0.94	23.96 \pm 1.84		0.807 \pm 0.028			50 \pm 6	17 \pm 2

Sub-urban air CO ₂										
Academia Sinica Campus										
Date time	Conc. (ppm)	$\delta^{13}\text{C}(\text{‰})$ (VPDB)	$\delta^{18}\text{O}(\text{‰})$ (VSMOW)	$\delta^{47}(\text{‰})$	Std. err.	$\Delta_{47}(\text{‰})$ (ARF)	Std. err.	$\Delta_{48}(\text{‰})$	Estimated temp. (°C)	Air temp (°C)
10/17/2013 10:00	400	-7.83	40.44	28.47	0.015	0.899	0.008	3.7	30	25
10/17/2013 14:30	402	-8.05	40.25	28.07	0.017	0.889	0.008	2.2	32	25
10/17/2013 17:20	409	-8.44	39.90	27.26	0.019	0.877	0.020	2.3	34	22
10/30/2013 10:00	395	-8.48	40.57	28.47	0.012	0.876	0.010	2.8	35	25.2
10/30/2013 14:30	400	-8.25	41.08	29.03	0.016	0.893	0.016	3.9	31	27.4
11/04/2013 10:30	411	-8.78	40.51	28.67	0.011	0.902	0.009	2.7	29	22.5
11/04/2013 14:30	406	-8.64	40.62	28.97	0.017	0.895	0.016	2.2	31	22
11/04/2013 18:30	415	-9.02	40.38	28.33	0.013	0.907	0.009	2.8	28	22.5
11/09/2013 10:30	405	-8.34	41.09	29.79	0.019	0.917	0.015	1.9	27	28.5
11/09/2013 14:00	407	-8.25	41.25	30.63	0.015	0.919	0.009	1.6	26	30.6
11/09/2013 18:30	425	-9.43	40.32	27.49	0.020	0.923	0.019	2.1	25	28
11/19/2013 10:00	419	-8.74	40.60	29.27	0.012	0.927	0.011	3.7	25	19.5
11/19/2013 14:00	418	-8.71	40.52	29.59	0.019	0.881	0.012	1.2	33	19.6
11/19/2013 18:00	414	-8.91	40.56	28.58	0.012	0.872	0.006	1.1	35	18.5
01/27/2014 10:30	403	-8.52	41.32	30.13	0.008	0.897	0.010	2.9	30	19.2
01/27/2014 15:20	400	-8.68	41.23	30.03	0.011	0.914	0.010	0.7	27	19.6
01/27/2014 18:00	404	-8.64	41.32	29.29	0.017	0.923	0.010	4.6	25	18.5
02/03/2014 11:00	408	-8.80	41.20	29.67	0.015	0.957	0.017	1.7	19	24.5
02/03/2014 14:30	409	-8.86	41.39	NA		NA		NA		
02/03/2014 19:30	409	-8.95	41.41	30.57	0.011	0.972	0.010	3.0	16	19.3

02/17/2014 10:30	445	-10.30	40.40	27.60	0.016	0.878	0.010	3.0	34	22.4
02/17/2014 14:30	408	-8.74	41.53	30.58	0.014	0.895	0.011	0.6	31	25
02/17/2014 18:30	437	-9.92	41.07	28.49	0.012	0.893	0.008	1.3	31	22
02/19/2014 10:00	418	-9.12	40.61	29.12	0.020	0.895	0.018	0.9	31	13.3
02/19/2014 18:00	424	-9.38	40.40	28.49	0.020	0.895	0.013	2.4	31	12.4
02/20/2014 14:30	410	-8.81	40.96	29.68	0.023	0.866	0.010	1.9	37	12.9
02/20/2014 18:00	417	-9.02	40.66	29.59	0.018	0.863	0.014	1.6	37	12.5
02/22/2014 12:15	401	-8.44	41.49	30.63	0.013	0.872	0.013	0.6	35	17.5
02/22/2014 17:00	402	-8.36	41.51	30.63	0.013	0.853	0.012	4.2	40	17.1
02/24/2014 17:30	406	-8.63	41.57	30.70	0.014	0.863	0.013	3.8	37	22
Average $\pm 1\sigma$	411 \pm 11	-8.78 \pm 0.50	40.87 \pm 0.46	29.23 \pm 1.00		0.897 \pm 0.027			30 \pm 5	21 \pm 5
Grassland: NTU Campus										
11/14/2013 10:10	353	-7.95	40.96	30.18	0.02	0.885	0.013	0.4	33	23
11/14/2013 14:05	366	-8.02	41.31	30.79	0.01	0.906	0.014	0.4	29	26
11/14/2013 19:20	462	-9.94	38.33	25.64	0.02	0.907	0.019	0.2	29	24
11/15/2013 10:40	416	-9.12	39.42	29.51	0.01	0.954	0.013	0.6	20	22
11/15/2013 14:10	421	-9.19	39.36	29.78	0.02	0.942	0.018	0.3	22	21
11/15/2013 19:12	438	-9.92	38.28	28.08	0.04	0.989	0.009	0.0	13	20
11/16/2013 10:50	412	-8.78	40.03	28.54	0.02	0.948	0.018	1.8	21	21
11/16/2013 17:10	408	-8.70	40.26	26.06	0.02	0.969	0.021	1.6	17	20
Average $\pm 1\sigma$	409 \pm 33	-8.95 \pm 0.70	39.74 \pm 1.00	28.57 \pm 1.77		0.937 \pm 0.030			23 \pm 6	22 \pm 2
Forest site near Academia Sinica Campus										
07/07/2015 10:30	411	-9.07	41.43	11.54	0.01	0.890	0.017	0.3	32	32
07/14/2015 10:30	458	-10.43	39.74	9.01	0.02	0.890	0.017	0.4	32	31
07/28/2015 10:40	441	-9.99	40.86	10.07	0.02	0.887	0.015	0.2	32	30
08/11/2015 10:40	448	-10.46	40.09	9.50	0.01	0.920	0.009	0.5	26	30

08/18/2015 10:30	433	-9.99	39.80	8.99	0.02	0.888	0.016	0.4	32	30
Average $\pm 1\sigma$	438 \pm 16	-9.99 \pm 0.50	40.39 \pm 0.66	9.82 \pm 0.94		0.895 \pm 0.012			31 \pm 2	31 \pm 1
High mountain: Hehuan										
10/09/2013 13:20	364	-8.21	40.89	28.79	0.02	0.895	0.016	3.2	31	10
10/09/2013 17:00	NA	-8.25	40.28	28.41	0.01	0.914	0.014	2.9	27	10
Average $\pm 1\sigma$	364	-8.23 \pm 0.02	40.59 \pm 0.30	28.60 \pm 0.19		0.904 \pm 0.009			30 \pm 2	10

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