

Specific comments.

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-chain 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.

L68: "Evapotranspiration" should be replaced to "transpiration."

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

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.

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.

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

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.

L108-109: One or more references are necessary.

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

L123: Delete "amu"

L130: 2 L; 2 atmospheric pressure

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-process for flushing should be done with identical condition to sample collection. How long did you take for actual sample collection except for pre-flushing?

L139: What is "systematic analyses"?

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."

L150-155: Add the height of the canopy.

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

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

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

L212: What is "this limit"?

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

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

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.

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

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?

L250-252: Add references for demonstrating poor consensus.

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

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

L276: Diurnal variation..

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

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

L296: What does "daytime" correspond? Daytime on 12th October? Or other three days?

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.

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?

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.

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

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

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

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

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

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.

L331: 39.32 instead of 39.319

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

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.

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

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

4: The section and order of description is inconsistent with Results. This prevents readers from moving on smoothly. Consider above mentioned comment and reorganization.

L400-418: These blocks should move to introduction.

L422: "biological" instead of "biogeochemical"

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.

L446-454: Describe how consistent with previous studies. Consider same calculation mentioned above.

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.

L469: Remove "we believe"

L474: Yeung et al., 2015).

L490-498: This block should move to Summary.

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.

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

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).

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.

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.

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?

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

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

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

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

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

Table 2: Add relative humidity if available.