Dear Editor,

I would like to thank you very much for the comments which helped us to improve the manuscript. We very much appreciate the effort and amount of time spent by the reviewers to review this manuscript. We agree with most of the concerns of the reviewers and addressed in the revised manuscript. Content wise the revised manuscript is not very different except some changes in the calculations and extending the simple model works to clumped isotope data inside the greenhouse (in Section 4.1) as suggested by the reviewers. The major changes are the presentation, English improvement and rearrangement and restructuring the manuscript as per the reviewers' suggestions.

Three major suggestions by the reviewers are as follows:

1. Clumped isotope effect associated with photosynthesis especially in relation to the findings in Eiler and Schauble (2004) and explore the ways to reconcile the findings from the two studies.
2. Application of Keeling plot for source identification when the source and sink coexist. Discussions about D47 results are mostly concluded to "unknown" enzymatic reaction during photosynthesis. Therefore, any quantitative discussion, such as estimating individual fluxes from/to the urban CO2, is not offered.
3. The discussion about the clumped isotope effect is mostly qualitative. The reviewer suggested to construct a simple (semi-) quantitative model to simulate the evolution of the concentration and isotopic composition of CO2 in the greenhouse experiments.

Our response to the first query is as follows: We elaborately discussed the effect of photosynthesis on the clumped isotope signatures in the residual CO2 and compared our findings with that of the Eiler and Schauble (2004) (see Sec 4.1). We are gathering more data at leaf level which will help to understand the effect of photosynthesis on clumped isotopes and the results will be presented in future publication. Meanwhile we linked more the ambient CO2 results to the greenhouse data which we have learned a lot more thank to a better controlled environment.

To reply to the second query, we agree with the reviewer that the identification of source using Keeling plot in the cases where both source and sinks co-exists is not valid. However, in most of the cases either source or sink is dominant. e.g., in the case of greenhouse, day time is dominated by photosynthesis and night time by respiration. In the revised manuscript, we considered all these aspects and did the appropriate calculation (Sec Sec 4.1).

To reply the third query, we want tell that we have carried out more in-depth discussion in the revised manuscript. Some simple modelling works were carried out with the traditional isotopes; we extended it to the clumped isotope data obtained inside the greenhouse (Sec 4.1 and Figure 8 in the revised manuscript). Definitely this is a new direction and has lot of scopes to carry research in more controlled environment.

I would like to mention that we have recently published a manuscript on clumped isotopes (Laskar et al., 2016, Terra Nova) where we discussed all details about the data quality and clumped isotope measurements including CO2 purification. As a result we have removed some of the contents in the method section and Supplement of the revised manuscript. The published paper is cited at appropriate places.

Below, please find our point-by-point response to referee's comments (referee's comments are in italics).

Sincerely yours,

Mao-Chang Liang
Academia Sinica

Anonymous Referee #1

This study provides excellent dataset for almost all of CO2 isotopologues in the atmosphere. Air samples were collected quite extensively, from open ocean, coasts, mountain, forest, grassland, sub-urban and urban traffic. Moreover, closed terrarium experiment and collecting exhaust from cars were conducted as well. Research plan and obtained results are very nice. While authors provides very valuable dataset, the individual discussion seems not always nice. My major comments on their discussion are; 1) They apply Keeling plot to most cases for source identification. If the case is simple two-source mixing, Keeling plot must be effective. However, this is generally not applicable for the case that source and sink coexist, except that both are the same isotopic composition (fractionation) and fluxes. I guess greenhouse experiment and grassland observation may be the cases. When Keeling analysis does work well, then authors seek the reason of inconsistency and develop some discussion. Some of these discussions are not so effective. Authors should pay attention that Keeling plot is not a universal tool. 2) On a related matter of 1), developed discussions about D47 results are mostly concluded to "unknown" enzymatic reaction during photosynthesis. Therefore, any quantitative discussion, such as estimating individual fluxes from/to the urban CO2, is not offered. Another approaches may be possible, I guess.

We thank the reviewer for appreciating the data. We agree with the points raised by the reviewer and answered the query at the beginning where we summarised the major points. We provided a detail assessment in the revised manuscript. However, it is too early to estimate individual fluxes using these limited data. Definitely, this will be our next plan with more detailed study including leaf level data.

I think this manuscript is worth-publishing to the journal Biogeosciences after addressing specific comments supplied as a separate file. Specific comments involve these issues, too. Please also note the supplement to this comment: http://www.biogeosciences-discuss.net/bg-2016-106/bg-2016-106-RC3-supplement.pdf

We agree with most of the comments and modified the manuscript accordingly. Point to point reply of the queries of the reviewer are given below.

L56, 85, 110, 301, 427, 482, 583: Authors used a term "bulk" for d13C and d18O, implying that clumped isotope (D47) is not bulk isotopic composition. To my knowledge, the term "bulk" is often used to distinguish between "weighted-average (bulk) isotope ratio of a material" and "compound-specific isotope ratio of a material", such as d13C for "organic matter" versus "protein, lipids, sugar, etc."; or "weighted-average (bulk) isotope ratio of a compound" versus "position-specific isotope ratio of a compound" such as d13C of long-hain hydrocarbon for "all carbon" or "1,2,3,4,..,n th carbon". In this sense, D47 of CO2 is also "bulk", or D47 is neither part of d13C or d18O but a integration of d13C and d18O to some extent. Thus I think authors should avoid using the term "bulk" for d13C and d18O. Instead, "conventional", "traditional" or without any adjective may be better.

We agree with the terminology of the reviewer and used “conventional” isotopes in the revised manuscript.

L68: "Evapotranspiration" should be replaced to "transpiration."
Done (L 74)

L68-69: This sentence is out of context. I guess it may follow the sentence of L58-62.

Modified in the revised manuscript (L 63)

L76-79: Contextually, this sentence should describe about d18O. But this sentence mentions general characteristics of CO2, not only d18O. Revise or move it to more appropriate place. In addition, I request one or more references to mention that present biogeochemical models remain inconclusive.

We agree with the reviewer, this is a general statement removed from the revised manuscript.

L85-87: "..limited because of the challenge.." Somewhat strange. "..limited due to the demand of very high precision.." or "..limited but several challenges have conducted to apply it to the atmospheric study.." might be more suitable.

The sentence is modified (L 84)

L92: "..have similar time-scales for the isotope exchange between CO2 and water.."

The sentence is modified (L 90)

L91-94: I agree that effect of photosynthesis and respiration on clumped isotope has not been studied well, but I disagree that corresponds to d18O as well. At least, their backgrounds are not equal.

We agree with the reviewer about d18O and modified the sentence accordingly (L 91-94)

L108-109: One or more references are necessary.

Additional references are provided (L 107)

L117-119: This is concluding remark. Move it to conclusion.

These two sentences are removed from here

L123: Delete "amu"

Done (L 119)

L130: 2 L; 2 atmospheric pressure

Done (L 126)

L130-133: I could not understand collection procedures well. Was the flask flushed out prior to sample collection without dehumidifier before collection? I believe such kind of pre-rocess for flushing should be done with identical condition to sample collection. How long did you take for actual sample collection except for pre-flushing?

Yes flasks were flushed out prior to sampling for ~10 minutes and flushing was done through the perchlorate (dehumidifier) column. The flasks were equipped with two stopcocks and after flushing the end stopcock was closed and allowed the pressure to build to 2 atm and then isolated by closing the other stopcock. This is discussed briefly in the revised manuscript (L 126-134). We also refer the details to our previously published papers such as Liang and Mahata (2015).

L139: What is "systematic analyses"?

“Systematic” refers to the study performed systematically, i.e., more regular and intensive sampling. To remove possible confusion, the word systematic is removed (L 138).

L141-142; L146-147: Just to recommend, "..5 m high. It was closed at least one day before each experiment and the ventilation was kept as minimum as possible."

Done (L 140)

L150-155: Add the height of the canopy.

Done (L 150)

L155-157: Add each sampling height above sea level.

Done (L 155-158)

L169-174: If you used a vacuum line, add which process is in vacuo. If not, I'm sorry.

Yes, we used vacuum line. CO_2 was extracted from air using a glass vacuum line connected to a turbo molecular pump by cryogenic technique. The vacuum line as well as the sample flask connection assembly including its head space was pumped to high vacuum before starting the CO_2 extraction. The details are mentioned in the revised manuscript (L 169-176). We also refer the details to our previously published papers such as Liang and Mahata (2015).

L194-196: Specify the names of the standard (VPDB, VSMOW, etc., for each).

Done (L 197)

L212: What is "this limit"?

The limit here refers to the full scrambling state. In this revised version, we replaced the term by “random distribution” (L 216)

L217-219: Just to recommend, "Masses 48 and 49 were monitored to confirm isobaric interferences due to contamination of hydrocarbons (Ghosh..).

Modified the sentence (L 221)

L221-233: Refer Yoshida et al. (2013) RCM27, 207-215, for the evidence of independence from d47 on D47.

Dependence of d47 on D47 varies from mass spectrometer to mass spectrometer. Therefore, this is not relevant, we discussed this in a previous publication (Laskar et al., 2016).

L235, 237: I am not so sure whether this term is really appropriate or not, however "empirical transfer function" is often based on the field observation, such as marine foraminifer community structure versus habitat temperature. Authors obtained a relation experimentally, thus I think "reference frame equation", "laboratory equation" or "local equation" should be more appropriate instead of empirical transfer function.

Though “empirical transfer function” is used by Dennis et al. (2011), we agree with the reviewer that the “reference frame equation” is more appropriate. This paragraph has been removed from the revised manuscript as it was discussed in another recent publication (Laskar et al., 2016).

L237-239: Authors need not to discuss in detail, but should compare their results with former study.

The reference frame equation varies between mass spectrometer to mass spectrometer, even it differs for a given mass spectrometer at different time. It is known to the community. This part is removed from the revised manuscript as it was discussed in a recent publication (Laskar et al., 2016).

L245: The 1-sigma values of d13C and d18O seem too large whereas that of d47 seems in agreement with previous studies (Table S1). Huntington et al. (2009) described that d13C or *d18O uncertainties were roughly an order of magnitude better than d47, because of those higher abundance. Actually, Yoshida et al. (2013) showed these lower uncertainties accordingly. To my knowledge, in any way, if one measures d13C with [44] signal of 12V and integration time of 2.5 hour, the standard deviation may be better than 0.01 permil, not only for single gas but also for several aliquots. Actually, results of CO2 digested from carbonates (Table 1) are similar accordingly. Do you have any idea why uncertainties of cylinder CO2 became so high, or d47 uncertainty became lower relatively?*

For carbonates, it is possible to achieve a std. dev. of 0.01 (Table 1). For air CO2 (compressed cylinder air or atmospheric air), handling/purification worsen the precision. Though efforts have been put (see Liang and Mahata, 2015, for example), the best precision we can get so far for d13C and d18O is ~0.05 per mil. The precision we agree that is not sufficient for CO2 long term monitoring, but is sufficient for the current study. Possible cause is likely that slight fractionations during the extraction cause this variation in d13C and d18O. However, this possible fractionation does not impair the D47 analysis.

L250-252: Add references for demonstrating poor consensus.

Dennis et al., (2011), the inter-laboratory comparison shows D47 values of NBS-19 from 0.373 to 0.404‰ for three laboratories. This part is removed from the revised manuscript as it was discussed in a recent publication (Laskar et al., 2016)

L254-255: Not only showing deviations from expected temperature, specify the reproducibility of D47 thermometry.

This is discussed in a previous publication (Laskar et al., 2016) and removed from the revised manuscript

L267-272: Lack of data source of temperature at South China Sea.

Actual measurements during sample collection, mentioned in the revised manuscript (L 157).

L276: Diurnal variation..

Corrected (L 256)

L282: Define Keeling plot and describe its purpose before the first use for readers from different fields.

A brief description of Keeling plot and purpose is incorporated in the revised manuscript (L 261).

L288: What is expected (potential) contamination of anthropogenic CO2 in the greenhouse?

The potential contaminants are the ambient air with significant anthropogenic components which was found absent from [CO2] and all the isotope signatures.

L296: What does "daytime" correspond? Daytime on 12th October? Or other three days?
It is from morning 9 am to evening 5 pm, statement is modified in the revised manuscript (L 286).

L297-299: The criteria of separation between weak/strong for photosynthesis or respiration in Fig. 4 is quite unclear. It seems very arbitrary. Define it clearly, otherwise delete this sentence and Fig. 4.

By weak photosynthesis we wanted to mean that the photosynthetic activity was reduced artificially. This was done by covering the greenhouse with a double layered black cloth on a dark cloudy day. This is more clearly explained in the revised manuscript (276-294).

3.2: Catalytic converter in the exhaust plays a role to convert CO to CO2. Is there any possibility this catalytic reaction may affect d18O value as same as D47, not only by exchanging oxygen with water?

The change in d18O in the exhaust was also observed (Sec. 3.2). We are not aware of any process other than exchange of oxygen isotopes between CO2 and condensed water which can cause the change in the d18O or D47 of the exhaust CO2.

3.3: This section should be divided into each field and reorganize to avoid confusion. For example, marine (including SCS and coastal sites), urban (Roosevelt Road), sub-urban (AS), grassland (NTU) and mountain. I guess authors might confuse a bit. For example, the relations between CO2 (1/CO2) and d18O as well as d13C and d18O for grassland are significant (regressions were done with data from Table 5), unlike its statement found in L346-349. Incidentally, the order to explain d13C and d18O results is marine, urban, sub-urban, grassland, mountain then forest. On the other hand, that to explain D47 results is marine, sub-urban, grassland, forest, mountain then urban. Easy to confuse.

We reorganized the sections (Sec 3.2 to 3.4) and presentation is consistent in the revised manuscript. Section 3.4 is divided into several paragraphs to remove confusion.

L314-328, L368-372: These should be reorganized as a separate section "marine CO2" for example.

Marine and coastal CO2 data are presented in a new section (Sec 3.3)

L330-333, L386-390: These should be reorganized as a separate section "urban CO2" for example.

Urban, sub-urban, grass-land, forest and high mountain CO2 data are presented under one section (Sec 3.4) but separated into paragraphs.

L333-339, L372-376: These should be reorganized as a separate section "sub-urban CO2" for example.

Urban, sub-urban, grass-land, forest and high mountain CO2 data are presented under one section (Sec 3.4) but separated into paragraphs.

L339-349, L376-379: These should be reorganized as a separate section "grassland CO2" for example.

Urban, sub-urban, grass-land, forest and high mountain CO2 data are presented under one section (Sec 3.4) but separated into paragraphs.

L353-357, L379-384: These should be reorganized as a separate section "forest CO2" for example.

Urban, sub-urban, grass-land, forest and high mountain CO2 data are presented under one section (Sec 3.4) but separated into paragraphs.

L314-328: The analysis based on the Keeling plot and subsequent source identification may be problematic. First, authors did not clarify whether the ocean of the study area/period is source or sink of CO2. Second, data range both of CO2 and d13C are narrow and number of data is limited, thus intercept of regression line must have large uncertainties. Therefore, some sentences from L324 to 328 and associated discussion in Section 4 may not be so meaningful. Moreover, authors should consider marine air interacts with ocean surface layer (mixed layer), not with deep ocean directly. The inconsistency between opaque Keeling intercept and d13C value from unconnected deep ocean is not surprising at all.

We agree with the reviewer about the application of Keeling plot with a few data points covering a small range. The region is a net source of CO2 in the atmosphere, discussed in the revised manuscript (Sec 4.3). We put less emphasis on the Keeling plots over the ocean in the revised manuscript.

L331: 39.32 instead of 39.319

Done (L 328)

L332-333: The average d18O value is not different significantly from that of grassland, thus this explanation is partly incorrect.

The mean values are significantly different though the uncertainty associated with the values is large. d13C values are significantly different, but it is difficult to conclude based on d18O as mentioned in the later part of the section. The statements are modified in the revised manuscript (L 328).

L344-345: I agree with this conclusion, however not by the result from Keeling plot, but by strong relations of CO2-d18O and d13C-d18O as mentioned above. D47 result may support this, thus I would like to emphasize that all results from same field should be described at once (in same block), should not be separated. However, this kind of concluding remark is supposed to be in the discussion.

We agree that this should be discussed as a block in the discussion; this is moved to discussion (Sec. 4.5).

L346-349: I totally disagree with this sentence. Authors should verify data again.

Away from, for example, significant anthropogenic sources, due to presence of a variety of water sources (leaf water, soil water, etc), correlation between 1/[CO2] and d18O is always not observable.

L358-367: This block and Fig. 6 may not be necessary.

This paragraph along with Fig. 6 has been removed from the revised manuscript.

4: The section and order of description is inconsistent with Results. This prevents readers from moving on smoothly. Consider above mentioned comment and reorganization.
We thank the reviewer for the suggestion. This section is totally reorganized in the revised manuscript.

L400-418: These blocks should move to introduction.

Removed from the revised manuscript

L422: "biological" instead of "biogeochemical"

Done (L 376)

L437-446: The obtained fractionation factor of -15.3, which is significantly different from expected C3-type fractionation, clearly demonstrated that this calculation is not applicable to the photosynthesis-respiration coexisting process. Authors should consider the different approaches. For example, assuming constant respiration rate for whole day (applying night time respiration rate to daytime), then obtaining gross productivity.

We agree with the reviewer that the calculation should include respiration also. We modified our calculation assuming a constant respiration and presented the estimate in the revised manuscript (L 396).

L446-454: Describe how consistent with previous studies. Consider same calculation mentioned above.
Calculation is modified as per the suggestion and the calculated d13C and d18O discriminations have been compared with previous studies in the revised manuscript (L 401-409).

L455-489: Authors demonstrated that d18O of respired CO2 is out of equilibrium with ambient temperature (water is supposed to have constant value, thus disequilibrium is due to temperature variation). If so, D47 of respired CO2 must be always out of equilibrium as well unless d13C is disequilibrium in a same manner (difficult to postulate due to the different fractionation process). However, authors mentioned that respired CO2 is in equilibrium with temperature because data in the early morning or night-time show close to equilibrium. This is a contradiction in principle. With keeping this contradiction, authors developed further discussion with respect to catalytic reaction. I cannot say whether the discussion is correct or not, however, I can say authors ignores a significant contradiction in the same block. Temperature change during night-time and cloudy (sun-shaded in addition) daytime were small whereas sunny days had wide range of temperature. Simply considering, larger magnitudes of disequilibrium during sunny daytime may be attributed this large temperature variation. Alternatively or additionally, authors had better consider that air temperature may *be different from body temperature inside leaves. Plants have homeostatic function with respect to temperature, a transpiration. CO2 is respired inside the leaf in partial isotope equilibrium with body temperature, not ambient temperature. I believe authors could develop much more deep and quantitative discussion with data shown in this study, before measuring clumped isotope of O2.*

We did not say that d18O of respired CO2 is out of equilibrium. We only showed that the respired CO2 is in thermodynamic equilibrium with the leaf and soil water using the obtained D47 values. We agree with the reviewer that the plant body temperature could be different from the air temperature but with progress of the day we expect change in the D47 values. As stated in the later part of this section, this needs to be tested at leaf level which we are planning and hopefully, the results will help to understand/model the effect of photosynthesis on the D47 values.

L469: Remove "we believe"

Done (L 429)

L474: Yeung et al., 2015).

Done (L 444)

L490-498: This block should move to Summary.

Done (L 665)

L501-513: As mentioned above, I find it difficult to understand why authors would like to link atmospheric CO2 to respired CO2 in the deep ocean. I think this is unnecessary, and recommend to remove entire this block.

We agree with the reviewer and reduced the discussion in the revised manuscript. However, we think that some explanation of the observed is required and kept a paragraph on this (L 494-507).

4.3: As mentioned above, authors had better consider the possibility of catalytic reaction between CO and CO2 at the converter.

Yes reaction between CO and CO2 inside the catalytic converter at the temperature of the converter could also lead to the change in the D47 values, though this would not change in the d18O values as the source of O2 in both CO and CO2 is the atmospheric O2. This is discussed in the revised manuscript (Sec. 4.2).

4.4: Authors gave f, anthropogenic contribution, in the two-source component equation from the difference between observed (urban) and marine CO2. This assumption ignores photosynthetic uptake or influence of other sources completely. Authors should get f by solving simultaneous equations based on the concentration and isotopic composition, conversely, then discuss. This approach may be more purposeful, quantitative and premised (why isotope study is needed).

We agree with the reviewer that a more quantitative estimate for CO2 cycling fluxes between reservoirs is possible. However we note that for example, atmospheric transport, that we mentioned at the end of the section, can easily interfere the calculation (box model interpretation, for example). This is the main reason that we give a more quantitative assessment for the greenhouse data, but not ambient CO2 data.

5 or new 4.6: A trial to estimate individual fluxes of combustion, respiration and photosynthesis for C3 and C4, respectively, from/to the urban (or sub-urban) CO2 is very welcome by using [CO2], d13C, d18O and D47.

Please see the previous response. We agree that the multiple CO2 isotopologues can help to constrain the CO2 fluxes of combustion, respiration and photosynthesis for C3 and C4, etc. However, incomplete knowledge on meteorological influence and lack of systematic dataset around the region prevent us from full assessment. From the available data presented, we showed that D47 behaves differently from [CO2], d13C, and d18O. To minimize regional and/or global interference (due to atmospheric transport, for example), we use greenhouse as a testbed for assessing the associated biological CO2 fluxes. For combustion, there are other tracers more useful than the presented CO2 isotopologues, such as VOCs and 14C.

Fig. 1: Detail map of collection site in the Taipei city is desirable instead of right panel. Coastal and mountain sites can be involved into the left panel.

Done (Fig 1)

Fig. 3C: Although there appears a fair negative relation between d18O and D47 in Figs. 3A, B and D, coordinated rapid drops subsequent increases of these values are found on 4th August (3C) as well as 31st July. Do you have any idea what happened at these periods?

Actually the correlation is significant only in Figure 3D. The reason for the rapid decrease in the D47 values in the early in response to photosynthesis is not very clear. We are doing more study at leaf level to identify the possible cause.

Fig. 4: As mentioned above, the criteria to separate A and B is unclear.

Here we wanted to show that D47 values are similar to that expected thermodynamically when respiration is strong and photosynthesis is weak but not the other way round. This is elaborated in the revised manuscript (Sec 4.1)

Fig. 5: Data from urban site should be added. Ocean and coastal sites can be merged.

Urban site data incorporated (Fig 7A). Ocean and coastal site merged in Fig 5.

Fig. 6: This figure is unnecessary (see above).

Removed from the revised manuscript

Fig. 7: Reorganize (rearrange) according to the order of results and discussions.

Done

New Fig. 9?: The summarizing diagram for individual fluxes (schematic box diagram) is welcome.

We agree that a summarizing diagram of individual flux will enhance the presentation. However, with the present data it will be too early to assign D47 values to individual fluxes. We will keep this suggestion in mind and try in future with more data.

Table 2: Add relative humidity if available.

We occasionally measured the relative humidity, not for all samples. We don’t think that relative humidity can have major role in clumped isotopes.

Anonymous Referee #2

The manuscript "Clumped isotopes in near surface atmospheric CO2 over land, coast and ocean in Taiwan and its vicinity" provided a valuable dataset of clumped isotopes in atmospheric CO2 and the authors did a good job. For the comments please see the attached file.

We thank the reviewer for appreciating our effort. All the reviewers queries from the pdf and modifications/changes made in the revise manuscript are listed below. Also the other minor suggestions such as changing present/past tenses in the sentences, deleting/adding texts in the manuscript are be made in the revised manuscript.

Line 28: The sentences should be in past tense.

Done (L 29)

Line 32: Not clear which processes. mention them i.e. photosynthesis, fossil fuel combustion ...

The different processes are photosynthesis, respiration, local anthropogenic emissions, modified in the revised manuscript (L 32-33).

Line 33: Split the sentence

The sentence is modified (L 30-34)

Line 34: Restructure the sentence: for example, the contribution of various sources of CO2 on D47 ...

The sentence is restructured (L 34)
Line 41: Split the sentence

Done (L 40)

Line 61: Split the sentence because it is hard to follow what you mean. Maybe: ... ocean and landbiosphere. The photosyn... 13C in plants is higher than ... .

The sentence is divided into two for making it simple and easily understandable (L 61)

Line 63: It is not clear what you mean. You should explain how photosynthesis and respiration may change 18O of CO2 in vicinity of plants, if it is what you wanted to say. Is there any discrimination against 18O during assimilation of CO2 for photosynthesis which may lead to enrichment or depletion in CO2 besides the leaves? In the next sentence your explanation just shows enrichement because of evapotranspiration but what is the effect of photosynthesis? Would be this isotopic discrimination due to evapotranspiration against 18O still present if the plant was not under water stress at all?

The statements are modified as follows (L 68):
δ^{18}O is used for partitioning net CO_2 terrestrial fluxes between soil respiration and exchange with the plant leaves, the exchange is enhanced by the presence of carbonic anhydrase in plants and soils (Francey and Tans, 1987; Farquhar and Lioyd, 1993; Yakir and Wang, 1996;

Ciais et al., 1997; Peylin et al., 1999; Murayama et al., 2010; Welp et al., 2011). This is because $\delta^{18}O$ of CO_2 fluxes originated from soil respiration are different from that exchanged with the leaf water. $\delta^{18}O$ in soil water reflect the $\delta^{18}O$ value of the local meteoric water while leaf water is relatively enriched due to transpiration.

Line 69: need reference

Appropriate references are included (L 63)

Line 71: This sentence should be in line 62 before 18O is used for partitioning ... .

Done (L 66)

Line 79: You mean reservoirs with different 18O?

Yes, the statement is modified in the revised manuscript (L 78).

Line 85: Split the sentence. You mixed many things together.

Done (L 80)

Line 86-96: Very well! This makes your study unique and valuable.

We thank reviewer for appreciating the work

Line 271: Materials and Methods is good.

Thank you

Line 277: The lowest CO2 concentration, [CO2] and the highest ...

Corrected (L 257)

Line 296: equilibrium with what? split the sentence.
Thermodynamic equilibrium with the leaf and soil water, sentence modified and split (L 285).

Line 300: my suggestion: The correlation between D47 and CO2... was observed only when the photosynthesis was weak.

Suggestion implemented (L 291)

Line 302: very good finding.

Thank you

Line 399: This paragraph can be deleted. It is not discussing any of the observation and measurements.

This paragraph has been removed from the revised manuscript, in fact the first three paragraphs of the discussion are removed.

Line 404: The sentences after "however" are not kind of discussion. I did not get why they should be mentioned here.

These three paragraphs have been removed from the revised manuscript.

Line 418: I think the whole these 3 paragraphs should be deleted. It is not clear what you wanted to say. Even if it was like an introduction for the discussion (which is not really necessary) you should follow to emphasis on the main issues respctively to what you will mention later for example effect of photosynthesis on D47, antropogenic effects in urban regions, ...

These three paragraphs have been removed from the revised manuscript.

Line 477: Split the sentence

Done (L 352)

Line 505: put the reference here and split the sentences.

Done (L 496)

Line 507: It is better to mention the intercept value here

The intercept value is mentioned now (L 499)

Line 511: write the value

Done (L 505)

Line 521: refer to the fig. or value here

Done (L 516)

Line 529: So D47 values in CO2 over oceans at nights should show no deviation from thermodynamic equilibrium. Is that true? How would be this effect in coastal areas where because of shallow water aquous plants may live as well?

Yes, there should not be any deviation in the D47 in night also. The effect of photosynthesis on clumped isotopes is observable when photosynthesis is very strong e.g., in a confined greenhouse. Probably effect is present everywhere but not detectable with the measurement precision. Therefore, in the coastal areas we expect similar D47 values as observed over the open ocean unless there is a significant CO2 is contributed from the other sources such vehicle and industrial emissions.

Line 559: It seems logical but how? Do you have an estimation of isotopic composition of condensed water? How CO2 isotopic composition can change? I mean CO2 will dissolve in water but how its isotopic composition can change?

Unfortunately we don’t have any measurement of the d18O value of the condensed water but it is expected to be similar to the atmospheric O2 plus the fractionation associated with the condensation (atmospheric O2 is used for combustion). CO2 readily exchanges oxygen isotopes when comes in contact with water, here probably a partial exchange takes place causing the deviation from the expected d18O and D47 values. This section is more elaborately discussed (Sec 4.2).

Line 562: Split the sentence! It is hard to follow you.

This section is rewritten (Sec 4.2) in the revised manuscript

Line 566: mention the temperature

Temperature is mentioned (L 489)

Line 583: reference needed

Done (L 556)

Line 589: split the sentence

Done (L 564)

Line 604: Can it be also less anthropogenic contribution?

This value was obtained after subtracting the anthropogenic contribution. It can also be due to underestimation of the anthropogenic CO_2 at the sampling spot. The regional background [CO_2] here could be lower than that assumed and the actual anthropogenic fraction of CO_2 could be higher than that assumed here. Discussed in the revised manuscript (L 576).

Line 620: split the sentence.

Done (L 597)

Line 625: How could be anthropogenic effects in a dense and isolated forest area?

It is very unlikely to have anthropogenic CO2 in an isolated place, but we did not neglect a priory. Later using D47 we showed that there is no anthropogenic CO2 in the forest site.

Line 628: I think still you cannot exclude the photosynthesis effect. Furthermore, the humidity in such condition should be high which may modify the effect of respiration and may affect the temperature. You need to discuss about these issues.

We agree that we cannot exclude photosynthetic effect. The issue is discussed more elaborately in the revised manuscript (L 625).

Line 648: You need to discuss here about the photosynthetic effect on D47 values, especially that you took the samples just above the grasses.

We agree with this suggestion and discussed more on this in the revised manuscript (L 620).

Line 657: The fig. 8 is really a good job.
Thank you

Line 671: explain it here also how and through which mechanism.

The explanation is also given here (L 660)

Line 678: You did not discuss about this before. Delet this or explain the relation in the text. Why not "atmospheric CO2 budget" instead?

This is removed from the revised manuscript.

Anonymous Referee #3

This manuscript reports new measurements of clumped isotope compositions of atmospheric CO2 collected from different environments and settings. Studies of clumpedisotope composition of atmospheric CO2 were among the first applications of clumped isotope methods, but have received less attention in recent years compared to other applications. It's great to see another focused study on this subject. The dataset presented in this study is quite extensive, and mostly confirms the major findings from previous studies. However, the conclusion the authors draw regarding the effect of photosynthesis on the clumped isotope composition of CO2 differs significantly from previous studies, and could potentially open many research opportunities. Overall, this manuscript improves our understanding of the various controls on the clumped isotope composition of atmospheric CO2, and can help future efforts to better constrain the atmospheric CO2 budgets. I have several specific comments about this manuscript, as detailed below, and would recommend these issues be addressed prior to publication.

We thank the reviewer for appreciating the work. Effect of photosynthesis on the clumped isotopes of atmospheric CO2 is an interesting finding and will be discussed more elaborately in the revised manuscript. We agree with all the concerns of the reviewer and addressed them in the revised manuscript.

Major comments:

1. Separation of N2O from CO2. A GC column was used to separate N2O from CO2 in this study. The authors showed a reasonable separation of the two in Fig. S2, but didn't mention the exact CO2 trapping time in their experiments. It's possible the CO2 yield was compromised in order to achieve the optimal separation of N2O. The authors need to provide more details and discuss how the compromised yield and/or residual N2O might affect their clumped isotope data.

We collect CO2 during 14 – 23 min. Yes CO2 yield was slightly compromised in order to achieve the optimal separation of N2O. The recovery of CO2 was always greater than 95 %. The residual N2O is checked comparing the sample and reference 48 and 49 signals. If value of D48 is large (>5) we did not consider the measurement, either we clean the sample again or just through. When the signal voltage for 49 between sample and reference is more than 0.3 mV we also neglected those numbers. We have discussed this in a recently published article (Laskar et al. Terra Nova, 2016) and cited at appropriate place.

2. Photosynthesis effect. In their greenhouse experiments, the authors observed that the clumped isotope compositions of CO2 were higher than what expected from thermodynamic equilibrium when photosynthesis was active. This finding is very intriguing and differs from what observed in previous studies (e.g. Eiler and Schauble 2004), where the clumped isotope compositions of CO2 residual to photosynthesis were shown to generally decrease.

Please see a previous response where the issue is discussed.

a. *Given the importance of this finding, I think the authors need to provide D48 and D49 data of their measurements to show that the elevated D47 values were not related to any contamination issues. More generally, the authors are encouraged to include all their raw clumped isotope measurement data in the electronic supplementary material of their manuscript, which is becoming a convention in the clumped isotope community.*

We mainly monitor the contamination with D48 signals. We will include the D48 values for all the sample. We have D49 values also but our experience is that it is also controlled by the 44 signals.

b. The authors need to expand their discussion about the clumped isotope effects associated with photosynthesis they observed, especially in relation to the findings in Eiler and Schauble (2004), and explore ways to reconcile the findings from the two studies.

Please see a previous response where the issue is discussed.

c. The authors did a nice job estimating the carbon and oxygen isotope fractionations associated with photosynthesis in their greenhouse experiments. But their discussion about the clumped isotope effect is mostly qualitative. The authors might want to construct a simple (semi-)quantitative model to simulate the evolution of the concentration and isotopic composition of CO2 in their greenhouse experiments. Such a model might enable them to quantitatively estimate the clumped isotope effects associated with photosynthesis, which would be an important contribution of this study.

Please see a previous response where the issue is discussed.

Minor comments:
1. Line 440: the authors neglected the daytime respiration when estimating the isotope effects associated with photosynthesis. They need to provide evidence to support this approach.

We agree that this is a crude assumptions, we have done the calculations incorporating the day time respiration in the revised manuscript (Sec 4.1).

2. *In section 4.1, the authors estimated the rates of respiration, photosynthesis, and CO2-water exchange in their greenhouse experiments, in the unit of molecules cm-2 s-1. But it's not entirely clear how those values were derived. More details are needed.*

We have provide more details about the calculations in the revised manuscript (L 401).

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

Amzad Hussain Laskar[1] and Mao-Chang Liang[1,2,3~~,4~~*]

[1]Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan

[2]Graduate Institute of Astronomy, National Central University, Taiwan

~~[3]Institute of Astronomy and Astrophysics, Academia Sinica, Taiwan~~

~~[4]Department~~[3]Department of Physics, University of Houston, USA

*Correspondence to: Mao-Chang Liang (mcl@rcec.sinica.edu.tw)

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Abstract

Molecules containing two rare isotopes (e.g., $^{13}C^{18}O^{16}O$ in CO_2), called clumped isotopes, in atmospheric CO_2 are powerful tools to provide an alternative way to independently constrain the sources of CO_2 in the atmosphere because of their unique physical and chemical properties. We ~~present~~presented clumped isotope data (Δ_{47}) in near surface atmospheric CO_2 from urban, sub-urban, ocean, coast, high mountain (~3.~~3~~2 km a.s.l.) and forest in Taiwan and its vicinity. The primary goal of the study ~~is~~was to use the unique Δ_{47} signature in air CO_2 to show the extents of its deviations from thermodynamic equilibrium due to different processes ~~in a variety of environments~~such as photosynthesis, respiration, local anthropogenic emissions, which the commonly used tracers such as $\delta^{13}C$ and $\delta^{18}O$ cannot provide. We also ~~explore~~explored the potential of Δ_{47} ~~in air CO_2~~ to identify/quantify the contribution of CO_2 from various sources. Atmospheric CO_2 over ocean ~~is~~was found to be in thermodynamic equilibrium with the surrounding surface sea water. ~~Also respired~~Respired CO_2 ~~is~~was also in close thermodynamic equilibrium at ambient air temperature. In contrast, photosynthetic activity ~~results~~result in significant deviation in Δ_{47} values from that expected thermodynamically~~ demonstrated using CO_2 collected from a controlled greenhouse~~. The disequilibrium could be a consequence of kinetic effects associated with the diffusion of CO_2 in and out of the leaf stomata. We ~~also observe~~observed that $\delta^{18}O$ and Δ_{47} ~~behave differently in response to~~do not vary similarly when photosynthesis was involved unlike simple water-CO_2 exchange~~ where the time scale of equilibration of the two is similar.~~. Additionally~~, the measured~~ we obtained Δ_{47} values ~~in~~of car exhaust CO_2 ~~are~~that were significantly lower than the atmospheric CO_2 but higher than that expected at the combustion temperature. In urban and sub-urban regions, the Δ_{47} values ~~are~~were found to be lower than the thermodynamic equilibrium values at the ambient temperature, suggesting contributions from local combustion emissions.

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

1. Introduction

The budget of atmospheric CO_2 is widely studied using the temporal and spatial variations ~~of the~~in concentration and ~~bulk~~conventional isotopic compositions (δ^{13}C and δ^{18}O) of CO_2 (Francey and Tans, 1987; Francey et al., 1995; Yakir and Wang, 1996; Ciais et al., 1995a,b, 1997; Peylin et al., 1999; Cuntz et al., 2003; Drake et al., 2011; Welp et al., 2011; Affek and Yakir., 2014). δ^{13}C is useful to differentiate the exchange of CO_2 with the ocean and land~~-~~-biospheres~~ as~~. This is due to the fact that the photosynthetic discrimination against ^{13}C during exchange with land plants is higher than that associated with the chemical dissolution of CO_2 in the ocean (e.g., Tans et al., 1993; Ciais et al., 1995a; Francey et al., 1995; Ito, 2003; Bowling et al., 2014). ~~δ^{18}O is used for partitioning global-scale net CO_2 terrestrial fluxes between photosynthesis and respiration (Francey and Tans, 1987; Farquhar and Lioyd, 1993; Yakir and Wang, 1996; Ciais et al., 1997; Peylin et al., 1999; Murayama et al., 2010; Welp et al., 2011). This is because oxygen isotopes in CO_2 exchanges readily with water and hence the values of δ^{18}O are different when exchanging with soil water or relatively enriched leaf water; the enrichment in ^{18}O in the leaf water occurs during evapotranspiration. ~~The major limitation of δ^{13}C is that it cannot distinguish ~~between ~~CO_2 produced ~~from~~by high temperature combustion ~~and~~or low temperature respiration~~.~~ (Affek and Eiler, 2006; Laskar et al., 2016a). δ^{18}O in atmospheric CO_2 is mainly controlled by various water reservoirs (ocean, leaf~~,~~ and soil). In urban locations, a significant fraction of CO_2 may have combustion origin possessing δ^{18}O signature of atmospheric O_2 (Kroopnick and Craig, 1972; Ciais et al., 1997; Yakir and Wang, 1996). δ^{18}O is used for partitioning net CO_2 terrestrial fluxes between soil respiration and that exchange with plant leaves, the exchange rate is enhanced by the presence of carbonic anhydrase in plants and soils (Francey and Tans, 1987; Farquhar and Lioyd, 1993; Yakir and Wang, 1996; Ciais et al., 1997; Peylin et al., 1999; Murayama et al., 2010; Welp et al., 2011). ~~; Barkan and Luz, 2012). The δ^{18}O values from these processes and interactions are different. As a result, δ^{18}O in atmospheric CO_2 has been widely used for constraining the budget~~This is because δ^{18}O of CO_2 fluxes originated from soil respiration are different from that exchanged with leaf water. δ^{18}O in soil water reflect the δ^{18}O value of local meteoric water while leaf water is relatively enriched due to transpiration. The δ^{18}O values from these processes and interactions are different and hence the tracer is widely used for constraining the gross production of CO_2 (Francey and Tans, 1987; Ciais et al., 1997; Gillon and Yakir, 2001; Cuntz et al., 2003; Welp et al., 2011). However, due to ~~its short turnover time in the atmosphere, mainly affected by presence~~rapid exchange of ~~enzyme carbonic anhydrase in plants, soils, and surface ocean, the definite determination of the associated fluxes in~~oxygen isotopes between CO_2 ~~biogeochemical models remains inconclusive. The presence of~~and different water reservoirs with diverse δ^{18}O ~~reservoirs~~ and processes such as evapotranspiration ~~also complicates the~~ complicate its interpretation~~.~~ (Riley et al., 2003).

The doubly substituted isotopologues or clumped isotopes such as $^{13}C^{18}O^{16}O$ in CO_2~~, whose excess over the stochastic isotopic distribution~~, denoted by Δ_{47}, provides an additional and independent constraint to study the atmospheric CO_2 budget~~ and~~. Δ_{47} in air CO_2 can help to identify the mechanisms for CO_2 production and consumption. Unlike ~~bulk~~conventional isotopes, clumped isotope studies for the atmospheric CO_2 are very limited mainly because of ~~the~~ challenges to ~~acquire~~apply it ~~precisely~~to the atmospheric study (Eiler and Schauble, 2004; Affek et al., 2007; Yeung et al., 2009). The available data are not sufficient to address some key issues such as quantification of CO_2 from different sources and to what extent the air CO_2 is in thermodynamic equilibrium with leaf and surface waters, especially in regions with strong anthropogenic activities such as urban areas. Also the effect of photosynthesis on the Δ_{47} of air CO_2 has not been studied rigorously. δ^{18}O and Δ_{47} were reported to have similar time-scales for the isotope exchange ~~time scales with pure~~ between CO_2 and water (Affek, 2013; Clog et al., 2015), but ~~how they behave~~no comparative study on their behavior in presence of other processes such as photosynthesis and respiration ~~has not been studied well.~~was done. A combined assessment from all~~ of~~ the three aforementioned isotopic tracers can better constrain the budget of CO_2 and associated processes than δ^{13}C or δ^{18}O alone.

Theoretically it is shown that in thermodynamic equilibrium, Δ_{47} values of CO_2 are temperature dependent (Eiler and Schauble, 2004; Wang et al., 2004), verified over a wide range from 10 to 1000 °C (Dennis et al., 2011). Processes that involve CO_2 and liquid water as medium, such as isotopic exchange with ocean water are expected to have Δ_{47} values close to the thermodynamic equilibrium. Δ_{47} values in ambient air CO_2 should reflect a balance of

CO_2 fluxes between biosphere-atmosphere exchange, ocean-atmosphere exchange, and emissions from combustion sources. Photosynthesis involves gas phase diffusion of CO_2 into leaves, fixes ~1/3 of the CO_2, and returns the rest back to the atmosphere. CO_2 molecules inside a leaf are generally expected to be in thermodynamic equilibrium with leaf water because of presence of enzymatic carbonic anhydrase that greatly enhances the isotopic exchange (Cernusak et al., 2004). Δ_{47} values of soil respired CO_2 is also not well constrained, though it is believed to be in thermodynamic equilibrium with the soil water~~.~~ (Eiler and Schauble, 2004).

Here, we present clumped and ~~bulk~~conventional isotope data in near surface air CO_2 covering a wide variety of processes and interactions. Air samplings were made in South China Sea, two coastal stations in northern Taiwan, an urban traffic street, a sub-urban location, a forest site, a greenhouse, top of a high mountain and car exhausts. The study ~~is~~was designed and aimed to show the extents of the deviations of near surface atmospheric CO_2 from thermodynamic equilibrium with local surface water. Possible influences from other processes such as anthropogenic emission, respiration, and photosynthesis on clumped isotopes ~~are explored. We show that CO_2 respired from root and soil is in close thermodynamic equilibrium with the soil waters but photosynthesis tends to deviate it. Therefore, utilizing Δ_{47} for partitioning fluxes between photosynthesis and respiration/soil invasion is possible~~were explored.

2. Materials and methods

Stable isotopic compositions of CO_2 including mass 47~~ amu~~ were measured using a Finnigan MAT 253 gas source stable isotope ratio mass spectrometer configured to measure ion beams corresponding to M/Z 44 through 49. The instrument registers the major ion beams (44, 45 and 46) through resistors 10^8, 3×10^{10}, and 10^{11} Ohm, respectively, and minor ion beams (47, 48 and 49) through 10^{12} Ohm. All the measurements were carried out at Research Center for Environmental Changes, Academia Sinica, Taiwan.

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

To show how photosynthesis and respiration affect the abundances of CO_2 isotopologues and to demonstrate what different information the Δ_{47} can give from the other isotopologues, we performed ~~systematic~~ analyses for CO_2 collected in a controlled greenhouse with cemented floor located in the top (3rd) floor of the Greenhouse Building, Academia Sinica. The size of the greenhouse was about 8m long, 5m wide and 5m high~~,~~. It was closed at least one day before each experiment and ~~was in a condition to have minimal air exchange with the surroundings by switching off~~ the ventilation ~~system~~was kept off. More than 70 % of the ground area inside the greenhouse was occupied with *Cinnamomum cassia* plants, each of ~2 m height kept in pots. Samples were collected at intervals of less than half an hour to a few hours on three sunny days and one cloudy day to investigate the influence of photosynthesis and respiration on the isotopologues of CO_2. ~~The greenhouse was isolated from the surroundings at least a day before the sample collection;~~Inside the room relative humidity was ~50-70 % for the three sunny days and was above 90 % for the cloudy day.

Forest air CO_2 was collected from a dense natural forest at the west end of the Academia Sinica Campus. The vegetation mainly consists of medium to big size trees with canopy heights varying between 10 to 20 m. The samples were collected ~100 m inside the forest on a small plateau at a height of ~30 m from the ground in the slope of a hill; the dense vegetation allowed little sunlight penetrating to the surface. The relative humidity at the site was 80-90 % during the sampling days and wind speed was nearly zero due to presence of hills on three sides of the sampling spot. Marine air was collected during a cruise in the South China Sea (for the cruise track see Figure 1) at a height of ~10 m a.s.l. and from two coastal stations: Keelung (25°09′6″ N, 121°46′22″ E) and Fuguei Cape (25°18′ N, 121°32′ E) (Figure 1~~).~~) at a height of ~5 m and ~20 m a.s.l. respectively. Sea surface temperatures were measured at the time of sampling. Urban air was collected at a bus stop on Roosevelt Road, a busy street in Taipei. Sub-urban air was collected from an open roof (~30 m above ground) of Institute of Earth Science Building, Academia Sinica (AS; 25°2′41″ N, 121°36′52″ E); grassland air was collected from a grass field in front of the Department of Atmospheric Science, National Taiwan University Campus (NTU; 25° 1′ N, 121°30′ E), Taipei. In addition, we collected air from the summit of the Hehuan mountain (24°8′15″ N, 121°16′32″ E, 3.~~3~~2 km a.s.l.) (Figure 1) on 9th October, 2013. All air samplings were made when there was no rain to avoid direct interaction with the rainwater. Car exhausts were collected from a Mazda 3000cc TRIBUTE and a Mitsubishi 2400cc New Outlander, using evacuated 2L glass flasks from ~20 cm inside the exhaust pipes through a column of magnesium perchlorate.

CO_2 was extracted from air ~~by cryogenic technique.~~using a glass vacuum line connected to a turbo molecular pump by cryogenic technique. The vacuum line as well as the sample flask connection assembly including its head space was pumped to high vacuum before starting the CO_2 extraction. Air in the flask was pumped through a series of five coiled traps, with the first two immersed in dry ice-acetone slush (-77 °C) for trace moisture removal followed by three in liquid nitrogen (-196 °C). CO_2 was collected from the traps immersed in liquid nitrogen by repeated freeze-thaw technique at liquid nitrogen and dry ice temperatures for further removal of traces of water (see Mahata et al., 2012 and Liang and Mahata, 2015 for details). The air was pumped for 40-45 minutes at a controlled rate of ~90 mL/min using a mass flow controller; the pressure on the post mass flow controller was ~10 mm of Hg. No measurable isotopic fractionation caused by mass flow controller at this flow rate was observed, checked using several aliquots of air from a high volume compressed air cylinder (~40 L at 2000 psi). For car exhaust, an aliquot of exhaust air was transferred to a 60 mL bottle and CO_2 was fully extracted cryogenically following the same protocol as discussed above (but with mass flow controller step skipped).

CO_2 was further purified from other condensable species like N_2O, CH_4, and hydrocarbons by means of gas chromatography (Agilent 6890N, with a 3.0 m × 0.3 cm stainless steel column packed with PorapakQ 80/100 mesh, supplied by Supelco Analytical, Bellefonte, PA, USA) with the column kept at -10 °C. High purity helium (>99.9999 % supplied by Air Products and Chemicals, Inc.) at 20 mL/min was used as carrier gas. CO_2 was eluted first, followed forthwith by N_2O, and CH_4, hydrocarbons and traces of water came out much later.

To get an optimized condition for CO_2, we checked the separation of CO_2 from N_2O with varying proportions and at various temperatures (25 ^oC to -20 ^oC) and found a temperature of -10 ^oC at which column separated CO_2 from N_2O perfectly (see Laskar et al., ~~2016~~2016b for details). The column was baked at 200 ^oC for more than 2 hours prior to use. The conditioned column is good for purifying three samples. At the end of the day, long baking (8-10 hours) was performed. At the initial phase the working gas was taken from a high purity commercial CO_2 called AS-2 ($\delta^{13}C$ = -32.54 ‰ with respect to VPDB and $\delta^{18}O$ = 36.61 ~~‰)~~‰ with respect to VSMOW) procured from a local supplier (Air Products and Chemicals, Inc.). As the difference between the isotopic compositions of samples and AS-2 was high, we later changed the reference to Oztech CO_2 ($\delta^{13}C$ = -3.59‰ and $\delta^{18}O$ = 24.96 ‰) (Oztech Trading Corporation, USA) from December 2014 onward. No detectable difference in isotopic compositions including Δ_{47} was observed between the analyses from different working references. All $\delta^{13}C$ values presented in this work are expressed in VPDB scale and $\delta^{18}O$ in VSMOW scale, unless specified otherwise. Δ_{47} is calculated following (Affek and Eiler, 2006):

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

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

Field Code Changed

where R^{13} and R^{18} (ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$) are obtained by measuring the ~~traditional~~conventional masses 44, 45 and 46 in the same CO_2 sample and R^{17} is calculated assuming a mass dependent relation with R^{18} given by ~~$R^{17} = R^{17}_{VSMOW}\left(R^{18}/R^{18}_{VSMOW}\right)^{\lambda}$~~ $R^{17} = R^{17}_{VSMOW}\left(R^{18}/R^{18}_{VSMOW}\right)^{\lambda}$, where exponent λ=0.5164 is used for all Δ_{47} calculations (Affek and Eiler, 2006). The value of λ varies between 0.516 and 0.523 (Hoag et al., 2005; Barkan and Luz, 2012; Hoffmann et al., 2012; Thiemens et al., 2014). The variation in Δ_{47} ~~is~~was less than 0.01 ‰ at 25 ^oC when the exponent ~~is~~was varied over the aforementioned range. This variation ~~is~~was comparable to the measurement uncertainty and hence ~~is~~ not considered here; all the calculations ~~are~~were based on λ=0.5164. Δ_{47} is obtained by measuring CO_2 with respect to which the isotopes among various CO_2 isotopologues are distributed randomly (Δ_{47} ~ 0 ‰). Practically, this ~~limit~~random distribution is approached by heating

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CO_2 at 1000 °C for more than two hours (Eiler and Schauble, 2004; Affek and Eiler, 2006). Measurements were made with a stable ~12 volt signal at mass 44, with peak centring, background scanning, and pressure-balancing before each acquisition started. Each sample was analyzed for 10 acquisitions, 10 cycles each at an integration time of 8 s; ~~-~~the total analysis time was approximately 2.5 h. ~~Routine analysis of masses~~Masses 48 and 49~~, in addition~~ were monitored to ~~masses 44~~check isobaric interferences due to ~~47 was used to monitor the degree of possible interference of sample impurities on the measurements of Δ_{47}~~contamination of hydrocarbons (Ghosh et al., 2006). Details about the corrections due to nonlinearity related to Δ_{47} measurements in the mass spectrometer, ~~empirical transfer function~~reference frame equation for expressing the measured Δ_{47} values in absolute reference frame (ARF) ~~are~~were discussed in Laskar et al. (~~2016~~2016b). To obtain the temperature from the Δ_{47} values, we used the following relation (Dennis et al., 2011):

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

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

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The reproducibility (1-σ standard deviation) for air CO_2 measurements was established from three aliquots of CO_2 extracted from a compressed air cylinder with CO_2 concentration ($[CO_2]$) of ~388 ppmv. The 1-σ standard deviations were 0.07, 0.08, and 0.01 ‰ for $\delta^{13}C$, $\delta^{18}O$, and Δ_{47}, respectively (Table S1 in ~~supplementary information).~~Supplement). The long-term reproducibility in Δ_{47} measurements was found to be 0.014 ‰ (~~1-σ standard deviation; n=15~~Laskar et al., 2016b) and the accuracy in Δ_{47} values in terms of temperature, based on CO_2 equilibrated with water at known temperatures were better than 3 °C (see Table S2 in ~~supplementary information~~Supplement).

For $[CO_2]$ measurements, flasks of volume 350 cc were used. These small flasks were connected in series with the larger flasks used for isotopic measurements. $[CO_2]$ was measured using a LI-COR infrared gas analyzer (model 840A, LI-COR, USA) at 4 Hz, smoothed with 20-s moving average. The analyzer was calibrated against a working standard (air compressed in a cylinder) with a nominal $[CO_2]$ of 387.7 ppmv and a CO_2 free N_2 cylinder. The reproducibility of LI-COR ~~is~~was better than 1 ppmv. The working standard was calibrated using a commercial Picarro analyzer (model G1301, Picarro, USA) by a series of NOAA/GMD certified tertiary standards with [CO_2] of 369.9, 392.0, 409.2, and 516.3 ppmv, with a precision (1-σ standard deviation) of 0.2 ppmv. The [CO_2] in car exhausts were estimated by gravimetric technique using an MKS Baratron gauge.

Ambient temperatures were taken from the nearest governmental weather stations (operated by Central Weather Bureau, Taiwan): Nankang (for AS; station code: C0A9G0; 25°03′27″ N, 121°35′41″ E, 42 m a.s.l.), Taipei (for NTU; station code: C1A730; 25°00' 58″ N, 121°31' 53″ E; 22 m a.s.l.), Hehuan mountain (station code: C0H9C1; 24°08′41″ N, 121°15′ 51″ E, 3240 m a.s.l.), and Keelung coast (for the two coastal sites; station code: 466940; 25°08′05″ N, 121°43′56″ E, 26.7 m a.s.l.).

3. Results

3.1 Greenhouse CO_2

~~Intraday~~Diurnal variation in the concentration and isotopic compositions of CO_2 inside the controlled greenhouse is shown in Figure 2. The lowest ~~[~~CO_2 concentration [CO_2] and highest $\delta^{13}C$ and $\delta^{18}O$ values ~~are~~were observed during late morning hours while highest [CO_2] and lowest $\delta^{13}C$ and $\delta^{18}O$ values ~~are~~were observed during night time and early morning before sunrise (Table 1 and Figure 2A-2C), indicating that respiration and photosynthesis ~~play~~played the major role in controlling the variations of the [CO_2] and isotopic compositions. Keeling plot, a graphical approach plotted between isotopic composition and the inverse of the concentration is used to determine the isotopic composition of the source (Pataki et al., 2003). It is valid for a mixing of two components; the intercept of the plot gives the source isotopic composition. Respiration was the main source of CO_2 here added to the background CO_2. Keeling analysis for $\delta^{13}C$ ~~gives~~had an intercept of -26.32±0.40 ‰ (Figure 2D), a value expected for C_3 plant respired CO_2. The Keeling plot for $\delta^{18}O$ ~~gives~~had an intercept of 30.68±0.73 ‰ (Figure 2E), which could be explained by a combined effect of respired CO_2 equilibrated with soil water and kinetic fractionation associated with the diffusion of CO_2 from soil to the air. A Keeling plot for $\delta^{13}C$ with the early morning and night time greenhouse data, when photosynthesis was absent, was found to have same intercept as observed with all the data, only the correlation was better for the latter (R^2=0.999, not shown). The tight correlations among [CO_2], δ^{13}C and δ^{18}O (Figure 2D-2F~~), however,~~) suggest that photosynthesis~~/~~ and respiration ~~are~~were the dominant processes controlling their variations ~~and the~~while mixing with ambient air and anthropogenic contribution of CO_2 ~~are~~were insignificant.

In contrast, Δ_{47} shows different patterns of diurnal variability~~.~~ due to the effect of photosynthesis and respiration. Figures 3A-3D detail diurnal variations in Δ_{47} in the greenhouse CO_2 in four different days. The first three ~~are~~were bright sunny days with photosynthesis as the dominant process while the last one ~~is~~was a dark cloudy day~~; to~~ affected more by respiration. To further reduce photosynthetic activity on the last day, two layers of black ~~cloths~~cloth that cut down the incident sunlight by ~50% ~~are~~were deployed~~ for the last.~~. The measured Δ_{47} values ~~are~~were also compared with the thermodynamic equilibrium values. The maximum value of Δ_{47} ~~is~~was observed in the morning before ~8 AM and at night~~:~~ and the values ~~are~~were similar to ~~that expected~~the thermodynamic equilibrium values at the ambient temperatures~~, indicating~~. This indicates that the respired CO_2 ~~is~~was in close thermodynamic equilibrium~~.~~ with the leaf and soil water. The daytime (from 9 AM to 5 PM) Δ_{47} values~~ are, in general,~~, for the three sunny days were higher than the thermodynamic equilibrium values. The Δ_{47} values were observed to decrease steadily in the early morning before ~9 AM and increased afterwards (Figure 3). By comparing the Δ_{47} values acquired in the sunny days with that in the cloudy day, we ~~notice~~noticed that when photosynthesis ~~is~~was weak, the Δ_{47} value ~~is~~was close to the thermodynamic equilibrium with soil and leaf water (Figure 4). ~~No~~The correlation ~~(R^2 < 0.1) is observed~~ between Δ_{47} and [CO_2], δ^{13}C or δ^{18}O (Figure ~~3A-3C) except~~3D) was observed only when the photosynthesis ~~is~~was weak~~ (Figure 3D), which~~. This suggests that ~~the~~ Δ_{47} carries information different from concentration and ~~bulk~~conventional isotopic composition when photosynthesis occurs. See Section 4.1 for detailed discussion.

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3.2 Car exhaust

The ~~concentration,~~[CO_2], δ^{13}C and δ^{18}O values of car exhaust CO_2 ~~are~~were 39350±50 ppmv, -~~7~~27.70±0.03 ‰ and 25.35±0.07 ‰, respectively (Table 2). δ^{13}C value ~~is~~was similar to that reported elsewhere (Newman et al., 2008; Popa et al., 2014), the $\delta^{18}O$ ~~is~~was slightly higher than the atmospheric O_2 (~23.5 ‰), the source of O_2 for combustion. ~~This is probably due to post isotopic exchange with water present in the stream of the exhaust inside the catalytic converter and the exhaust pipe.~~ The average value of Δ_{47} for the exhausts from the two cars ~~is~~was 0.273±0.021 ‰, which ~~gives an average~~ gave a temperature of 282±17 °C (Table 2). This temperature is much higher than the fuel combustion temperatures (>800 °C). The possible reason for higher values of $\delta^{18}O$ and Δ_{47} in the exhaust CO_2 than expected was post combustion partial exchange with water and other gaseous species, released during combustion, inside the catalytic converter and the exhaust pipe (see discussion in Sec. 4.2).

3.3 Atmospheric CO_2 over ocean~~,~~ and coasts ~~and land~~

Isotopic compositions including Δ_{47} values obtained for CO_2 over ocean~~,~~ and coasts~~, sub-urban, urban and grassland are summarized~~ are presented in Table 3~~ and 4~~. The averaged [CO_2] over ocean between latitudes 18°03′ N and 21°17′ N ~~is~~was 395±7 ppmv, and the values of $\delta^{13}C$ and $\delta^{18}O$ ~~are~~were -8.43±0.19 ‰ and 40.72±0.20 ‰, respectively (Table 3). ~~Figure 5 shows a comparison of carbon Keeling analyses for the atmospheric CO_2 collected over different regions. The intercept for oceanic CO_2 is -15.96±1.95 ‰ (Figure 5A).~~ In the coastal stations, the averaged values of [CO_2], $\delta^{13}C$, and $\delta^{18}O$ ~~are~~were 397±10 ppmv, -8.48±0.11 ‰, and 40.70±0.29 ‰, respectively~~, with a $\delta^{13}C$ Keeling intercept of -12.20±1.11 ‰ (Figure 5B).~~. Both the [CO_2] and $\delta^{13}C$ values over the ocean and coasts ~~are~~were similar to those observed at Mauna Loa during the sampling period, suggesting little contribution from local/regional anthropogenic sources. ~~However, the intercepts of the Keeling plots is different from the $\delta^{13}C$ value of the CO_2 released by the remineralization of organic matter (-20 to -30 ‰) in the deep sea regions, the expected source of CO_2 over ocean. This is probably due to partial isotopic equilibration of the CO_2 with dissolved inorganic carbon before releasing to the atmosphere (see discussion~~ The Keeling analysis for $\delta^{13}C$ gave in intercept of -13.61 ‰ (Figure 5A) for ~~details).~~

~~The averaged values of [CO_2], $\delta^{13}C$, and $\delta^{18}O$ for~~ the air CO_2 collected over the ocean and coasts. $\delta^{18}O$ of air CO_2 over the ocean were close to the isotopic equilibrium values with the surface sea water at the sea surface temperatures (see Sec 4.3). The Δ_{47} values varied between 0.880 ‰ and 0.946 ‰ for the marine and coastal CO_2 (Table 3, Figures 5B), similar to that predicted at thermodynamic equilibrium at sea surface temperatures (obtained using Eq. (2)). Therefore, both δ^{18}O and Δ_{47} values suggest that the air CO_2 over the ocean was in close thermodynamic equilibrium with the underlying sea water.

3.4 Atmospheric CO_2 over land

To show how anthropogenic emission affects the isotopic composition especially the Δ_{47} values, we analyzed atmospheric CO_2 samples collected near Roosevelt Road, a busy street in downtown Taipei~~, are~~. The averaged values of [CO_2], δ^{13}C and δ^{18}O obtained were 500±50 ppmv, -11.05±0.90 ‰, and 39.~~319~~32±0.94 ‰, respectively (Table 4). ~~Both the [CO_2] and isotopic compositions show~~A significantly higher [CO_2] and lower δ^{13}C, and δ^{18}O values compared to the marine CO_2 showed signatures of a significant contribution from vehicular emissions. Δ_{47} values near Roosevelt Road were found to be in the range of 0.754‰ to 0.833 ‰, with an average of 0.807±0.028 ‰ (Table 4). The values were lower by ~0.15 ‰ compared to the thermodynamic equilibrium value at 20 ^{o}C, the ambient temperature around the sampling time, indicating a significant fraction of CO_2 produced at higher temperatures, i.e., of combustion origin.

In the sub-urban location (~~AS~~Academia Sinica Campus), [CO_2] averaged over four months ~~is~~was 410±10 ppmv (Table 4), which was ~15 ppmv higher than that observed over the South China Sea and that at Mauna Loa Observatory during the time of sampling. The higher [CO_2] suggests contribution from local anthropogenic emissions. δ^{13}C values ~~mainly vary~~varied between -7.83 ~~to~~and -10.30 ‰, with an average of -8.78±0.50 ‰. Keeling analysis for δ^{13}C ~~(Figure 5C) gives~~gave an intercept of -26.16±1.58 ~~‰,~~‰ (Figure 6), indicating source of CO_2 from C_3 plant respiration and/or combustion. Δ_{47} values here varied between 0.853 ‰ and 0.972 ‰ (Table 4) with an average of 0.897±0.027 ‰, which were significantly less than the thermodynamic equilibrium values (assuming water bodies had the same temperature as the ambient) (Figure 7).

The averaged [CO_2~~]~~], δ^{13}C and δ^{18}O over the grassland (~~NTU) is~~inside National Taiwan University Campus) were 410±33 ppmv~~.~~, -8.95±0.70 ‰ and 39.74±1.00 ‰, respectively.

The Keeling plot for δ^{13}C gave an intercept ~~is~~of -16.98±1.02 ‰ (Figure ~~5D~~6), indicating that a significant fraction of CO_2 originated from C_4 vegetation. This is not surprising as the CO_2 was sampled over a C_4 dominated grassland (area: ~50 m x 50 m). ~~We note that though the station is located in an urban region, the sampling location is at least ~150 m away from traffic streets, such as Keelung road, along with ~60 m wide, ~10 m high C_3 trees in between. As a result, anthropogenic signals are not very prominent. The averaged values of δ^{13}C and δ^{18}O are -8.95±0.70 ‰ and 39.74±1.00 ‰, respectively.~~ Unlike greenhouse CO_2, no statistically significant correlation between δ^{18}O and 1/[CO_2] in air CO_2 in these sites ~~is~~was observed (not shown), probably due to ~~various contributions from~~influence of multiple sources and processes ~~affecting~~on oxygen isotopes of atmospheric CO_2. Figure 7C shows the Δ_{47} values in air CO_2 over the grassland at National Taiwan University Campus. A large variation in Δ_{47} was observed (0.885 - 0.989 ‰) with an average of 0.937±0.030 ‰. Some of the values were close to the thermodynamic equilibrium while the others deviated significantly.

~~The [CO_2], δ^{13}C, and δ^{18}O values for two high mountain air CO_2 samples collected on 9th October, 2013 are 364 ppmv, -8.23±0.02 ‰ and 40.59±0.30 ‰, respectively (Table 4). The lower [CO_2] and higher δ^{13}C than Mauna Loa suggests photosynthetic uptake, which is also seen at NTU site and inside greenhouse on a few occasions. The air [CO_2], δ^{13}C and δ^{18}O are~~In a small and dense forest near Academia Sinica Campus (Figure 1), average values of [CO_2], δ^{13}C and δ^{18}O in air CO_2 were 438±16 ppmv, -9.99±0.50 ‰ and 40.39±0.63 ‰, respectively~~, for a dense forest site near the Academia Sinica (AS) Campus. Given the proximity of the site from AS, the higher concentration and~~ (Table 4) during summer (Jul-Aug) of 2015. A significantly higher [CO_2] and lower δ^{13}C values than ~~those at AS~~the background indicate ~~significant influence~~strong contribution of CO_2 from local respiration ~~(Table 4).~~

~~Figure 6 shows the time series of δ^{13}C and δ^{18}O at the sub-urban station where measurements were carried out for more than four months. Tentatively, [CO_2] level increases and δ^{13}C depletes from October to February (Figure 6A), likely a result of seasonal variation in photosynthesis/respiration. On average, the δ^{13}C value is slightly less than the global mean, implying influence from local/regional anthropogenic activities though the dominant role is played by biogeochemistry in affecting the variation. The time series of δ^{18}O (Figure 6B) shows variation between 39.40 and 41.57 ‰, with an average of 40.87±0.46 ‰. An~~

~~increasing trend is also observed in $\delta^{18}O$ from October to February. We attribute this to interactions with rain and surface waters which are heavier in winter time compared to the summer (~~.~~Peng et al., 2010; Laskar et al., 2014).~~

~~The~~ Δ_{47} values ~~vary between 0.880 ‰ to 0.946 ‰ for the marine and coastal CO_2 (Table 3, Figures 7A and 7B), similar to that predicted at thermodynamic equilibrium at sea surface temperatures (obtained using Eq. (2)). Similarly, $\delta^{18}O$ of air CO_2 shows the expected equilibrium values with the surface sea water (see discussion), suggesting that the air CO_2 is indeed in thermodynamic equilibrium with the underlying sea water. Figure 7C shows the measured Δ_{47} values at the sub-urban station along with the equilibrium values expected at the ambient temperatures. Here the Δ_{47} values vary between 0.853 ‰ and 0.972 ‰, which in contrast to the marine CO_2, are significantly less than the thermodynamic equilibrium values (assuming water bodies have the same temperature as the ambient) (Table 4). Figure 7D shows the Δ_{47} values in the grassland (NTU). A large variation in Δ_{47} is observed (0.885 - 0.989 ‰) with an average of 0.937±0.030 ‰; some of the values are close to the thermodynamic equilibrium while the others deviate significantly. The forest air CO_2 Δ_{47} values in summer~~ fall in the range of 0.887 ‰ to 0.920 ‰, with an average of 0.895±0.012 ‰ (Table 4). The values ~~are~~were similar to that expected at thermodynamic equilibrium (Figure ~~7E~~7D) except on 11th August, when a significant increase in Δ_{47} was observed. The deviation ~~is~~was probably due to influence of a super typhoon, which passed over the region on previous days mixing and transporting air masses regionally.~~ In the high mountain station, the averaged value of Δ_{47} is 0.904±0.009 ‰, slightly less than that expected at the ambient temperature (Table 4).~~

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~~To show how anthropogenic emission affects the background Δ_{47} values, we collected several air CO_2 samples from Roosevelt Road and the values are in the range of 0.754‰ to 0.833 ‰, with an average of 0.807±0.028 ‰ (Figure 7F). The value is lower by ~0.16 ‰ compared to the thermodynamic equilibrium value, indicating a significant fraction of CO_2 produced at higher temperatures.~~

Over the top of the Hehuan mountain (~3.2 km a.s.l), [CO_2], $\delta^{13}C$, and $\delta^{18}O$ values in air CO_2 samples collected on 9th October, 2013 were 364 ppmv, -8.23±0.02 ‰ and 40.59±0.30 ‰, respectively (Table 4). The lower [CO_2] and higher $\delta^{13}C$ than Mauna Loa suggests photosynthetic uptake, which was also seen at grassland site and inside greenhouse on a few occasions. Here the averaged value of Δ_{47} was 0.904±0.009 ‰, slightly less than that expected at the ambient temperature (Table 4).

4. Discussion

~~As stated earlier, the Δ_{47} has the unique physical property of representing the formation temperature of a CO_2 molecule, providing an alternative tool for constraining the budget of CO_2 in the atmosphere. We present in detail the data of multiple CO_2 isotopologues obtained from a controlled greenhouse, where atmospheric mixing and transport are largely reduced, to demonstrate the advantage of utilizing Δ_{47} for flux partitioning between photosynthesis and respiration over other CO_2 isotopologues. The data collected from other natural environments are also presented, compared, and discussed.~~

~~In urban and industrial places where anthropogenic emission is significant, all the three isotopic tracers, viz., $\delta^{13}C$, $\delta^{18}O$, and Δ_{47}, provide information about the anthropogenic fraction of CO_2 due to distinct values of their sources. For example in a traffic street, a two end member (background and anthropogenic CO_2) mixing of any of these tracers may provide sufficiently good estimate of the anthropogenic fraction of CO_2. However, if a significant fraction of CO_2 is respired from soil under C_3 plants, $\delta^{13}C$ cannot distinguish between the respired and anthropogenic sources. $\delta^{18}O$ is always not applicable due to complexity of multiple oxygen-containing sources.~~A detailed discussion of the results obtained from different locations is presented below.

~~Anthropogenic CO_2 can also be quantified using radiocarbon (^{14}C) as fossil fuels are highly depleted in ^{14}C (Miller et al., 2012); however, it cannot distinguish difference between CO_2 from two sources with modern carbon.~~

~~The un-catalyzed isotopic exchange time scale between CO_2 and water is similar for both $\delta^{18}O$ and Δ_{47} (e.g., see Affek, 2013), and therefore, we expect that the two provide similar information when CO_2 in air simply exchanges with water. But it is not well understood if they behave similarly when biogeochemical processes such as photosynthesis and respiration~~

~~are involved. We note that ^{18}O is highly variable between reservoirs such as leaf water affected by evapotranspiration even when temperature variation is not very large. Thus, Δ$_{47}$ can complement δ^{18}O and ^{14}C data to probe the associated processes in the CO$_2$ cycling. A detailed analysis of the results from different locations is presented below.~~

4.1 Greenhouse air CO$_2$

To minimize anthropogenic alteration and air mixing/transport and to maximize the variations of CO$_2$ isotopologues by ~~biogeochemical~~biological processes, a controlled greenhouse provides an ideal environment. Diurnal variation ~~is~~was observed in [CO$_2$], δ^{13}C, δ^{18}O (Figure 2), and Δ$_{47}$ (Figure 3) in the greenhouse. Good correlations between [CO$_2$], δ^{13}C and δ^{18}O suggest common processes affecting all of them, and ~~we believe~~ they ~~are~~were photosynthesis and respiration. Giving July 31st as an example, we ~~estimate~~estimated the rates of night-time respiration and daytime photosynthetic uptake using the ~~bulk~~conventional isotopic compositions (analysis of Δ$_{47}$ ~~which will be~~ is discussed separately below). The dimension of the greenhouse room ~~is~~was 8m, 5m and 5m (length, width and height). The night-time respiration rate ~~is~~was then estimated to be about ~10 ppmv per hour (considering change of [CO$_2$] from 5:30 PM to 9:30 PM; Figure 2A), or ~4×10^{13} molecules cm^{-2} s^{-1}. ~~The~~Using simple isotopic mass balance, this increase of [CO$_2$] ~~can~~could be satisfactorily explained assuming C$_3$ respiration as the main source of CO$_2$ (δ^{13}C ≈ -26 ‰; intercept in Figure 2D) added to the background (-8.5 ‰). Similarly, the same conclusion ~~is also arrived~~could be derived by analyzing δ^{18}O ~~(the~~ considering δ^{18}O of respired and background CO$_2$ ~~is~~of 30.68 ~~‰,~~ ‰ (intercept in Figure 2E~~, and background δ^{18}O of air CO$_2$ outside which is~~) and ~40 ~~‰).~~‰ respectively. Thus, we conclude that the main factor that ~~affects~~affected the changes in concentration as well as the isotopic compositions in night-time ~~is~~was respiration.

The daytime net uptake rate can be estimated by taking the changes from early morning to noon time; the [CO$_2$] ~~reduces~~reduced by 110 ppmv, δ^{13}C ~~increases~~increased by 3.46 ‰, and δ^{18}O by 2.23 ‰ in about six hours. We calculated the number of molecules and their changes inside the greenhouse assuming simple gas laws. The estimated net photosynthetic uptake ~~is ~7×10^{13}~~was ~1×10^{14} molecules cm^{-2} s^{-1}~~. Neglecting~~ assuming constant respiration ~~during~~

~~daytime, the~~rate that was observed in the night. The photosynthetic discrimination can be calculated using the Rayleigh distillation model

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

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where R_o and R are the initial and modified $^{13}C/^{12}C$ or $^{18}O/^{16}O$ ratios (due to photosynthetic activity), respectively, f is the fraction of the material left, and α is the fractionation factor. The estimated discrimination in ^{13}C defined by (α-1), following equation (3), ~~is -15.3 ‰, similar to~~was -16.5 ‰, which was slightly higher than that expected for C_3 type vegetation~~.~~ (~ -20 ‰) (Farquhar et al., 1989). For ^{18}O, in addition to photosynthetic uptake, one has to consider an additional effect due to temperature-dependent water-CO_2 equilibrium fractionation. That is, the process decreases δ^{18}O by ~0.2 ‰ for an increase of 1 °C in temperature (Brenninkmeijer et al., 1983); from morning to noon time, the temperature effect ~~reduces~~reduced δ^{18}O by ~~-~~4.4 ‰. Adding this factor to the observed change in δ^{18}O ~~yields~~yielded a discrimination factor of ~~about -27~~-12.0 ‰; the value becomes -~~9.5~~7.0 ‰, if this additional temperature-dependence is ignored. ~~The obtained discrimination factors for ^{13}C and ^{18}O are in good agreement~~The value (-12.0 ‰) observed considering the additional exchange with ~~those reported~~the soil water was slightly higher than that observed previously ~~(Farquhar et al., 1989;~~ (-14.4 ‰) (Flanagan et al., 1997~~; Cuntz et al., 2003; Affek~~). Here the δ^{13}C and δ^{18}O values of the respired components were assumed to be -26 ‰ and ~~Yakir, 2014~~30 ‰ respectively (see Sec. 3.1).

~~Assuming~~We assume that ca. 1/3 of the CO_2 molecules in stomata are fixed photosynthetically~~,~~ and the remaining retro-diffuse back to the atmosphere (Farquhar and Lloid, 1993~~),~~) implying that the CO_2-water isotopic exchange rate ~~is~~was ~2×10^{14} molecules cm^{-2} s^{-1}~~, or 9~~. Also we assume that the CO_2 molecules that enter into the leaf stomata get isotopically equilibrated with the leaf water before diffusing back to the atmosphere. This implies an approximately 8 hours of oxygen isotope exchange time for CO_2 in the greenhouse room. As a result, we do not expect that CO_2 ~~reaches~~reached to complete isotopic equilibrium with the substrate water in a few hours~~.~~ inside the room. Δ_{47} values in the leftover CO_2 ~~can~~could be used to check the disequilibrium. The respired CO_2 ~~are~~were found to be ~~always~~ in thermodynamic equilibrium at the ambient temperature, shown by the Δ_{47} values of CO_2 in the early morning and night-time (Figure 3A-3C) and that collected on a cloudy day with suppressed photosynthetic activity (Figure 3D). The close-thermodynamic equilibrium at reduced photosynthetic condition is also shown in Figure 4A that deviation in Δ_{47} from that expected at ambient temperature is small. On sunny days, the [CO$_2$], δ^{13}C, and δ^{18}O values change by 50-115 ppm, 2-4 ‰, and 1.1-2.2 ‰, respectively, in a time period of ~5 hours in the morning (Figure 2). Figure 3 shows that the Δ_{47} values ~~retain~~retained the thermodynamic equilibrium values in the morning hours (until 9 AM) and then deviate from the thermodynamic equilibrium later ~~on~~of the day. The maximal reduction ~~and deviation~~ in the Δ_{47} values during ~~the time period is~~ these morning hours was ~0.05 ‰ (Figures 3A-3C~~); the changes we believe are~~) which is significant, as ~~the values are~~this value is much higher than the uncertainty of the measurements. An increase in Δ_{47} values after ~9 AM was observed. We attribute ~~this deviation~~these changes in the Δ_{47} values of the residual CO$_2$ to photosynthesis as it is seen when photosynthesis is strong. Also we note that there was no significant correlation/anti-correlation between δ^{18}O and Δ_{47} when photosynthesis was strong (Figure 3A-3C), but became significant when the photosynthesis was weak (Figure 3D). Therefore, the plant photosynthesis decouples Δ_{47} and δ^{18}O; in contrast to pure water-CO$_2$ isotopic exchange where the two behave similarly as far as isotopic equilibration is concerned (Affek, 2013; Clog et al. 2015).

Strong influence of photosynthesis on Δ_{47} was also reported ~~previously (~~by Eiler and Schauble~~,~~ (2004). They observed decrease in the Δ_{47} values of the residual CO$_2$ due to photosynthetic assimilation though the effect observed was different for different species. Here we observed a decrease in Δ_{47} value of the residual CO$_2$ initially (first 2 hours) due to photosynthesis similar to that observed by Eiler and Schauble (2004) but later it starts increasing in response to the photosynthesis. Photosynthesis as a source of disequilibrium was ~~further~~also shown recently by analyzing the clumped isotopes of O$_2$ (Yeung et al., ~~2005~~2015). Though enzymatic carbonic anhydrase catalyzes the water-CO$_2$ isotopic exchange toward equilibrium (Peltier et al., 1995; Cernusak et al., 2004~~), the reaction may not complete, limited by the enzymatic activity inside leaves;~~) its activity varies. A large variation in the activity of carbonic anhydrase in different vegetation types (C$_3$, C$_4$) or within the same type ~~is observed~~was noted previously (see Gillon and Yakir, 2001 and references therein). Therefore, the reaction may be incomplete which is limited by the enzymatic activity inside leaves. Furthermore, a box ~~modelling~~modeling by Eiler and Schauble (2004) demonstrated that gas diffusion through leaf stomata during photosynthesis fractionates the remaining air CO$_2$ Δ_{47} ~~values~~value deviating it from the thermodynamic equilibrium set by leaf water. Mixing of more than one component can also cause change in Δ_{47} when ~~bulk~~

~~isotopic compositions~~δ^{13}C and δ^{18}O of the components are different (Affek and Eiler, 2006; Laskar et al., 2016a), but this can easily be ruled out as it ~~is~~was not observed when photosynthesis ~~is~~was not very strong (Figure 3D). More rigorous investigations with controlled experiments using different plants with diverse carbonic anhydrase activities are needed to resolve the issue. ~~We note that no significant correlation between δ^{18}O and Δ_{47} is observed (Figure 3). Therefore, the plant photosynthesis decouples Δ_{47} and δ^{18}O; in contrast, pure water-CO_2 isotopic exchange process shows that the two behave similarly as far as isotopic equilibration is concerned (Affek, 2013; Clog et al. 2015).~~

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

4.2 Car exhaust CO_2

Ideally, the Δ_{47} value of car exhaust CO_2 should reflect the temperature of fuel combustion inside the combustion chamber which is >800 °C. However, the temperature estimated from Δ_{47} was found to be 283±18 °C. It is likely that interaction of the sample CO_2 with the exhaust gases and water inside catalytic converter and exhaust pipe modified the Δ_{47} values. Catalytic converter which oxidizes CO and hydrocarbons to CO_2 probably reset the clumped signatures at relatively lower temperature. During combustion water-vapor is also released. We observed that the exhaust gas contained a large amount of water vapor, part of which got condensed on the exhaust pipe and the front part of the magnesium perchlorate column.

Partial equilibration with the stream of the exhaust gas and water inside catalytic converter and the exhaust pipe was the likely cause for higher Δ_{47} values than that expected. This was also supported by the higher $\delta^{18}O$ values than atmospheric O_2, the source of O_2 for water and CO_2 here. Normally isotopes in CO_2 do not exchange with water vapor, but exchange may take place at higher temperature in presence of catalyst. Inside catalytic converter, exchange could take place on the surface of the catalyst at elevated temperatures of 200 – 400 °C (Farrauto and Heck, 1999; Kašpar et al., 2003; Klingstedt et al., 2006). Affek and Eiler (2007) also observed elevated Δ_{47} values for car exhausts and estimated a temperature of CO_2 production to be ~200 °C. The temperature estimated here (283 °C) is significantly higher than that observed by Affek and Eiler (2007). Difference could be due to different car models and the variations in the temperatures of the catalytic converters from car to car.

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~~The Δ_{47} thus serves as an independent tracer for studying photosynthesis. Though the deviation from equilibrium during photosynthesis is also observed in oxygen clumped isotopes [*Yeung et al.*, 2015], CO_2 and O_2 are affected and produced from different processes and sources; the former is affected seriously by water (water-CO_2 isotopic exchange) while the latter is derived from water. We believe the analyses of the clumped isotopes for both CO_2 and O_2 are of great importance in the atmospheric carbon cycling study, providing a new angle for tackling the chemistry chain in photosynthesis. More systematic study in controlled environments including leaf level experiments will help to better understand the role of photosynthesis on Δ_{47}.~~

4.~~2~~3 Marine and coastal air CO_2

~~The concentration and $\delta^{13}C$ values of~~ Carbon Keeling plot for marine and coastal air CO_2 ~~are close to the background atmospheric values reported at Mauna Loa, indicating little contribution from local/regional anthropogenic activities. The Keeling analysis for $\delta^{13}C$ gives~~gave an intercept of -~~15.9±2.0~~13.61±1.14 ‰ (Figure 5A~~) which is the $\delta^{13}C$ value of~~), the source signature. The South China Sea is net source of CO_2 ~~over~~to the ~~ocean.~~atmosphere (Zhai et al., 2005). The CO_2 released over ocean is mainly originated from the remineralization of organic matter in the deeper ocean~~, the~~ (Francois et al., 1993; Goericke and Fry, 1994). The δ^{13}C value of ~~which~~such organic matter ranges between -20 and -30 ‰ in the tropical to subtropical oceans~~ (Francois et al., 1993; Goericke and Fry, 1994),~~, the intercept observed here (-13.6 ‰) is much higher than this range~~.~~, though the associated uncertainty is high due to a small span of isotopic values of the samples. A possibility is that the remineralized CO_2 gets equilibrated with the dissolved inorganic carbon before releasing to the atmosphere. Again a complete equilibration of the CO_2 with the dissolved inorganic carbon would lead to a δ^{13}C value of released CO_2 to be -9 to -10 ‰ (Mook, 1986; Boutton, 1991; Zhang et al., 1995; Affek and Yakir, 2014), the observed value of the intercept ~~. Again a complete equilibration of the CO_2 with the dissolved inorganic carbon would lead to a δ^{13}C value of released CO_2 to be -9 to -10 ‰ (Mook, 1986; Boutton, 1991; Zhang et al., 1995; Affek and Yakir, 2014), the observed value of the intercept is much~~(-13.6 ‰) was significantly less than this. Therefore, we conclude that the CO_2 produced in the deeper ocean is partially equilibrated with the dissolved inorganic carbon before releasing to the atmosphere.

~~Therefore, we conclude that the CO_2 produced in the deeper ocean is partially equilibrated with the dissolved inorganic carbon before releasing to the atmosphere.~~

The δ^{18}O values of the surface sea water in the South China Sea region in summer (July-September) and winter (December-February) ~~are~~were about -1.7 ‰ and -0.6 ‰ (Ye et al., 2014). The sea surface temperatures in the summer and winter are about 28 and 24 °C, and the equilibrated δ^{18}O values of the atmospheric CO_2 should be 38.9 ‰ and 40.7 ‰, respectively assuming fractionation factors at the respective temperatures (Brenninkmeijer et al., 1983). Our observed values lie in the range of 40.4 ‰ to 41.0 ‰ (Table 3), consistent with the isotopic equilibrium values with the surface water. Therefore, we conclude that oxygen isotopes in near surface air CO_2 over ocean are close to the isotopic equilibrium with the surface sea water. This conclusion ~~is~~was further supported by the observed Δ_{47} values~~.~~ which were found to be close to thermodynamic equilibrium with the underlying sea surface water at the sea surface temperature (Figure 5B). This is due to the same water-CO_2 exchange time for the two species (Affek, 2013; Clog et al., 2015). Comparing this observation with the greenhouse data above, we ~~therefore ~~conclude that δ^{18}O and Δ_{47} behave similarly when equilibrium is achieved by simple water-CO_2 exchange but respond differently when photosynthesis is the main governing factor~~ and behave similarly when exchange occurs due to simple water-CO_2 equilibration~~. Though carbonic anhydrase are also present in the surface

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ocean and marine phytoplankton does photosynthesis, $\delta^{18}O$ and Δ_{47} in air CO_2 over the ocean show the values at thermodynamic equilibrium unlike greenhouse. The degree of deviation from thermodynamic equilibrium ~~likely~~probably increases with the ~~strength of~~increase in photosynthetic activity. Normally photosynthesis~~, and normally the~~ by oceanic ~~photosynthesis~~plants is much less compared to ~~the~~their terrestrial ~~plants. Therefore, Δ_{47} can be used as a tracer for estimating terrestrial carbon uptake~~counterparts, the deviation from thermodynamic equilibrium by the oceanic photosynthesis, if present, is probably not detectable with the present measurement precision. Compared to $\delta^{18}O$, Δ_{47} is process sensitive and is not affected by the isotopic composition of substrate water. Given that the surface air temperature is better measured, we believe the clumped isotopes potentially provide good tracers for global carbon flux study involving CO_2, complementing the commonly used species like $[CO_2]$, $\delta^{13}C$, and $\delta^{18}O$.

~~The isotopic values including Δ_{47} in the two coastal stations are similar to those observed for the marine CO_2. The carbon Keeling analysis yields an intercept of -12.20±1.11 ‰ (Figure 5D), consistent with that for the marine $\delta^{13}C$ (removing one outlier from Figure 5A gives an intercept of -13.3 ±1.0 ‰). The Δ_{47} values here are~~In the coastal stations, Δ_{47} values were similar to the thermodynamic equilibrium with the sea surface water at the temperature of ~27 °C (Figure ~~7B~~5B). The recoded air temperature during the sampling period over the coasts ~~varies~~varied between 14 and 24 °C and ~~is~~was not reflected in the Δ_{47} values. We note that the samples ~~are~~were collected from two open spaces in the coasts where strong north and northeasterly winds ~~overwhelm~~overwhelmed, carrying air masses from the oceans towards the sampling locations (See Table S3 in ~~supplementary information).~~Supplement). Therefore, we expect the major contribution ~~is~~was marine air with little influence from local processes, which could occasionally cause deviation from the thermodynamic equilibrium values.

~~4.3 Car exhaust CO_2~~

~~The Δ_{47} value of car exhaust CO_2 should reflect the temperature of fuel combustion inside the combustion chamber which is >800 °C. However, the temperature estimated from Δ_{47} is found to be 283±18 °C. It is likely that interaction of the sample CO_2 with the condensed water in the exhaust pipe modifies the Δ_{47} value: during sample collection, we observed that the exhaust gas contains a large amount of water vapor and some of which get condensed on~~

~~the exhaust pipe and the front part of the magnesium perchlorate column. Precautions, such as opening the evacuated flask for a short time (<1 min) and careful holding of the sampling tube inside the exhaust pipe without touching the wall of the pipe, were taken to minimize CO_2-water interaction during sample collection.~~

~~The higher Δ_{47} value for the exhaust CO_2 indicates isotopic re-equilibration of CO_2 with water in the stream of the exhaust gas and inside catalytic converter, also supported by the observed enriched $\delta^{18}O$ than atmospheric O_2; the oxygen atoms in the two most abundant species, water and CO_2 here, are mostly originated from atmospheric O_2 and are expected to inherit the isotopic composition of atmospheric O_2. Normally isotopes in CO_2 do not exchange with water vapor, but inside catalytic converter, exchange may take place on the surface of the catalyst at certain temperature (which is usually much less than the combustion temperature). Affek and Eiler (2007) also observed elevated Δ_{47} values for car exhausts and estimated a temperature of CO_2 production to be ~200 °C. The temperature estimated here is significantly higher than that observed by Affek and Eiler (2007). Difference could be due to different car models and the variations in the temperatures of the catalytic converters from car to car.~~

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4.4 Urban and sub-urban air CO_2

A significant fraction of anthropogenic CO_2 ~~is~~was present in the air CO_2 over the urban site, indicated by the [CO_2] as well as isotopic compositions including Δ_{47}. ~~Limits to the anthropogenic~~Anthropogenic contribution can be estimated following a two component mixing: $\delta = f_{anth}\times\delta_{anth}+(1-f_{anth})\times\delta_{bgd}$, where δ's can be $\delta^{13}C$ or $\delta^{18}O$ or Δ_{47} and f's, the corresponding weighting factor, and subscripts 'anth' and 'bgd' refer to anthropogenic and background, respectively. We take the 'anthropogenic' ~~and 'background'~~ end member as the isotopic compositions ~~from~~of the car exhaust values (Table 2) and ~~marine CO_2 (~~'background' end member as that values observed over the ocean (for $\delta^{13}C$ and $\delta^{18}O$, Table 3~~),~~) and thermodynamic equilibrium value at the mean ambient temperature of ~20 °C in December (0.95 ‰ for Δ_{47}) at the sampling site, respectively. Assuming that the excess in [CO_2] above the background ~~is~~was originated from vehicular emissions, the values of the $\delta^{13}C$, $\delta^{18}O$, and Δ_{47} in the urban site obtained using the mixing equation ~~are~~were -12.26 ‰, 37.68 ‰, and 0.~~791~~809 ‰, respectively, which ~~are~~were similar to those observed (Table 4). Δ_{47} is not a conserved quantity and a linear mixing is not valid when the ~~bulk isotopic compositions~~δ^{13}C and δ^{18}O of the components are widely different~~.~~ (Affek and Eiler, 2006; Laskar et al., 2016a). In the present case, the isotopic compositions of the two components ~~are~~were not drastically different and fraction of anthropogenic CO_2 ~~is~~was much less (<1/4) than the background CO_2, and hence the error due to linear approximation ~~is smaller than~~was small (comparable to the uncertainty of measurement). Anthropogenic CO_2 can also be quantified using radiocarbon (^{14}C) as fossil fuels are highly depleted in ^{14}C (Miller et al., 2012); however, it cannot distinguish difference between CO_2 from two sources with modern carbon.

No systematic diurnal or temporal trend ~~is~~was observed in the Δ_{47} values in the sub-urban CO_2 during the sampling period (Figure ~~7C) though~~7B). However a weak trend ~~is~~was seen in δ^{13}C and δ^{18}O (not shown) in response to the seasonal variation of the carbon assimilation and oxygen isotopes in the rainwater (Peng et al., 2010; Laskar et al., 2014).~~Figure 6),~~ This furthermore ~~demonstrating~~demonstrates that Δ_{47} behaves differently from [CO_2], δ^{13}C, and δ^{18}O. Almost all measured Δ_{47} values ~~are~~were lower than that expected at the ambient temperature except two days: 9th November, 2013 and 3rd February, 2014. δ^{13}C values ~~are~~were also slightly lower than the background values. The reduced values of Δ_{47} could be due to contribution of CO_2 from combustion processes which ~~produce~~produced CO_2 with low Δ_{47} values as discussed in Section 4.~~3~~2. We ~~estimate~~estimated the contribution of local anthropogenic emissions in δ^{13}C and Δ_{47} using the two components mixing discussed above. The components ~~are~~were the background air CO_2 and car exhausts. The expected δ^{13}C and Δ_{47} values of the mixture ~~are~~were -9.1 ‰ and 0.92 ‰, respectively. The observed Δ_{47} value ~~is~~was significantly different from that estimated from simple two component mixing, though it ~~is~~was not different for δ^{13}C~~, suggesting other processes like photosynthesis present in affecting Δ_{47}~~. After subtracting the local anthropogenic contribution from the observed Δ_{47} values, a difference of ~0.026 ‰ between the observed and estimated remains for sub-urban station and it ~~disappears~~disappeared for urban station (see Table S4 in ~~Supporting Information).~~Supplement). This ~~is~~was not obvious in δ^{13}C probably due to larger variation. The lower Δ_{47} values in sub-urban station could possibly be due to kinetic effect during photosynthetic assimilation, partial contribution of marine air, or a combination of them. It could also be due to underestimation of the anthropogenic CO_2 at the sampling spot. The regional background [CO_2] here could be lower than that assumed and the actual anthropogenic fraction of CO_2 could be higher. The marine air in the vicinity of Taiwan, which ~~is~~was at thermodynamic equilibrium with the surface sea water as discussed earlier, ~~may contribute~~might have contributed partially to the air CO_2 at the sampling site. Varying contribution of marine air could explain the lower Δ_{47} values to some extent. ~~The respired CO_2 is in thermodynamic equilibrium as shown above (Section 4.1). Therefore, the~~The most plausible cause for observed deviation in the Δ_{47} values that cannot be accounted for by anthropogenic and marine alterations ~~is~~was photosynthesis, as discussed earlier for greenhouse CO_2. This is not unreasonable, as the Academia Sinica Campus is surrounded by thick greeneries.

On 9th Nov, 2013 and 3rd February, 2014, the Δ_{47} values ~~are~~were close to that expected at thermodynamic equilibrium (Figure ~~7C~~7B). The Δ_{47} values on 9th November ~~are~~were not very different from the values reported for the previous or next days. However, the calculated thermodynamic equilibrium values on that day ~~are~~were relatively low due to high ambient temperatures~~ (Figure 7C);~~; air CO_2 probably did not get enough time to equilibrate. On 3rd Febrauray, 2014, the Δ_{47} values ~~are~~were higher and comparable to the thermodynamic equilibrium values expected at ambient temperatures. A likely explanation is that the air on that day was a mixture of two components at the sampling region. A relatively strong wind from the southern land (Table S3 in ~~Supporting Information~~Supplement) contributed the air CO_2 and the higher Δ_{47} values ~~are~~were probably due to mixing of the local air with that transported from the south of Taipei.

4.5 ~~Forest, grassland~~ Grassland, forest and high mountain air CO_2

~~An elevated CO_2 concentration and low $\delta^{13}C$ and $\delta^{18}O$ values indicate significant contribution of respiration and/or anthropogenic CO_2 in the forest station (Table 4) near the Academia Sinica Campus. Though the samples are collected at 10-11 AM under bright sunlight, the vegetation is so dense that little sunlight reached the ground. As a result, photosynthesis is weakened at the ground level. Also poor circulation of air due to presence of high heels on the three sides of the sampling spot makes the site nearly isolated from the surroundings. The Δ_{47} values are similar to the thermodynamic equilibrium expected at the ambient temperatures except on 11th August, 2015 on which a significantly higher Δ_{47} value is observed (Figure 7F). The higher value is likely due to the influence of the super Typhoon~~

~~Soudelor which passed over Taipei during 8-10 August, 2015 causing a decrease in temperature by 3-4 °C and air masses mixing in a larger spatial scale.~~

In the grassland station in Taipei city, the Keeling plot ~~for δ^{13}C gives an~~ intercept ~~of -~~for δ^{13}C (-17.0±1.0 ~~‰~~‰) (Figure 5D~~). This indicates~~) indicated some sources of CO_2 with higher δ^{13}C values compared to the most expected sources, namely, C_3 vegetation and vehicle emission with a δ^{13}C value of ~ -27 ‰. Though the sampling station was located in an urban region, the sampling spot was at least ~150 m away from traffic streets, such as Keelung road, along with ~60 m wide, ~10 m high C_3 trees in between. As a result, anthropogenic signals were not very prominent. The samples were collected just above the surface of the grasses. Tropical warm grasses are mainly C_4 type with δ^{13}C in the range of -9 to -19 ‰ and a global average of -13 ‰ (Deines, 1980). We measured δ^{13}C values of a few grass samples and found values in the range of -15 to -17 ‰. The soil and grass respired CO_2 with higher δ^{13}C contributed significantly to the near surface CO_2, resulting in ~~an elevated~~ a higher value of intercept ~~of -~~(-17 ~~‰.~~‰). The concentration ~~is sometimes~~was observed to be less than the background level sometimes, probably due to strong CO_2 uptake by plants. The temperature gradually decreased from 26 to 20 °C during the consecutive three days and clumped isotope followed similar trend, reflecting the influence of temperature on CO_2 Δ_{47} and rapid equilibration with the leaf and surface waters. One low value observed on the second day ~~is~~was probably due to plumes of vehicle exhausts, also supported by the elevated level ~~in~~of [CO_2] and depletion in δ^{13}C and δ^{18}O (Table 4). Effect of photosynthesis on the CO_2 was also expected specifically due the collection of samples at the grass level. However, in an open system, it is difficult to assess this with limited data points.

An elevated CO_2 concentration and low δ^{13}C and δ^{18}O values indicated significant contribution of respiration and/or anthropogenic CO_2 in the forest station (Table 4) near the Academia Sinica Campus. Though the samples were collected at 10-11 AM under bright sunlight, the vegetation was so dense that little sunlight reached the ground. Probably photosynthetic activity was not very strong at the ground level in the morning hours and the dominant process was respiration. Also poor circulation of air due to presence of high heels on the three sides of the sampling spot made the site nearly isolated from the surroundings. As a result the Δ_{47} values were observed to be similar to the thermodynamic equilibrium expected at the ambient temperatures except on 11th August, 2015 (Figure 7F). This also supports our hypothesis, made in the case of greenhouse CO_2, that respired CO_2 is always in close thermodynamic equilibrium with the substrate water. On 11th August, 2015 a significantly higher Δ_{47} value was observed. The higher value was likely due to the influence of the super Typhoon ‘Soudelor’ which passed over Taipei during 8-10 August, 2015 causing a decrease in temperature by 3-4 °C and air masses mixing in a larger spatial scale.

For high mountain CO_2, the observed Δ_{47} ~~value~~values (Table 4) ~~is~~were lower than that expected at ~10 °C, the ambient temperature at the top of the mountain site during sampling. The Δ_{47} values ~~are~~were similar to that observed in the plain and over the ocean. We note that during the sampling period, the site was affected significantly by winter monsoons. HYSPLIT 24 hours back trajectory ~~shows~~showed marine origin of air (not shown) during the sampling time. The air CO_2 on the mountain probably ~~does~~did not get sufficient time to isotopically equilibrate with the local surface and leaf water but ~~show~~showed the signature of the marine CO_2.

The deviations in Δ_{47} from the thermodynamic equilibrium values in different atmospheric environments and processes are summarized in Figure ~~8~~9. It is obvious that the urban and sub-urban CO_2 deviate the most towards lower Δ_{47} values, mainly contributed by CO_2 originated from high temperature combustions, i.e., vehicular emissions. The respired CO_2 are always in close thermodynamic equilibrium at the ambient temperature. On the other hand, CO_2 affected by strong photosynthesis show significant ~~deviation from~~increase in the Δ_{47} values compared to the thermodynamic equilibrium values~~. Kinetic isotopic fractionation during diffusion of CO_2 in and out of leaf stomata is a probable reason~~.

5. Summary

We presented a compilation of Δ_{47} analyses for car exhaust, greenhouse and air CO_2 over a wide variety of interactions in tropical and sub-tropical regions including marine, coastal, urban, sub-urban, forest, and high mountain environments. Near surface marine air CO_2 is in close thermodynamic equilibrium with the underlying surface water at the sea surface temperature. Car exhaust, urban, sub-urban and greenhouse air CO_2 significantly deviate from the thermodynamic equilibrium values. While respired CO_2 is in thermodynamic equilibrium with leaf and soil surface waters, photosynthesis significantly deviates the Δ_{47} values from the thermodynamic equilibrium~~.~~ or more precisely increases the Δ_{47} values probably due to kinetic effect associated with the diffusion of CO_2 out of leaf stomata. The Δ_{47} values in urban and sub-urban air CO_2 are lower than that expected under thermodynamic equilibrium at the ambient temperature. The deviation is mainly due to contributions from fossil fuel emissions and to some extent due to photosynthesis especially in regions with dense vegetation. ~~We expect Δ_{47} can shed light on the estimation of anthropogenic contribution to the atmospheric CO_2 and the activity of photosynthesis. The latter deserves further investigation, to establish how exactly Δ_{47} is affected by photosynthesis, before the tracer can be used for estimating gross primary productivity.~~

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

Data availability

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

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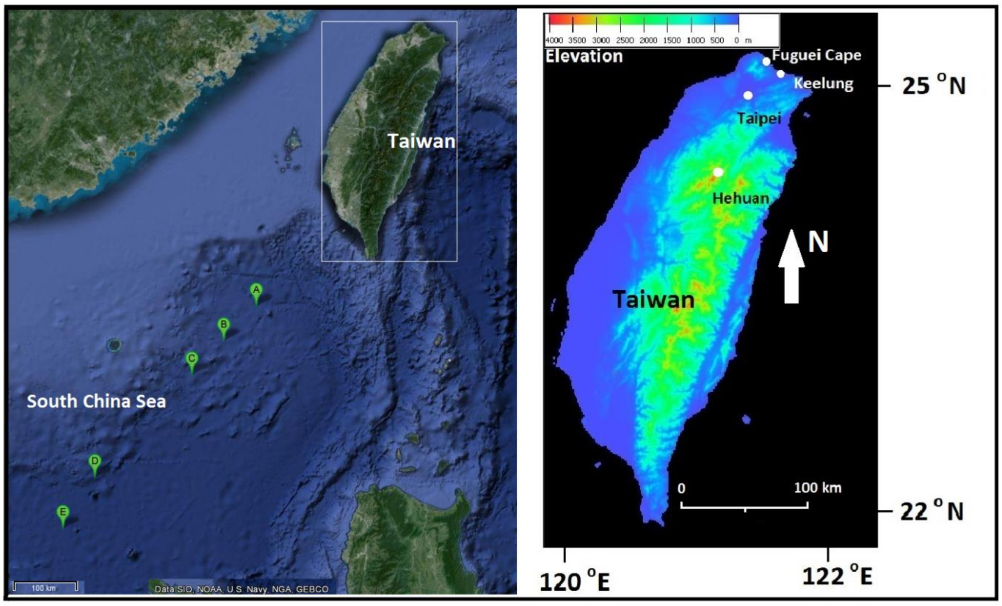
Figures



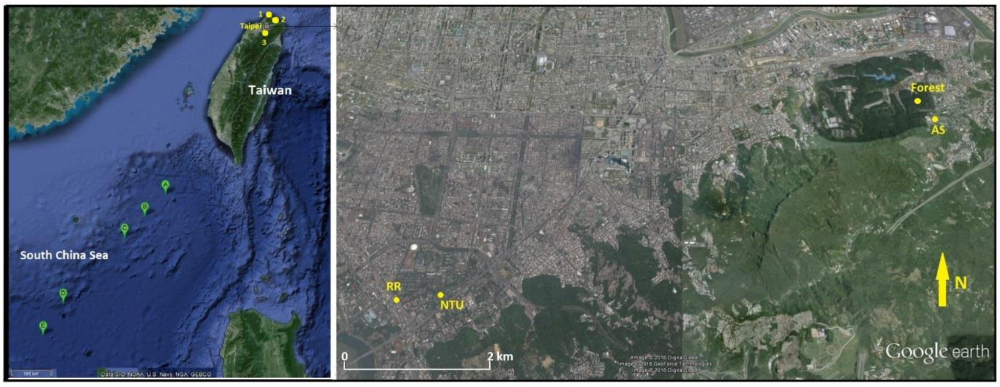


Figure 1. ~~Map~~Left panel: map of Taiwan and South China Sea with the locations of marine air sampling~~. Marine air CO_2 sampling~~ stations (A to E~~) in the South China Sea~~). The coastal stations 1 and 2 are ~~shown on the left.~~ Fuguei Cape and Keelung ~~are two coastal stations, urban site (~~and 3 is the high mountain station Hehuan (~3.2 km a.s.l.). Right panel: Part of Taipei city with sampling stations Roosevelt Road~~) and~~ (RR), grassland ~~(~~in the National Taiwan University (NTU) Campus~~) are located at the centre of Taipei City and~~ , sub-urban site ~~(~~inside the campus of Academia Sinica ~~Campus) at the outskirt of the city~~ (AS) and ~~Hehuan is a high mountain station (~3000 m a.s.l.); all are shown on the right~~Forest site.

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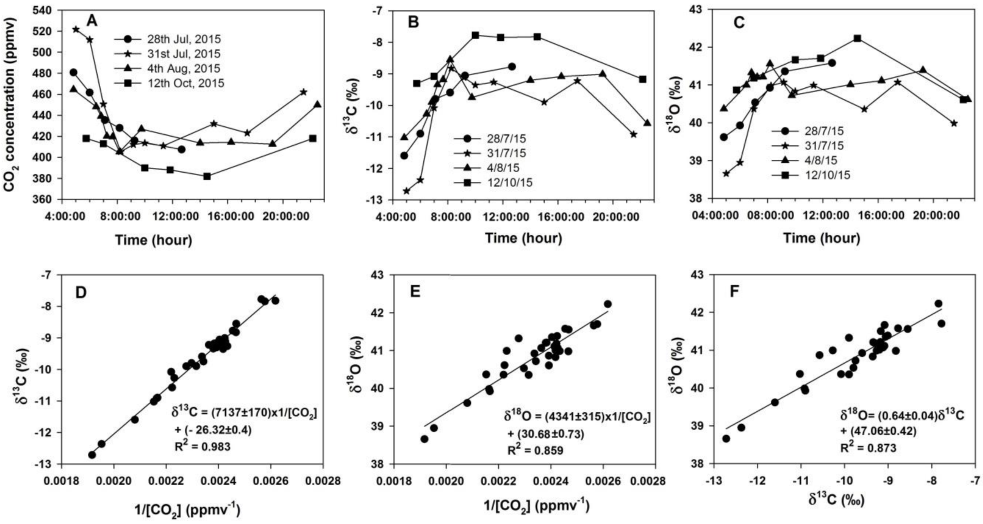

A
28th Jul, 2015
31st Jul, 2015
4th Aug, 2015
12th Oct, 2015
CO$_2$ concentration (ppmv)
360 380 400 420 440 460 480 500 520 540
4:00:00 8:00:00 12:00:00 16:00:00 20:00:00
Time (hour)
B
28/7/15
31/7/15
4/8/15
12/10/15
δ^{13}C (‰)
-13 -12 -11 -10 -9 -8 -7
4:00:00 8:00:00 12:00:00 16:00:00 20:00:00
Time (hour)
C
28/7/15
31/7/15
4/8/15
12/10/15
δ^{18}O (‰)
38 39 40 41 42 43
04:00:00 08:00:00 12:00:00 16:00:00 20:00:00
Time (hour)
D
δ^{13}C = (7137±170)x1/[CO$_2$] + (- 26.32±0.4)
R^2 = 0.983
δ^{13}C (‰)
-13 -12 -11 -10 -9 -8 -7
0.0018 0.0020 0.0022 0.0024 0.0026 0.0028
1/[CO$_2$] (ppmv^{-1})
E
δ^{18}O = (4341±315)x1/[CO$_2$] + (30.68±0.73)
R^2 = 0.859
δ^{18}O (‰)
38 39 40 41 42 43
0.0018 0.0020 0.0022 0.0024 0.0026 0.0028
1/[CO$_2$] (ppmv^{-1})
F
δ^{18}O= (0.64±0.04)δ^{13}C + (47.06±0.42)
R^2 = 0.873
δ^{18}O (‰)
38 39 40 41 42 43
-13 -12 -11 -10 -9 -8 -7
δ^{13}C (‰)

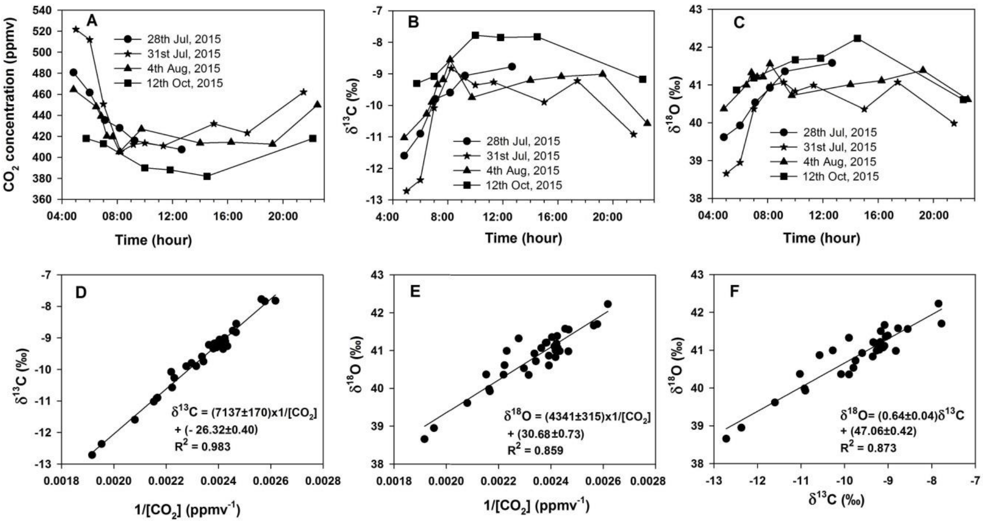
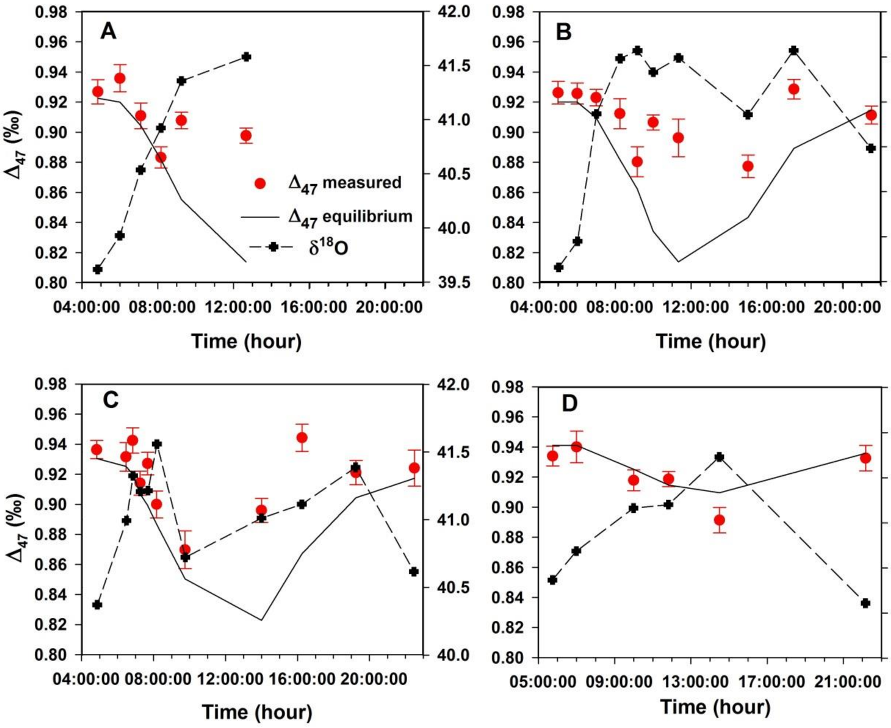

A
28th Jul, 2015
31st Jul, 2015
4th Aug, 2015
12th Oct, 2015
CO$_2$ concentration (ppmv)
360 380 400 420 440 460 480 500 520 540
04:00 08:00 12:00 16:00 20:00
Time (hour)
B
28th Jul, 2015
31st Jul, 2015
4th Aug, 2015
12th Oct, 2015
δ^{13}C (‰)
-13 -12 -11 -10 -9 -8 -7
4:00 8:00 12:00 16:00 20:00
Time (hour)
C
28th Jul, 2015
31st Jul, 2015
4th Aug, 2015
12th Oct, 2015
δ^{18}O (‰)
38 39 40 41 42 43
04:00 08:00 12:00 16:00 20:00
Time (hour)
D
δ^{13}C = (7137±170)x1/[CO$_2$] + (- 26.32±0.40)
R^2 = 0.983
δ^{13}C (‰)
-13 -12 -11 -10 -9 -8 -7
0.0018 0.0020 0.0022 0.0024 0.0026 0.0028
1/[CO$_2$] (ppmv^{-1})
E
δ^{18}O = (4341±315)x1/[CO$_2$] + (30.68±0.73)
R^2 = 0.859
δ^{18}O (‰)
38 39 40 41 42 43
0.0018 0.0020 0.0022 0.0024 0.0026 0.0028
1/[CO$_2$] (ppmv^{-1})
F
δ^{18}O= (0.64±0.04)δ^{13}C + (47.06±0.42)
R^2 = 0.873
δ^{18}O (‰)
38 39 40 41 42 43
-13 -12 -11 -10 -9 -8 -7
δ^{13}C (‰)

Figure 2. Top panels show the diurnal variation of (A) concentration, (B) δ^{13}C, and (C) δ^{18}O of CO_2 sampled in the greenhouse. Bottom panels are the Keeling plots for (D) δ^{13}C and (E) δ^{18}O and (F) scatter plot of δ^{13}C and δ^{18}O to show their covariance.



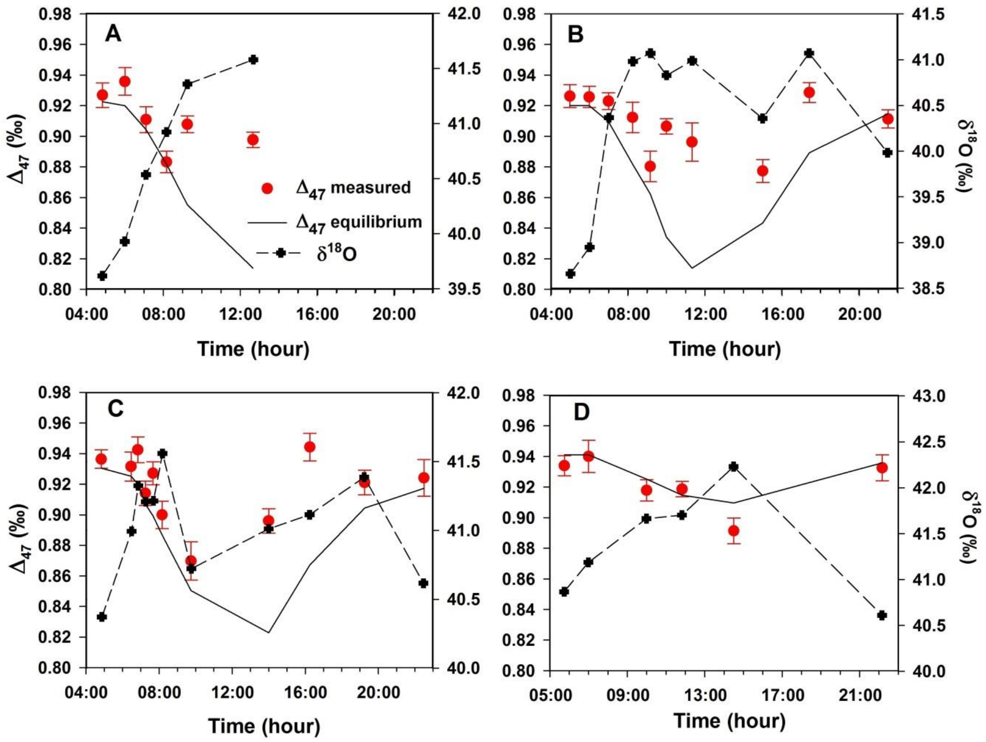


Figure 3. Diurnal variation of the Δ_{47} and δ^{18}O values in the greenhouse for samples collected on four days of 2015: (A) 28th July, (B) 31st July, (C) 4th August, and (D) 12th October. The first three days (A-C) were bright sunny days and the last one (D) ~~on~~ a cloudy day with covered rooftop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

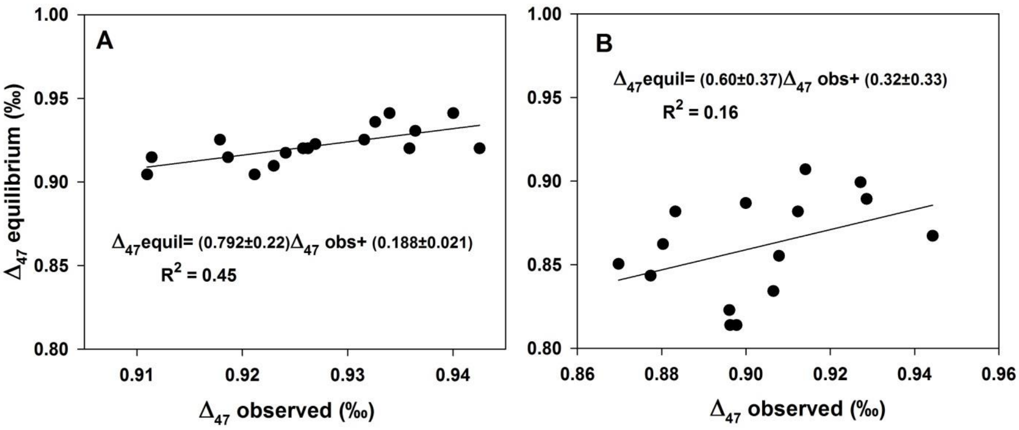
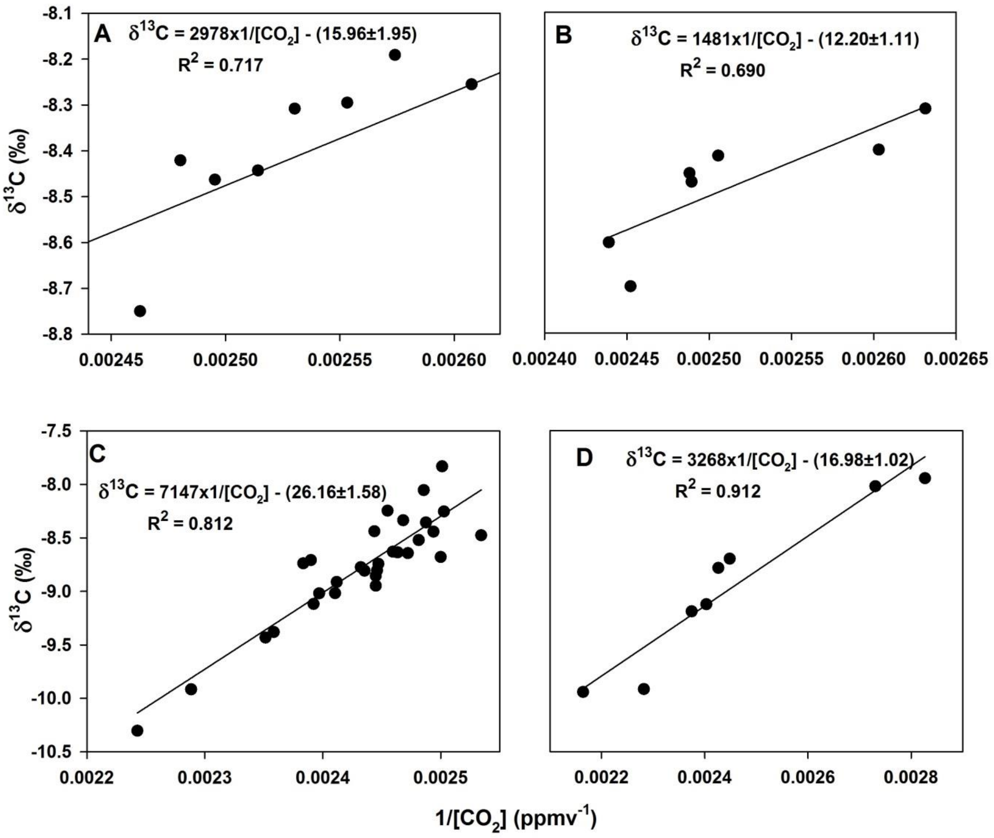


Figure 4. Correlation between the observed and thermodynamic equilibrium Δ_{47} values for greenhouse CO_2 samples collected when (A) photosynthesis ~~is~~ass weak and respiration ~~is~~was strong and (B) photosynthesis ~~is~~was strong and respiration ~~is~~was weak.


A
$\delta^{13}C = 2978x1/[CO_2] - (15.96\pm1.95)$
$R^2 = 0.717$
B
$\delta^{13}C = 1481x1/[CO_2] - (12.20\pm1.11)$
$R^2 = 0.690$
C
$\delta^{13}C = 7147x1/[CO_2] - (26.16\pm1.58)$
$R^2 = 0.812$
D
$\delta^{13}C = 3268x1/[CO_2] - (16.98\pm1.02)$
$R^2 = 0.912$
$\delta^{13}C$ (‰)
-8.1
-8.2
-8.3
-8.4
-8.5
-8.6
-8.7
-8.8
0.00245
0.00250
0.00255
0.00260
0.00240
0.00245
0.00250
0.00255
0.00260
0.00265
$\delta^{13}C$ (‰)
-7.5
-8.0
-8.5
-9.0
-9.5
-10.0
-10.5
0.0022
0.0023
0.0024
0.0025
0.0022
0.0024
0.0026
0.0028
$1/[CO_2]$ (ppmv^{-1})

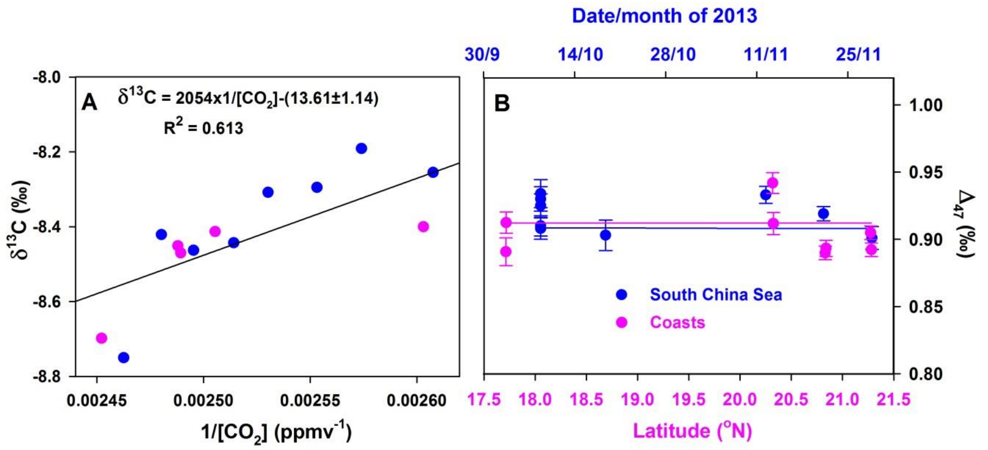
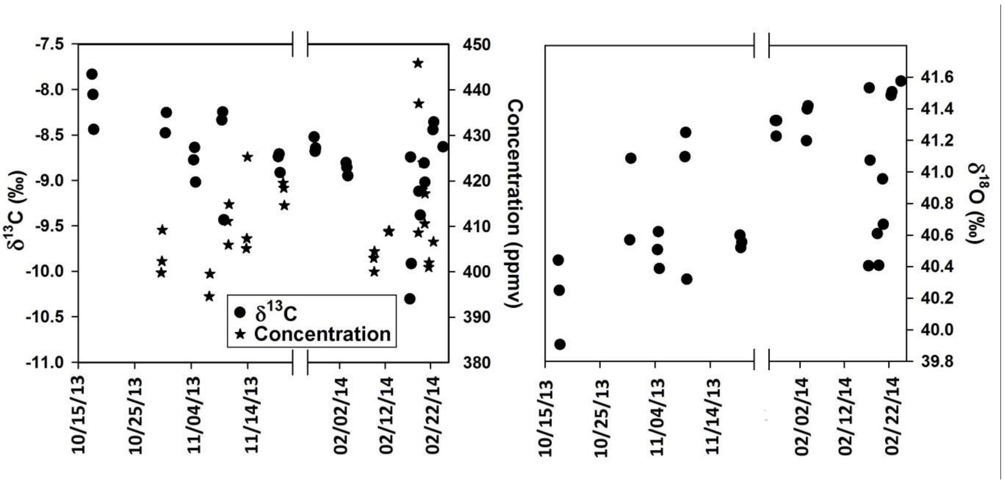
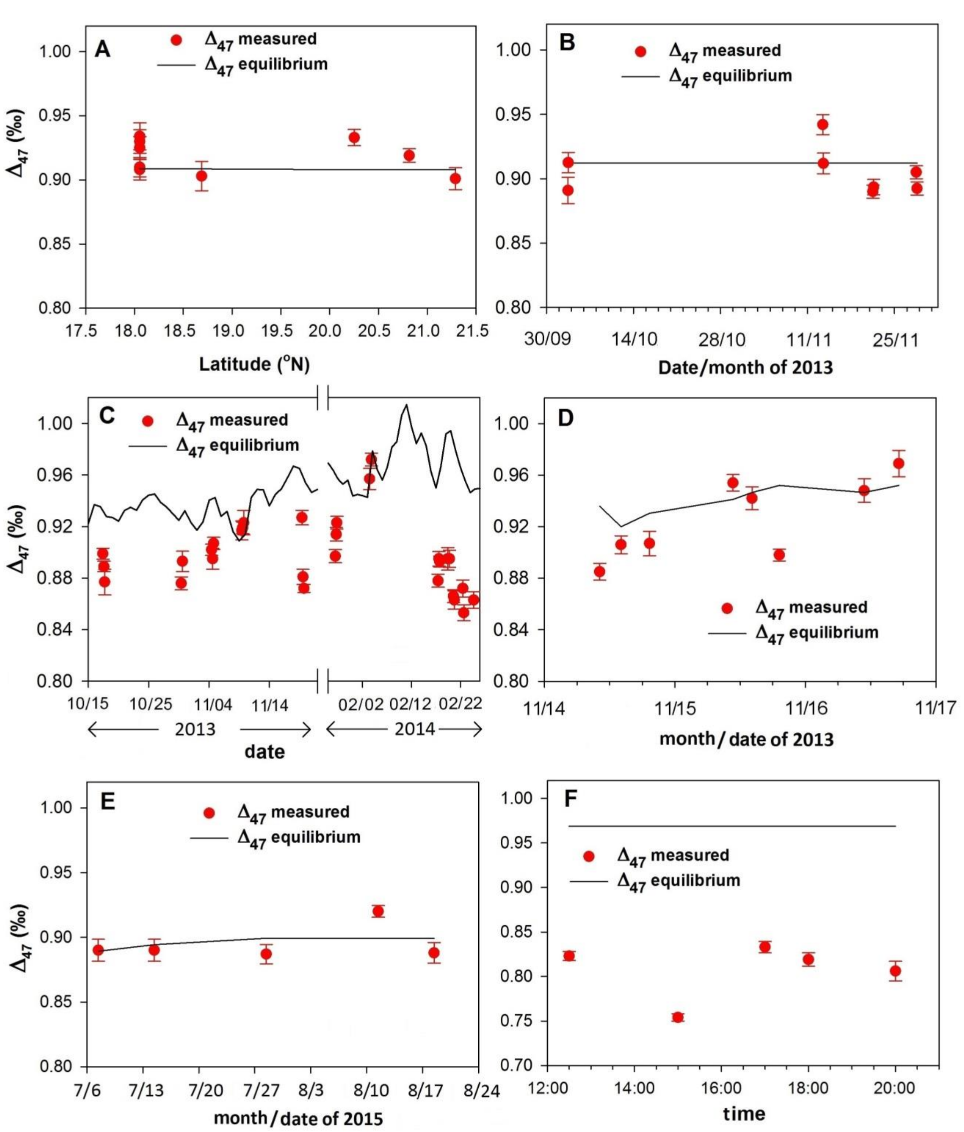


Figure 5. (A) Carbon Keeling ~~plots~~plot for ~~atmospheric~~air CO_2 collected ~~at (A)~~over South China Sea ~~(B) Keelung and Fuguei Cape, (C) sub-urban station, Academia Sinica Campus, and (D) grassland, National Taiwan University. For more details about the sites, see the texts and Figure 1.~~



~~Figure 6. Time series of (A) concentration and stable carbon and (B) stable oxygen isotopes for CO_2 collected at Academia Sinica Campus.~~



and~~Figure 7. Δ_{47} values in the near surface atmospheric CO_2 from (A) South China Sea, (B)~~ coastal stations (Keelung and Fuguei Cape~~), (C) sub-urban station (Academia Sinica campus), (D) grassland in the National Taiwan University campus, (E) forest site near the Academia Sinica Campus and (F) urban site (Roosevelt Road).~~). (B) Δ_{47} values observed over the South China Sea and coastal stations. The error bars are the 1 standard ~~errors~~error associated with the measurements. Lines show Δ_{47} values for the CO_2 in thermodynamic equilibrium at ambient temperatures.

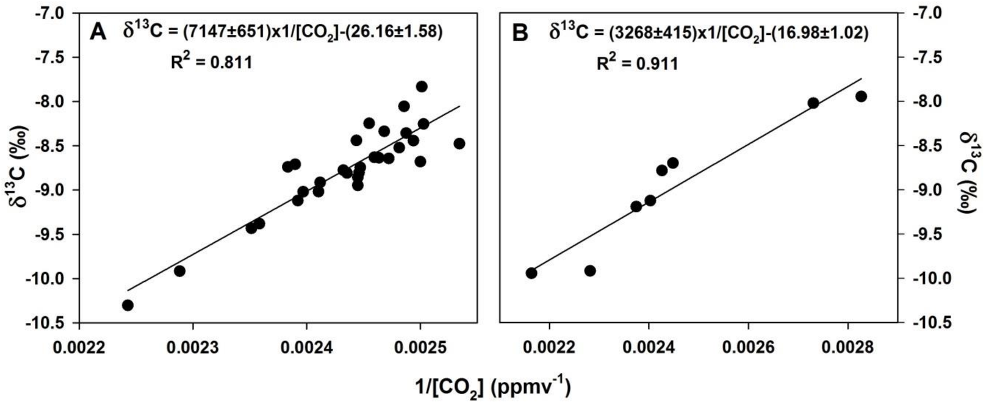


Figure 6. Carbon Keeling plots for air CO$_2$ collected over (A) sub-urban Academia Sinica Campus and (B) grassland at National Taiwan University Campus.

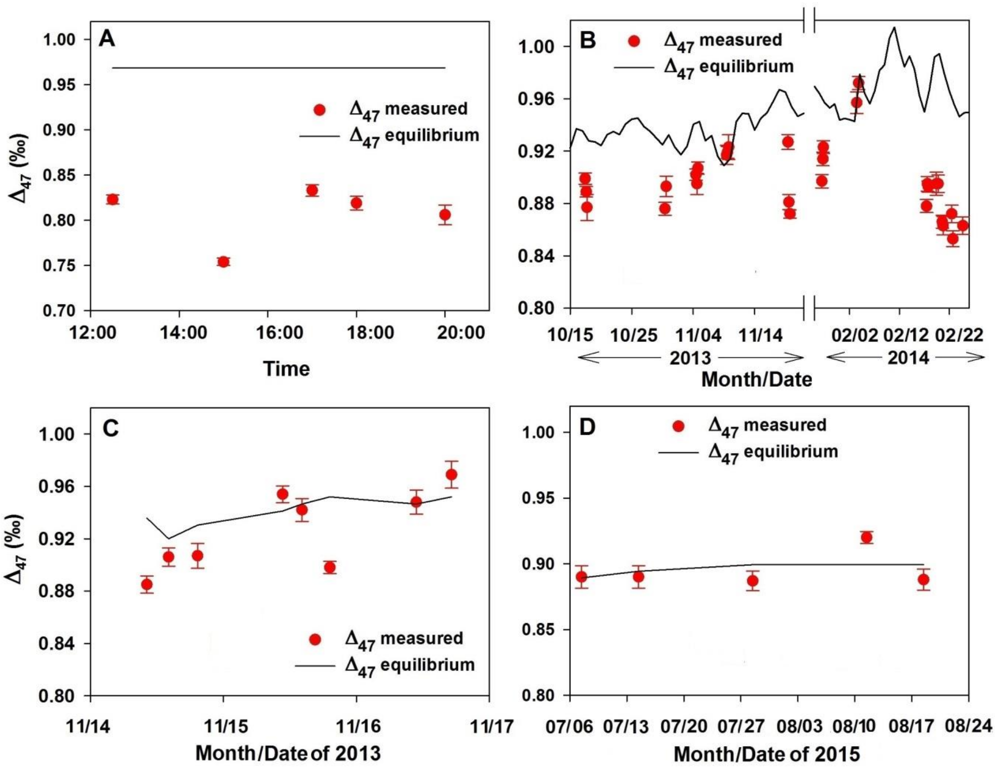
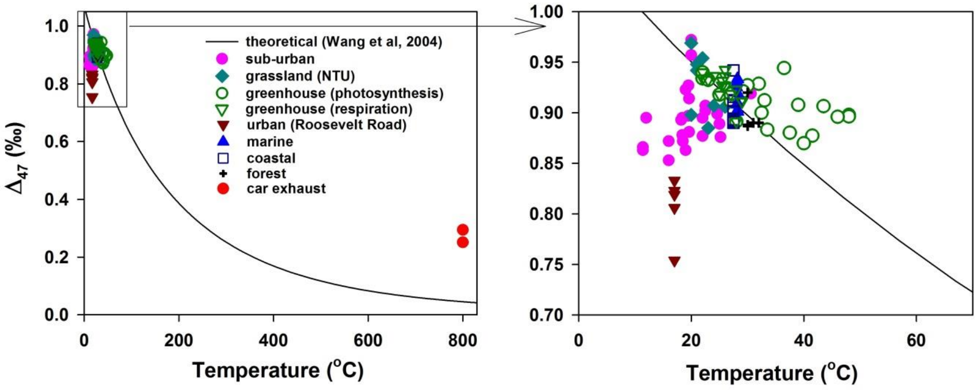


Figure 7.



~~Figure 8.~~Δ_{47} values in the near surface atmospheric CO_2 from (A) urban site near Roosevelt Road on 30th December, 2015, (B) sub-urban station (Academia Sinica Campus), (C) grassland in the National Taiwan University Campus and (D) forest site near the Academia

Sinica Campus. The error bars are the 1 standard error associated with the measurements. Lines show Δ_{47} values for the CO_2 at thermodynamic equilibrium at ambient temperatures.

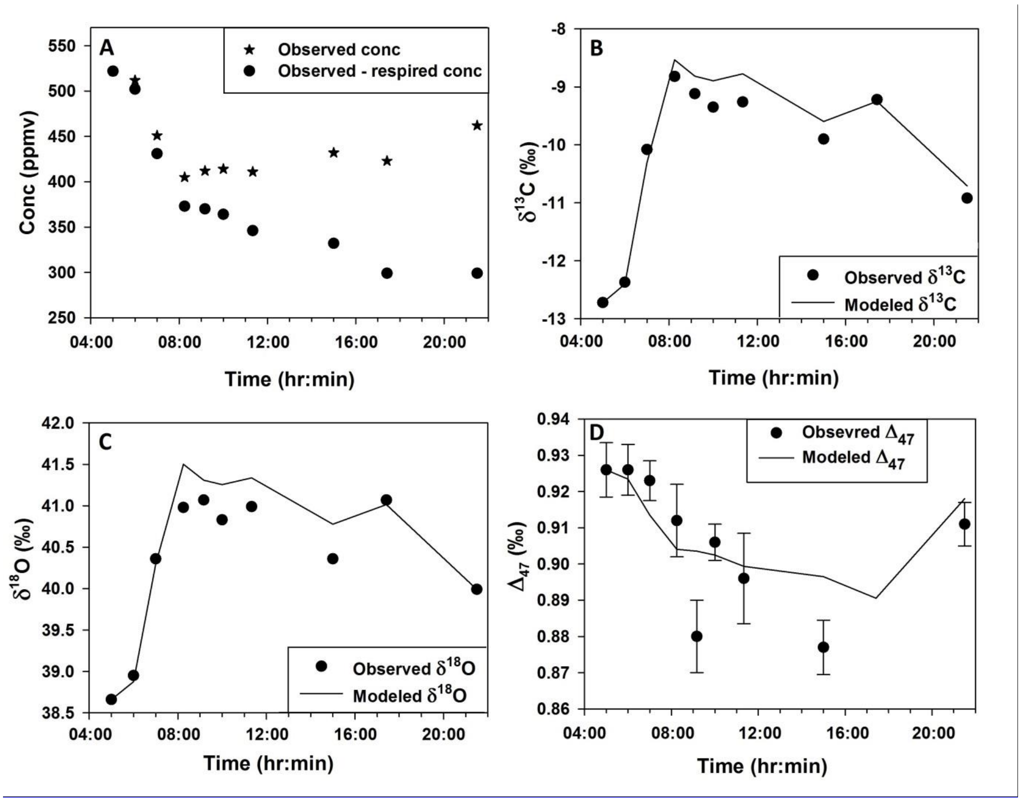


Figure 8: (A) CO_2 concentration inside greenhouse on 31st Aug, 2015: observed concentration (star) and decrease in concentration by photosynthesis after subtracting the respiration (solid circle) are also shown. Comparison of observed (B) $\delta^{13}C$, (C) $\delta^{18}O$ and (D) Δ_{47} values with that modeled using discrimination factors of -16.5 ‰, -12.0 ‰ and 0.065 ‰ for $\delta^{13}C$, $\delta^{18}O$ and Δ_{47} respectively.

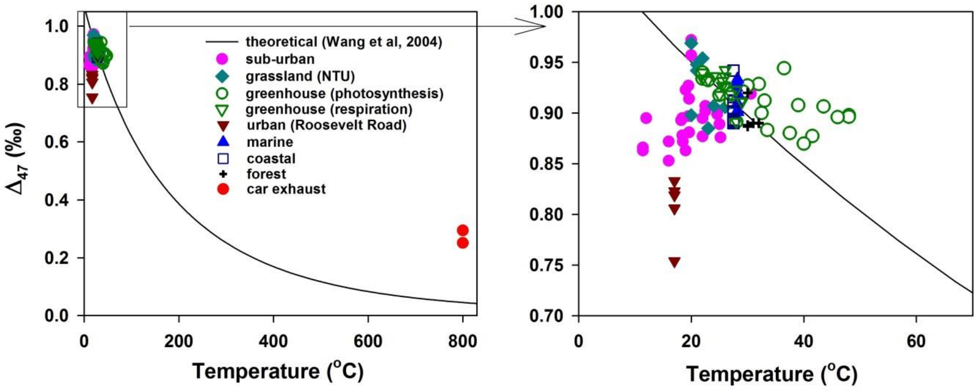


Figure 9. A summary of Δ_{47} values in near surface air CO_2 obtained at different environments and compared with the thermodynamic equilibrium values. Combustion temperature for car exhausts is assumed to be 800 °C (minimum value). Greenhouse CO_2 are divided into two categories: photosynthesis dominated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

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

Date	Time	Conc. (ppmv)	δ^{13}C(‰) (VPDB)	δ^{18}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

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	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

Table 2. Stable carbon and oxygen isotopic composition and clumped isotopes (Δ_{47}) for car exhaust CO_2. Temperatures estimated using Δ_{47} values and lowest possible combustion temperatures are given.

Car model	Conc. (ppm)	δ^{13}C(‰) (VPDB)	δ^{18}O(‰) (VSMOW)	δ^{47}(‰)	Std. err.	Δ_{47} (‰) (ARF)	Std. err.	Δ_{48} (‰)	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 ± 1σ	39350±50	-27.70±0.03	25.35±0.07	-22.64±0.44		0.273±0.021			283±18	

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Table 3. Stable isotopic composition including Δ_{47} for air CO_2 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 CO_2										
South China Sea										
Date time	Conc. (ppm)	δ^{13}C(‰) (VPDB)	δ^{18}O(‰) (VSMOW)	δ^{47}(‰)	Std. err.	Δ_{47} (‰) (ARF)	Std. err.	Δ_{48} (‰)	Estimated temp. (^{o}C)	Sea surface temp. (^{o}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 ± 1σ	395±7	-8.43±0.19	40.72±0.20	28.52±0.36		0.918±0.012			27±2	28.2±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

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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 ± 1σ	394±12	-8.45±0.09	40.57±0.26	29.12±0.63		0.911±0.020			28±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 ± 1σ	402±3	-8.53±0.12	40.94±0.16	29.68±0.29		0.894±0.015			31±3	27.5

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

Table 4. Stable isotopic composition including clumped isotopes (Δ_{47}) for air CO_2 collected in urban and sub-urban stations, grassland, forest and high mountain environments. Temperatures estimated using Δ_{47} values and air temperatures are also presented.

Urban CO_2: Roosevelt Road, Taipei City											
Date	Time	Conc. (ppm)	$\delta^{13}C$(‰) (VPDB)	$\delta^{18}O$(‰) (VSMOW)	δ^{47}(‰)	Std. err.	Δ_{47} (‰) (ARF)	Std. err.	Δ_{48} (‰)	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±1σ		500±50	-11.05±0.90	39.31±0.94	23.96±1.84		0.807±0.028			50±6	17±2

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Sub-urban air CO_2

Academia Sinica Campus

Date time	Conc. (ppm)	$\delta^{13}C$(‰) (VPDB)	$\delta^{18}O$(‰) (VSMOW)	δ^{47}(‰)	Std. err.	Δ_{47} (‰) (ARF)	Std. err.	Δ_{48} (‰)	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

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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 ± 1σ	411±11	-8.78±0.50	40.87±0.46	29.23±1.00		0.897±0.027			30±5	21±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 ± 1σ	409±33	-8.95±0.70	39.74±1.00	28.57±1.77		0.937±0.030			23±6	22±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

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08/18/2015 10:30	433	-9.99	39.80	8.99	0.02	0.888	0.016	0.4	32	30
Average ± 1σ	438±16	-9.99 ±0.50	40.39±0.66	9.82±0.94		0.895±0.012			31±2	31±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 ± 1σ	364	-8.23 ±0.02	40.59±0.30	28.60±0.19		0.904±0.009			30±2	10

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