Seasonal Variations in Clumped Isotope and $\Delta^{17}O$ of Atmospheric CO_2 at La Jolla, CA

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The budget of atmospheric CO_2 is commonly studied using records of CO_2 concentrations, $\delta^{13}C$ and $\delta^{18}O$. These measurements permit estimates of marine, biosphere and soil fluxes, but generally under-constrain the budget due to the large number, diversity and variability of sources and sinks. We present a new record of $\Delta^{17}O$ and clumped isotope composition of CO_2 from La Jolla, CA, covering multiple 1+ year periods between 2003 and 2013. These data, document seasonal variations that offer new insights into the atmospheric CO_2 budget.

Samples were collected from the La Jolla pier during strong stable onshore winds. We report the clumped isotopologues of CO_2 using Δ_{47} notation where Δ_{47} is defined as the deviation of the ratio of mass 47/mass 44 from that expected for a random distribution of isotopologues, reported here using the absolute reference frame. The $\Delta^{17}O$ data was normalized to concurrently run SMOW2 and SLAP2 water standards and are reported with a λ=.522.

In the years studied, we find that $\Delta^{17}O$ (mean value-0.11‰) and Δ_{47} (mean value-0.96‰) vary seasonally, and are correlated with the seasonal cycle of CO_2 and $\delta^{18}O$ in CO_2 respectively. The amplitude of the seasonal cycle in $\Delta^{17}O$ is .013‰ while in Δ_{47} it is 0.2‰. We use these two records, as well as $\delta^{13}C$ and $\delta^{18}O$, to construct a box model that constrains the sizes of gross mass fluxes of CO_2 into the atmosphere, including the size of gross primary production (GPP) and the soil invasion flux.

We find that to explain the mean value of our isotopic records, GPP must be 148-162/yr assuming a soil invasion flux of 30PgC/yr. To reconcile our GPP estimates with the IPCC estimate of 123PgC/yr, we find that soil invasion flux must be much larger of 240PgC/yr. These revisions to the sizes of gross carbon fluxes represent another independent benchmark by which to evaluate global biospheric carbon cycling models.