Supplementary Information

New constraints of terrestrial and oceanic global gross primary productions from the triple oxygen isotopic composition of atmospheric CO2 and O2

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**Leaf evapotranspiration for the triple-oxygen isotope variation in tropospheric CO2**

Exchanging oxygen isotopes with water is the major process in determining CO2 fluxes from the biosphere/hydrosphere. The associated λ is well defined experimentally1,2 and the fluxes (e.g., the terrestrial flux - the cycling flux between the terrestrial biosphere and atmosphere, inferred from the oxygen isotopic composition of CO2) can then be constrained (cf.3). Given that the carbon flux estimation presented in this paper is based on the deviations of the oxygen anomalies of reservoirs/processes from those measured in atmospheric CO2, it is natural to take the λ value best describing the variation of the triple-oxygen isotopic partitioning in tropospheric CO2. Processes that affect CO2 isotopocules in the troposphere are terrestrial, oceanic, and anthropogenic, with the first being dominant (e.g., see Figure 4B of Liang et al. 4 for their relative importance). In the terrestrial biosphere, leaf water largely governs the oxygen isotope composition of CO2 (ref.5-11). The leaf water isotopic composition is known to be affected by evaporation at reduced relative humidity. It has been found previously that the evapotranspiration λ value in water oxygen isotopic systematics is a strong function of ambient air relative humidity12, whereas dependence on other meteorological variables such as temperature and soil water isotopic composition has not been observed. We set λ = 0.516, as it represents the evapotranspiration λ at 75% relative humidity, a globally averaged humidity near the surface13. The regions where vegetation is dense generally have relative humidity 75±5% (ref.13), corresponding to λ = 0.5160±0.0004 (with all possible errors included; re-calculated from Landais et al. 12, following the linear definition of λ defined in the main text). As a result, we take 0.516 as our reference value.

Indeed, from the CO2 data acquired in the western Pacific (with a total of 327 good measurements, after excluding one outlier having an extremely low Δ17O value of -0.025 ‰), the linear regression yields a slope of 0.516±0.002 in the δ17O versus δ18O plot, conforming with the average relative humidity of 76±4% in the region. Sensitivity tests show that a shift of 0.001 in λ does not impact the finally derived tGPP much; a change of +0.001 in λ at ~0.516 yields a change of +8 PgC/yr in tGPP, or ~24 PgC/yr in the terrestrial gross flux, Ft which reduces the recycling time τ by 0.06 year.

**Sensitivity of the terrestrial and oceanic processes in the CO2 cycling**

The sensitivity of the terrestrial and oceanic processes can be assessed following equation (2) of the main text. That is,

(S3)

where “i” is the individual process being evaluated. In general, the greater the abs(Δ17Oi - Δ17O) value, the higher the sensitivity of the derived Fi to the process “i.” As a result, the anthropogenic is the most sensitive process and oceanic the least, a consequence of mass balance of the Δ17O isoflux. Overall, terrestrial processes are roughly equally sensitive. For example, with a reduction of 100 PgC/yr in soil invasion, to maintain the same level of the isoflux from the terrestrial biosphere, one has to increase either respiration by 100 PgC/yr, or leaf retroflux by 74 PgC/yr. For oceanic, the increase is 333 PgC/yr, in order to balance the reduction of isoflux from the terrestrial biosphere. For anthropogenic CO2, the increase is 21 PgC/yr only. The above exercise clearly demonstrates the sensitivity of the triple-oxygen isotope approach to the overall terrestrial processes, but the total budget is less sensitive to a particular biological process in the terrestrial biosphere due to the common source of water, meteoric water. A bar chart of the sensitivity is shown in Figure 3 of the main text.

**Evenness of the intra- and inter-hemispheric Δ17O in CO2**

Here, we estimate the spatial homogeneity of annually averaged Δ17O values and discuss how intra- and inter-hemispheric transport affects the terrestrial gross flux Ft and tGPP. The tropospheric mixing time in each hemisphere ranges from 2-3 weeks to ~4 months14. Largely affected by Hadley circulation, it is known that the exchange of air masses across ~30° latitude is inefficient and the efficiency of the mixing is seasonally dependent. As a result, the exchange time varies between ~0.3 and 4 months, with an average of ~3 months14; see also Figure S1 for the horizontal wind of the northern hemisphere of the order of 1 m s-1, implying the mixing time is about a few months. Within each latitude bin (0-30° and 30-90°), the mixing time is in general less than 3 weeks, in either hemisphere. Inter-hemispheric mixing time is about 1.1 years14,15. With these time scales, along with the oxygen isotope turnover time, the spatial homogeneity of Δ17O in CO2 can be estimated, even before an extensive set of global data comes available.

To start, we adopt the carbon cycling model results from the National Center for Atmospheric Research Community Climate System Model coupled with the Community Land Model 4.0 (CLM4) for 20th century runs16; there are 30 ensemble runs. The main reason for this model to be selected for comparison is that the model generates tGPP of 147 PgC/yr, one of highest values among the IPCC AR5 models16,17, closer to the new estimate derived in this work and reported by Welp et al. 3. The model can also produce a reasonable global response of the terrestrial biosphere to the changing climate reflected in temperature, precipitation, and atmospheric CO2 level (see Piao et al. 18 for details).

We first estimate the difference in Δ17O in CO2 between the hemispheres. The respective Δ17O budget, expanded from equation (S2) for each hemisphere (N denotes the northern hemisphere and S the southern hemisphere), following Hoag et al. 19, can be written as follows.

(S1)

, (S2)

where MN (give value) and MS (give value) are the CO2 mass loading of each hemisphere and τh the inter-hemispheric mixing time of 1.1 year. Using the tGPP obtained by CLM4 (northern tGPP is 84 PgC/yr and southern tGPP is 63 PgC/yr), the hemispheric Δ17O difference is 0.025 ‰, assuming absence of inter-hemispheric transport. Including the 1.1 year inter-hemispheric mixing time, the difference reduces to 0.006 ‰ (=0.025 ‰ × e-(1.5 year)/(1.1 year), at 1.5 year global oxygen isotope recycling time, τ). This difference would increase our best estimated τ by 0.04 year, much less than the error of 0.2 year reported in the main text. Here, we have assumed that the cross-tropopause exchange is the same between the hemispheres e.g., see Škerlak et al. 20.

We next estimate how intra-hemispheric transport and mixing affects the Δ17O values of atmospheric CO2. Given that the mixing time (<3 weeks) in each latitude bin is much less than the derived oxygen isotope residence time (1.2 years, derived in this work versus as short as 0.4 year reported by Welp et al. 3 in the northern hemisphere), the Δ17O inhomogeneity is less than e-(0.4 years)/(3 weeks) = 0.1 %. The largest contrast comes from the cross 30° latitude transport in the northern hemisphere. If the most conservative value of the oxygen isotope residence time of 0.4 year from Welp et al. 3 is taken, the percentage difference of Δ17O between 0-30° and 30-90° is e-(0.4 year)/(3 months) = 37 %. We then take the tGPP and soil respiration values from the CLM4 model and assume soil invasion is the same as soil respiration (the most active soil invasion scenario reported by Wingate et al. 9). The estimated Δ17O difference is about 0.1 ‰, or (0.1 ‰ ×37 %) = 0.037 ‰ after considering cross 30° latitude transport; the value at the low latitude band is lower than that at the high latitude band (a consequence of upwelling air transport at low latitudes due to Hadley cell circulation and downwelling transport of air masses from the stratosphere at high latitudes; e.g., see Holton et al. 21 and Škerlak et al. 20 for details). Such difference, however, has not been found. Instead, high latitude data from Hofmann et al. 22 show a lower value (by ~0.05 ‰) compared to lower latitude data; the data of Hofmann et al. 22 may be subject to some unknown systematic biases, and as a result, that conclusion of the high latitude depletion needs to be further verified. However, careful examination shows that Taiwan and SCS are likely in the low latitude band (0-30°), whereas Israel and USA are in the high latitude band. This separation is supported by the cross-tropopause exchange pattern analyzed and obtained by Škerlak et al. 20. Within error, no statistically meaningful difference between the two bands is observed (see Table 1 of the main text). If an error of 0.01 ‰ is assumed for the difference, the inferred oxygen isotope turnover time is 0.9 year in the northern hemisphere, consistent with the time of 1.2 year reported in the main text.

In short, our model predicts a negligible difference (<0.01 ‰) in annually averaged Δ17O between latitudes and between hemispheres, the same conclusion reported earlier by Hoag et al. 19.

**Terrestrial gross primary productivity, tGPP**

Plant uptake scenarios affect the estimates of GPP and soil invasion. GPP can be estimated as follows:

, (S4)

where Fs is soil invasion, *θeq* represents the degree of hydration of CO2 inside stomata, and *κc* is a measure of stomatal conductance which can be expressed by

*κc* = *Cc*/(*Ca* – *Cc*), (S5)

where *Cc* is the CO2 concentration in chloroplasts at the site of CO2 hydration and *Ca* is the atmospheric concentration. The factor 0.88 is used to account for leaf respiration23. For C3 plants, *Cc/Ca* = 2/3; for C4 plants, *Cc/Ca* = 1/3, assuming that *Cc* is equal to intracellular CO2 concentration24. A globally averaged *Cc/Ca* is 0.57 or *κc* = 1.33 (ref.3,11). *θeq*, however, is variable11,24 and a currently globally averaged value is 0.78 (ref.11). Sensitivity analysis shows that over the range of *κc* bound between C3 and C4 plants, the change in tGPP is -4 PgC/yr for every 0.1 increase in *κc*; the calculation is done at *θeq* of 0.78. The sensitivity is -8 PgC/yr per 0.1 increase in *θeq*; the calculation is performed at *κc* = 1.33. It was pointed out previously24 that the current estimate of *θeq*, reported by Gillon and Yakir 11 is likely overestimated, but we think the overestimation is not too much, given the extent of global C4 plants compared to C3 plants. A likely range of globally averaged *θeq* is ~0.6-0.7, which corresponds to the value of tGPP of ~175-185 PgC/yr.

Another factor mentioned above is the selection of λ. At λ ≈ 0.516, the sensitivity to the tGPP is +8 PgC/yr per +0.001 change. The dependence is not linear; the higher the value of λ, the larger the sensitivity of tGPP (and τ) to λ. At λ ≈ 0.520-0.523, the sensitivity increases to +16 PgC/yr, doubling the sensitivity of that at λ ≈ 0.516. The higher sensitivity is because of the equilibration slope of water-CO2 in the dual-oxygen isotope space, which is 0.5229. At λ of 0.518, *κc* of 1.33, and *θeq* of 0.7, the tGPP value is 200 PgC/yr.

Overall, based on the assessments presented above, a choice of λ value between 0.516 and 0.518 for describing the Δ17O budget is reasonable, and *θeq* value around 0.7 is preferred. The selection yields a best estimate of tGPP of ~170-200 PgC/yr.

**Global primary productivity**

Utilization of the triple-oxygen isotopic composition of molecular oxygen in the atmosphere for GPP has been established 25. Unlike CO2, O2 does not exchange isotopes with water in a traditional way. During photosynthetic biomass production, O2 preserves its isotopic composition before getting modified by respiration, following a well-defined slope in the triple-oxygen isotope plot. Following the exact analytical formula for GPP, the globally averaged O2 GPP at steady state can be written as follows:

GPP×(δ17Ope – 0.516×δ18Ope) + Fst×(δ17Ost – 0.516×δ18Ost) = 0, or (S6)

GPP×Δ17Ope + Fst×Δ17O = 0, (S7)

where δ17Ope and δ18Ope are the effective photosynthetic O2 delta values from the biosphere and δ17Ost and δ18Ost are the values for O2 from the stratosphere; all the delta values are referenced with respect to tropospheric O2. The coefficient 0.516 is taken from the recommendation of Luz and Barkan 26. The value of Fst×(δ17Ost – 0.516×δ18Ost) is taken from Liang et al. 27 derived for the CO2 Δ17O isoflux across the tropopause. Assuming steady state in CO2-O3-O2 coupled chemistry, the positive Δ17O isoflux in CO2 is balanced by the negative Δ17O isoflux in O2. The latter is then balanced by a positive isoflux from the biosphere.

GPP can be written as functions of tGPP and oGPP, i.e.,

GPP×Δ17Ope = tGPP×Δ17Op,t + oGPP×Δ17Op,o (S8)

The photosynthetic values of δ17Op and δ18Op (in the VSMOW substrate) taken from Luz and Barkan 26 are -10.126 ‰ and -20.014 ‰, respectively, with respect to atmospheric O2; the Δ17Op value is 0.201 ‰. The actual values include substrate water Δ17O. That is,

Δ17Op,t = Δ17Op + Δ17Omw = 0.149 ‰

Δ17Op,o = Δ17Op + Δ17Oo = 0.202 ‰

The final GPP depends on the partition of tGPP and oGPP. Assuming equally partitioned28, GPP is 283±30 PgC/yr (the error, calculated following the standard error propagation in equation (S8), is mainly from the measurement uncertainty in photosynthetic O2; see Table 1 of the main text for the errors). If we take the derived tGPP from the main text, the GPP increases to 293 PgC/yr. If Δ17Op is the same as the substrate water value, the GPP increases further to 335 PgC/yr. We think it is more reasonable to use the same photosynthetic O2 delta values as the marine ones26 for terrestrial photosynthetic O2. Therefore, the value of 293 PgC/yr should be taken. The sensitivity of the GPP to the tGPP/GPP ratio is insignificant. Changing the ratio of tGPP/GPP from 0.5 to 0.9 changes the GPP value weakly from 283 PgC/yr to 321 PgC/yr.

**Table S1:** VSMOW2-CO2 equilibration at 25 °C, determined following Liang et al. 4. The values of δ17O are calculated using the scale determined and adopted previously4,29.

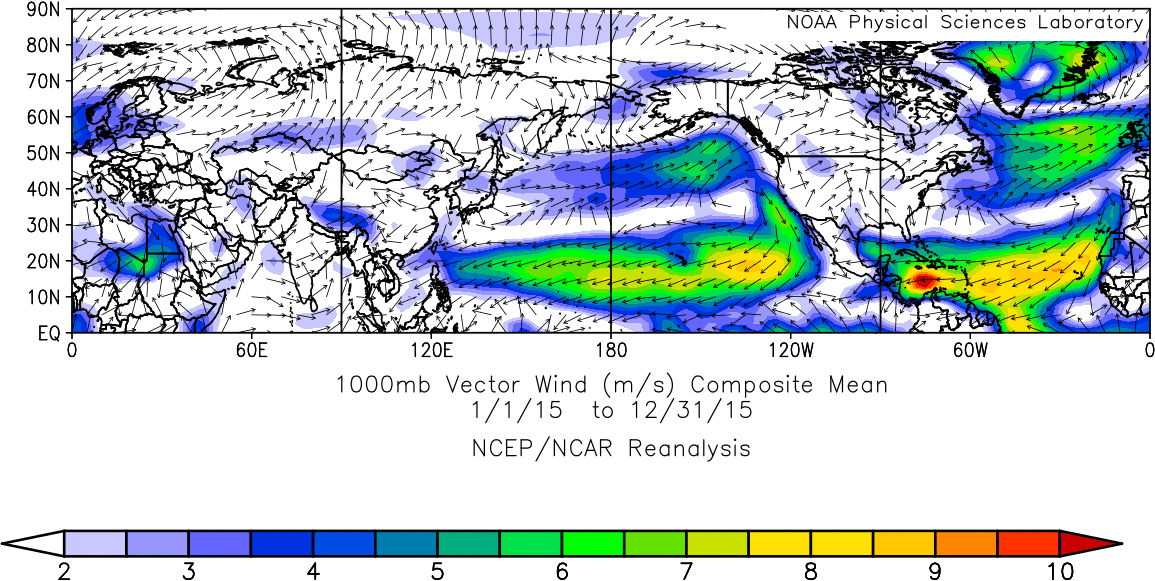
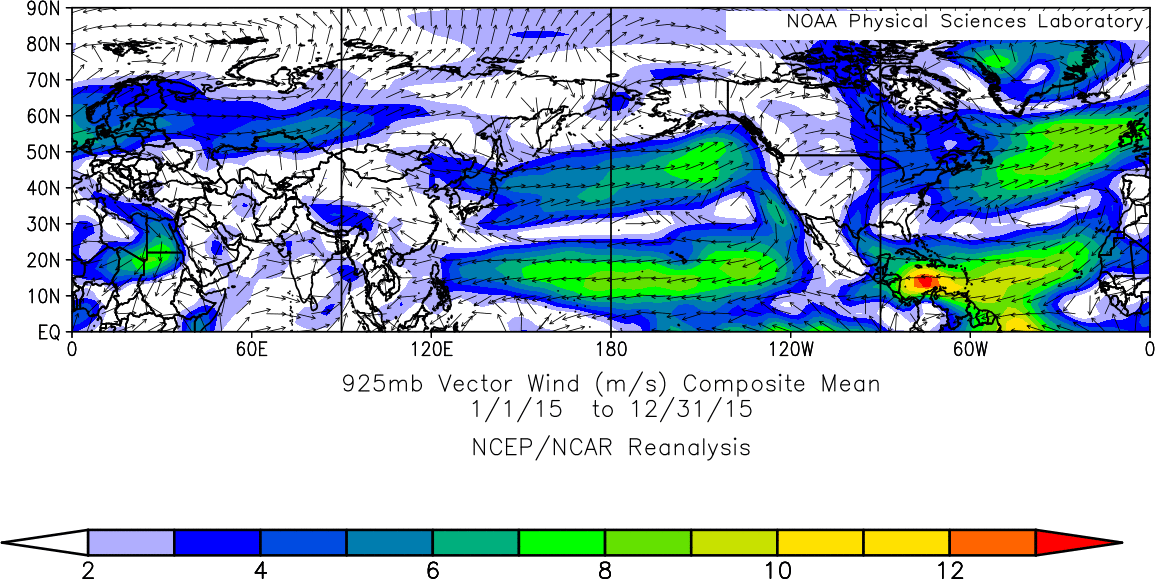
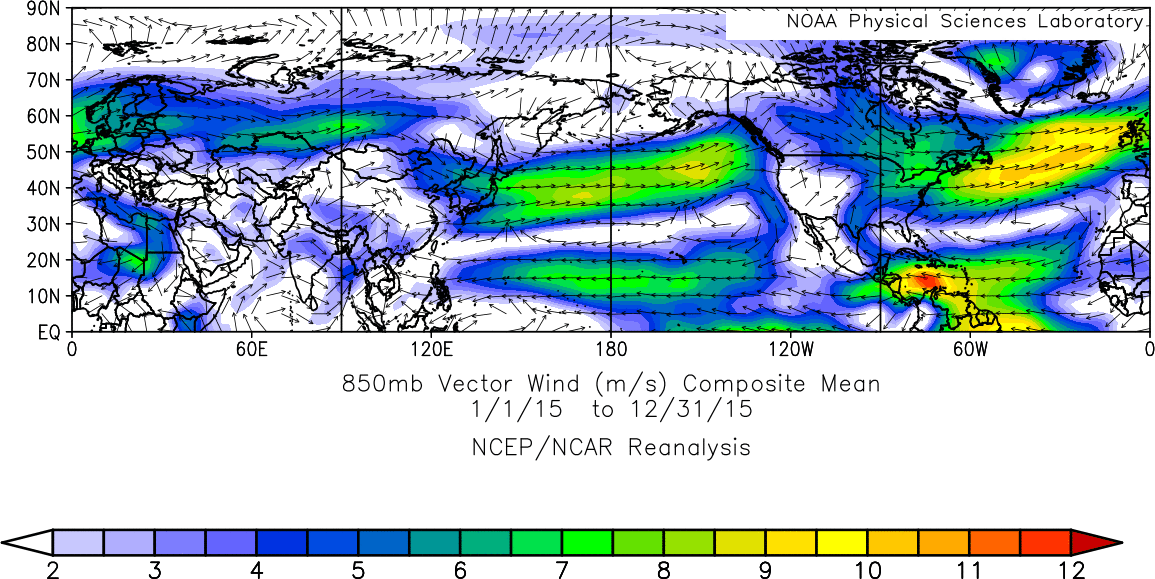
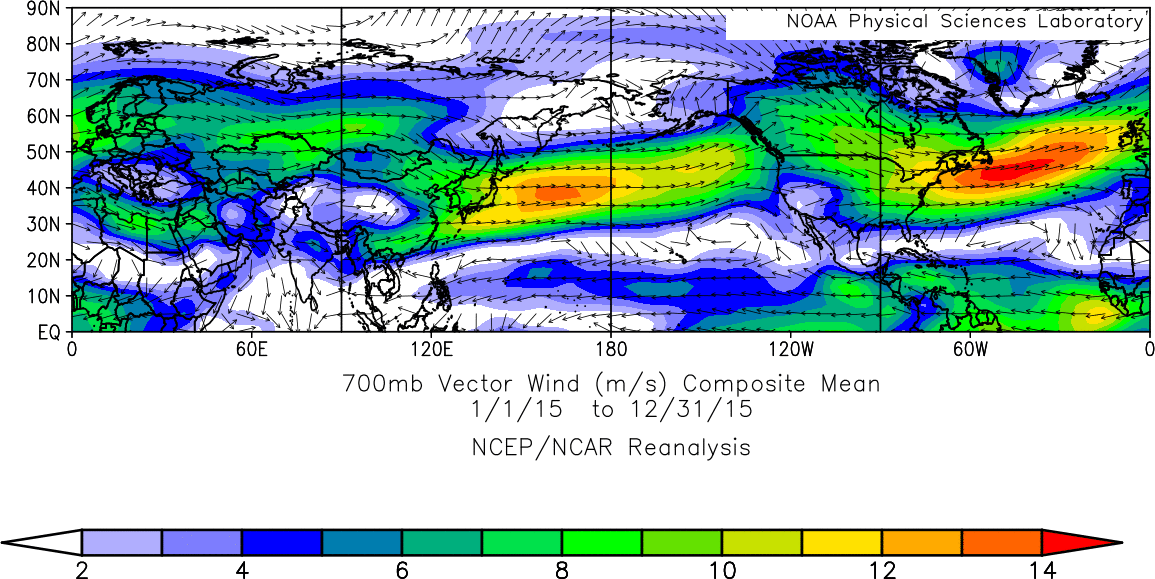
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| No. | δ17O (‰) | δ18O (‰) | 17α | 18α | ln(17α)/ln(18α) |
| 1 | 21.348 | 41.159 | 1.02135 | 1.04116 | 0.5237 |
| 2 | 21.361 | 41.159 | 1.02136 | 1.04116 | 0.5240 |
| 3 | 21.373 | 41.232 | 1.02137 | 1.04123 | 0.5234 |
| 4 | 21.384 | 41.180 | 1.02138 | 1.04118 | 0.5243 |
| 5 | 21.394 | 41.220 | 1.02139 | 1.04122 | 0.5241 |
| 6 | 21.365 | 41.180 | 1.02137 | 1.04118 | 0.5239 |
| 7 | 21.450 | 41.328 | 1.02145 | 1.04133 | 0.5241 |
| 8 | 21.455 | 41.328 | 1.02146 | 1.04133 | 0.5242 |
| 9 | 21.387 | 41.232 | 1.02139 | 1.04123 | 0.5237 |
| mean | 21.391 | 41.224 | 1.02139 | 1.04122 | 0.5239 |
| SD | 0.038 | 0.065 | 0.00004 | 0.00007 | 0.0003 |
| SE | 0.013 | 0.022 | 0.00001 | 0.00002 | 0.0001 |

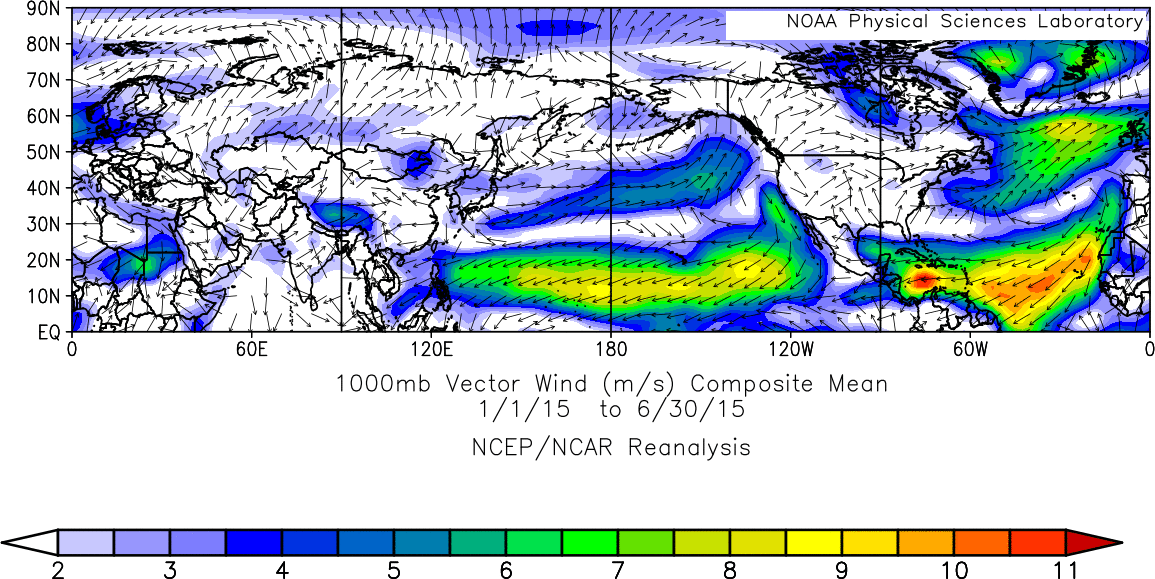
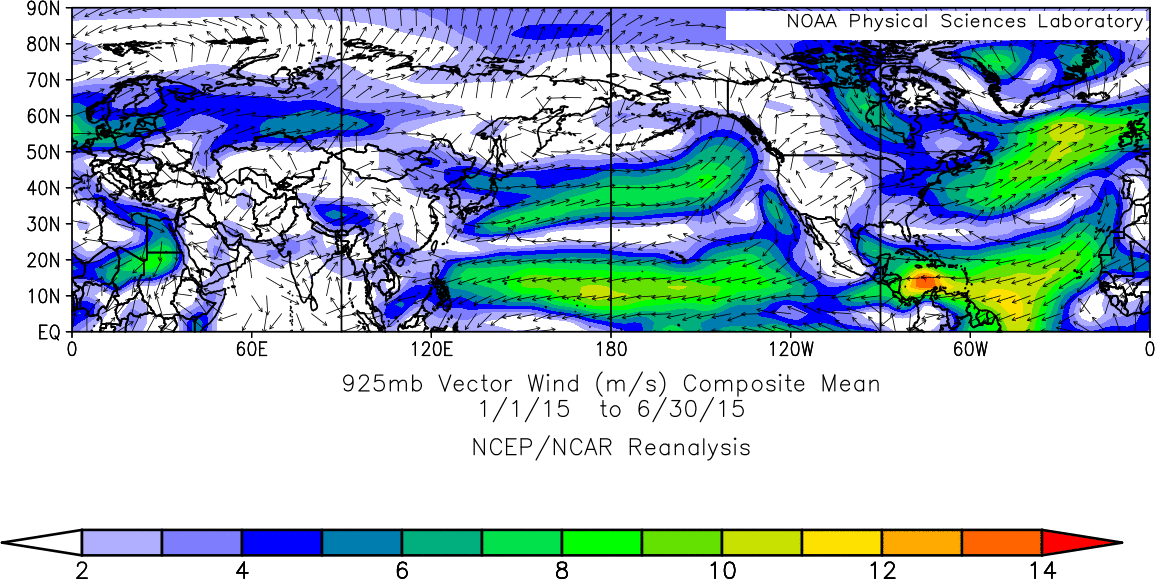
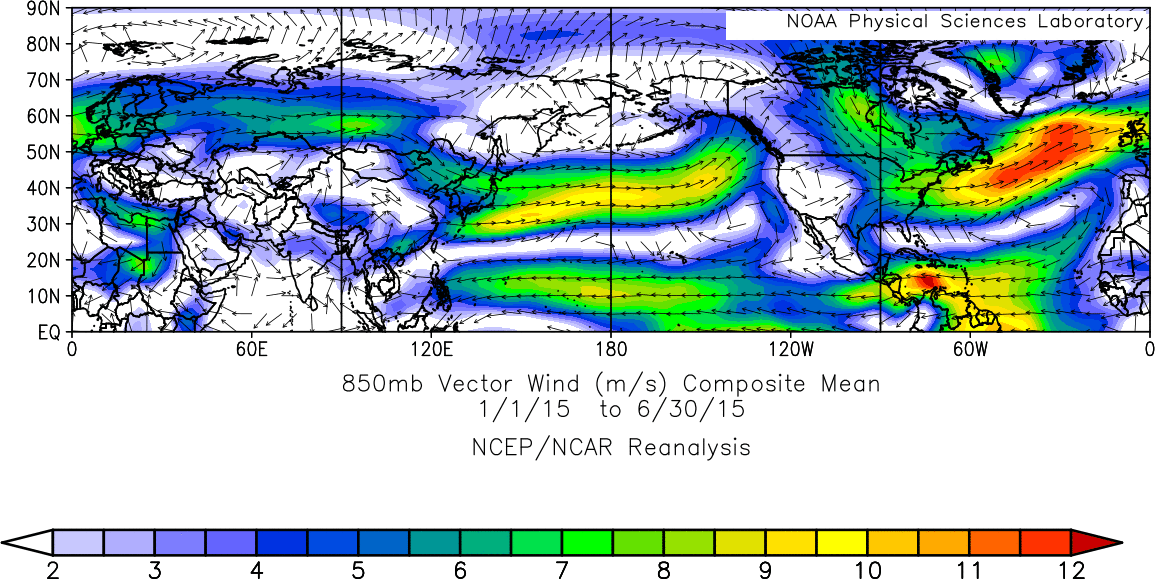
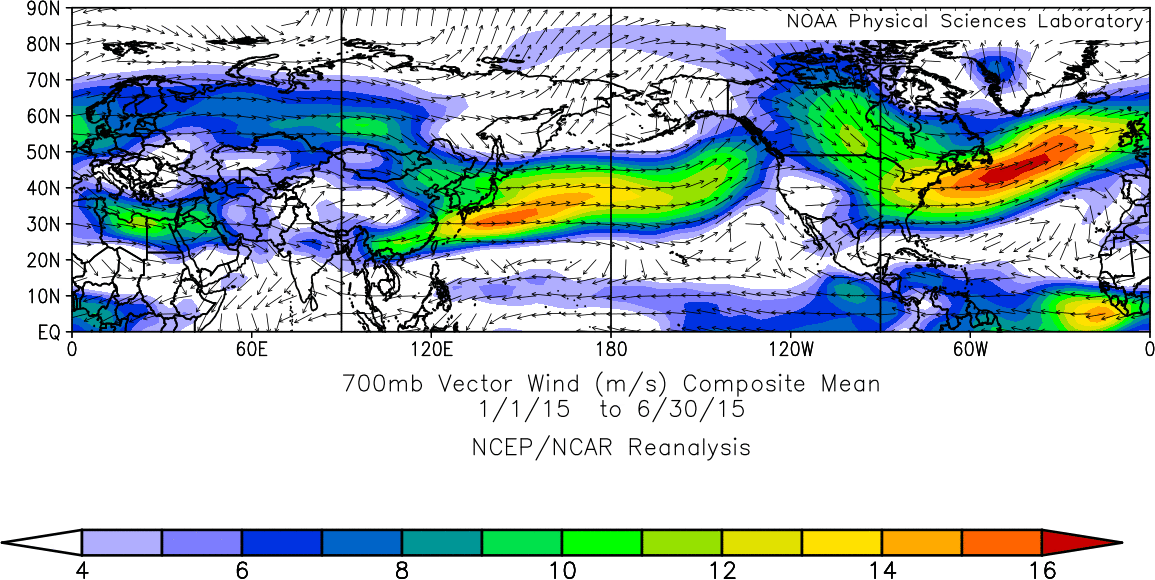
**Table S2:** AS-2 CO2 determined in Israel, following Barkan et al. 30. The values of δ17O are determined using 17α of 1.021254 and 18α of 1.041036. 17Δ = ln(1+δ17O) – 0.516×ln(1+δ18O). Our Academia Sinica nominal 17Δ value is 0.161 ‰, obtained with calibration against a determined AS-1 reported by Liang and Mahata 31.

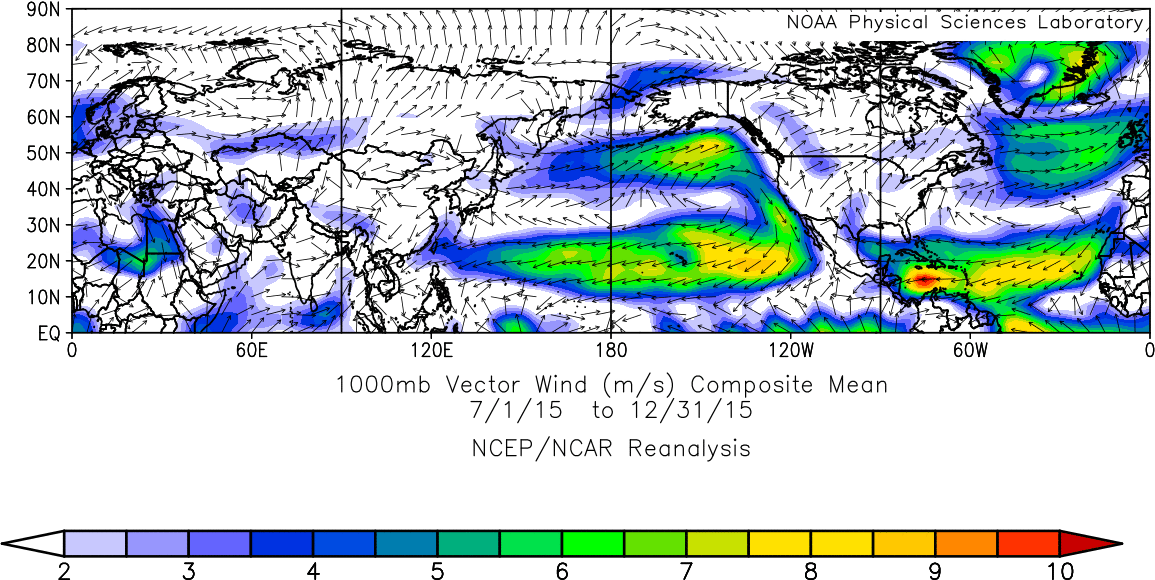
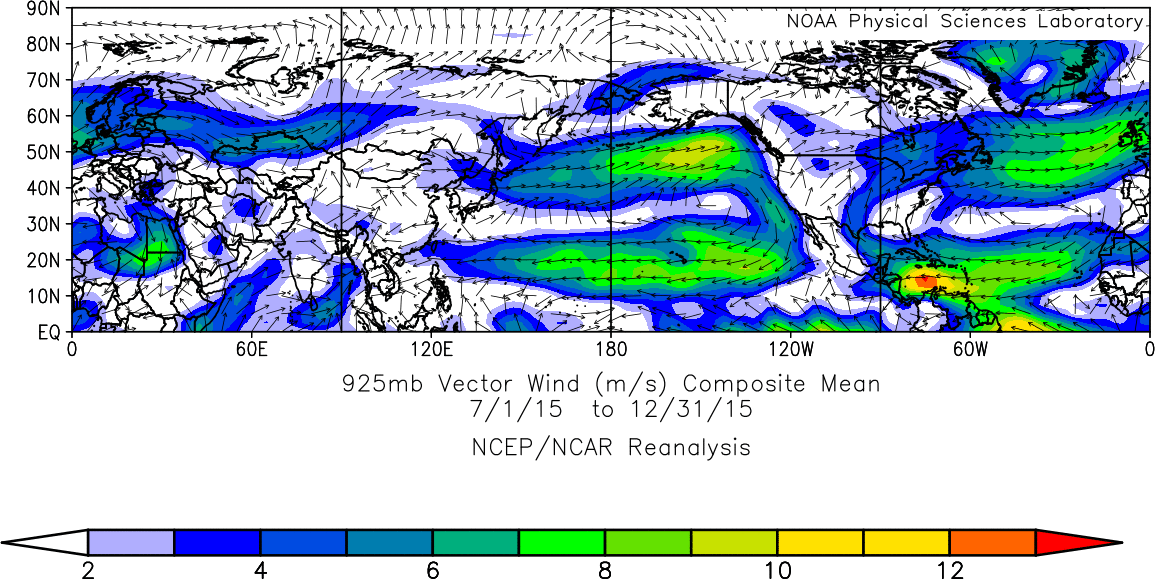
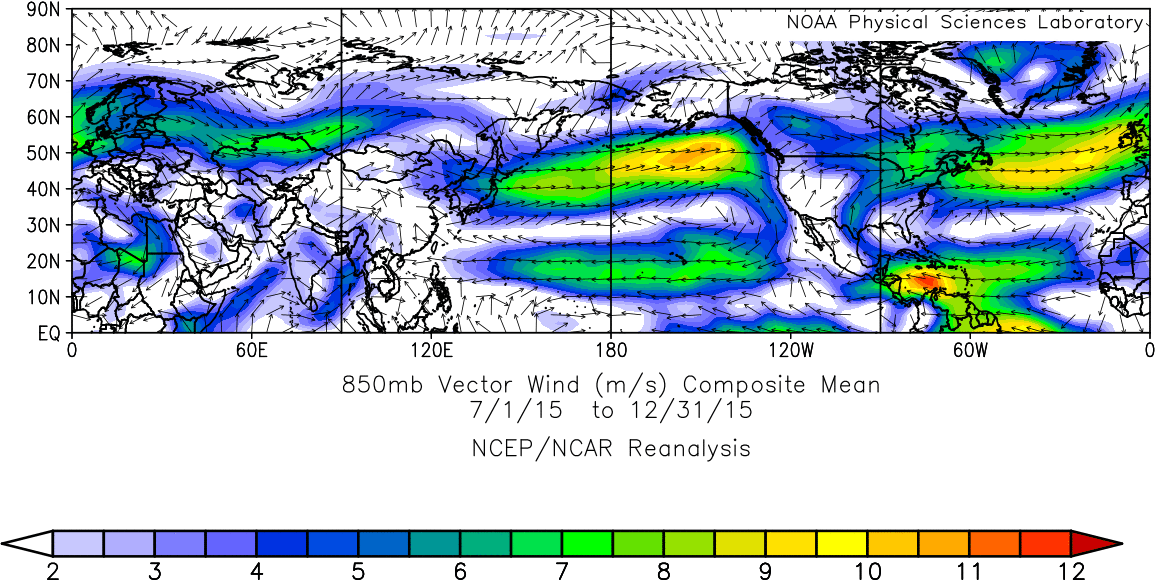
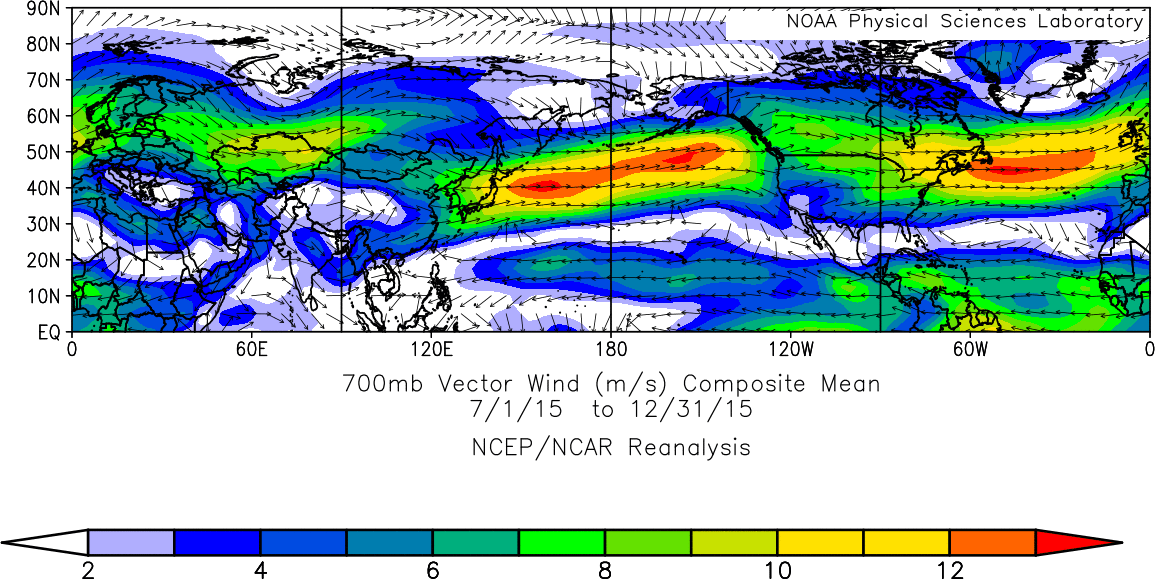
|  |  |  |  |
| --- | --- | --- | --- |
| No. | δ17O (‰) | δ18O (‰) | 17Δ (‰) |
| 1 | 18.857 | 36.61 | 0.128 |
| 2 | 18.859 | 36.61 | 0.131 |
| 3 | 18.863 | 36.61 | 0.134 |
| 4 | 18.858 | 36.61 | 0.129 |
| 5 | 18.854 | 36.61 | 0.125 |
| mean | 18.858 | 36.61 | 0.129 |
| SD | 0.003 | N/A | 0.003 |
| SE | 0.001 | N/A | 0.001 |

**Table S3:** Summary of the new CO2 data obtained in this work from South China Sea (SCS), Israel, and Palos Verdes (PVD), provided in a separate supplementary table file.

**Figure S1:** Wind vectors and wind speed (color coded, in m/s) taken from NCEP/NCAR Reanalysis32 for year 2015 at 700, 850, 925, and 1000 mbar. Three different time periods are averaged: annual, January-June, and July-December. NCEP Reanalysis data are provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.esrl.noaa.gov/psd/. The images are provided by the NOAA/ESRL Physical Sciences Laboratory, Boulder Colorado from their Web site at http://psl.noaa.gov/.

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