Changes in Concentration and Isotopic Composition of CO₂ in Air in Pasadena, CA, Between 1972 and 2003

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Air samples collected on the campus of the California Institute of Technology in Pasadena, CA, contained ~30 ppm more CO₂ in 1998-2003 than they did in 1972-1973 (averaging 369 ppm in 1972-1973 and 397 ppm in 1998-2003). Yet the ranges of the carbon and oxygen isotopic ratios have remained essentially constant (${}^{13}C_{VPDB}$ was -13.4 to -7.7‰ in 1972-1973 and -14.1 to -8.0‰ in 1998-2003; ${}^{18}O_{VPDB-CO2}$ was -4.0 to -0.3‰ in 1972-1973 and -4.0 to +0.5‰ in 1998-2003). A tighter distribution for most of the more recent measurements is consistent with fewer days with highly polluted air relative to 30 years ago. Both data sets display significant correlations between ${}^{13}C$ and $1/CO_2$, with end member ${}^{13}C$ values of -31.8 ± 0.4‰ for 1972-1973 and -30.6 ± 0.2‰ for 2002-2003. Based on mass balance considerations, this reflects a changing mix of natural gas and petroleum products burned in the region combined with a change in the isotopic composition of the bulk petroleum products burned.

The 13 C of the CO₂ inventory in Pasadena can be explained by a local addition to "clean" air of 16 to 36 ppm CO₂ from exhaust from burning of fossil fuels (petroleum products and natural gas) and minor emissions from cement production. Because of southern California's warm climate, larger amounts of isotopically light fossil fuel are consumed during the summer for energy generation for air conditioning; much smaller amounts are required during the winter for heating. This offsets the effects of vegetation due to photosynthesis/respiration and masks the periodic seasonal variation observed in clean air from oceanic/coastal sites at similar latitudes, although the error limits allow up to 32% of the local contribution to be derived from biological activity.

Unlike carbon, the isotopic composition of oxygen in the CO_2 of Pasadena air does exhibit seasonal variations, similar to those of clean air sites at similar latitudes, reflecting the global signal of the biosphere's annual cycle. Added to this is the high- CO_2 end member contributed locally, which is a product of fossil fuel combustion, whose oxygen is similar to atmospheric O_2 , as determined by analysis of plots of $1/CO_2$ vs. ¹⁸O.



Figure 1. Composition of CO_2 in air in Pasadena compared with air from clean southern California sites and NOAA ESRL oceanic and coastal sites located 25-40°N. Shaded bands indicate ±1 from the best fit lines.