Changes in mixing ratio and isotopic composition of CO_2 in urban air from the Los Angeles basin, California, between 1972 and 2003

Sally Newman,[1] Xiaomei Xu,[1,2] Hagit P. Affek,[1,3] Edward Stolper,[1] and Samuel Epstein[1,4]

[1] Atmospheric CO_2 mixing ratios and C and O isotopic compositions are reported for the Los Angeles basin in southern California, a region renowned for its air pollution. Air samples collected midday on the Caltech campus in Pasadena, California, contained ~30 ppm more CO_2 in 1998–2003 than in 1972–1973 (averaging 397 ppm in 1998–2003 and 366 ppm in 1972–1973) compared to a 47 ppm change in background air CO_2, yet the ranges of the carbon and oxygen isotopic compositions remained essentially constant. Because the 1998–2003 data show a significant progression through time, analysis was done on data from 2002 to 2003 complete calendar years (CO_2 mixing ratios increased 41 ppm between 1972 and 1973 and 2002–2003). Both 1972–1973 and 2002–2003 data sets display significant correlation between $\delta^{13}C$ and $1/[CO_2]$ with local CO_2 source end-member $\delta^{13}C$ values of -30.9 ± 0.5‰ for 1972–1973 and -29.9 ± 0.2‰ for 2002–2003 (1σ errors). Mass balance calculations explain that this apparently coincidental similarity reflects a change in the relative proportion of natural gas and petroleum products burned in the region combined with a change in the origin, and thus isotopic composition, of the petroleum burned. The $\delta^{13}C$ of the average CO_2 inventory in Pasadena can be explained by local addition to background air of 38 ± 4 ppm CO_2 in 1972–1973 and 29 ± 3 ppm in 2002–2003 from anthropogenic sources, in seeming contradiction to the known increase in CO_2 emissions between these two time periods.

1. Introduction

[2] Over the past 150 years, the mixing ratio of CO_2 in the Earth's atmosphere has been increasing owing to industrial and agricultural activities [e.g., *Keeling et al.*, 1995]. Given the importance of these changes to the Earth's climate, considerable effort has been directed toward characterizing spatial and temporal variations in atmospheric CO_2 mixing ratios. Because isotopic shifts accompany this concentration increase, reflecting the ^{13}C-depleted nature of organic matter used in combustion, owing to the preferred uptake of ^{12}C relative to ^{13}C in photosynthesis [e.g., *Farquhar et al.*, 1989; *Keeling*, 1961b; *Park and Epstein*, 1960], the carbon isotopic composition of atmospheric CO_2 is also often measured. Studies that couple measurements of the mixing ratio and isotopic composition of atmospheric CO_2 have focused on sites far from anthropogenic sources of atmospheric CO_2 [e.g., *Ciais et al.*, 1995; *Keeling et al.*,

1989, 1995; *Levin and Kromer*, 1997; *Mook et al.*, 1983; *Tans et al.*, 1990] (see ftp://ftp.cmdl.noaa.gov/ccg for information on NOAA Climate Monitoring and Diagnostics Laboratory, now part of the Global Monitoring Division of the Earth System Research Laboratory, Global Air Sampling; NOAA-ESRL). Only a few similar studies have been performed in urban areas (Dallas, TX [*Clark-Thorne and Yapp*, 2003]; Budapest, Hungary, and Krakow, Poland [*Demeny and Haszpra*, 2002; *Kuc*, 1986, 1989, 1991; *Kuc and Zimnoch*, 1998; *Kuc et al.*, 2007]; Salt Lake City, UT [*Pataki et al.*, 2003, 2006, 2007; *Bush et al.*, 2007]; and Paris, France [*Widory and Javoy*, 2003]), even though such regions are significant sources of anthropogenic CO_2 in the global system. Studying CO_2 in urban areas is important because these regions are the major source of anthropogenic CO_2. Since the amount of atmospheric CO_2 increases owing to anthropogenic contributions, it is relevant to understand how CO_2 concentrations in the atmosphere of urban source regions change with time. Do they change with the global change manifested in clean regions? Ground-based studies of urban environments complement remote sensing studies such as the Central Arizona–Phoenix Long-term Ecological Research project (http://elwood.la.asu.edu/grsl/lter/index.html) and the Advanced Spaceborne Thermal Emission and Reflectance Radiometer for the Urban Environmental Monitoring project (http://elwood.la.asu.edu/grsl/

[1]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA.
[2]Now at Earth System Science, University of California, Irvine, California, USA.
[3]Now at Department of Geology and Geophysics, Yale University, New Haven, Connecticut, USA.
[4]Deceased 17 September 2001.

UEM/; studying 100 cities worldwide, of which 22 are in the United States).

[3] In this paper, we report results of measurements of the mixing ratio and isotopic composition of CO_2 in air collected on the campus of the California Institute of Technology (Caltech) in Pasadena, California, between May 1972 and August 1973 and between October 1998 and December 2003. Situated in the Los Angeles basin (Figure 1), a major urban center that is known for its poor air quality, these measurements contribute to understanding the magnitude of variations in atmospheric CO_2 and the factors controlling them. These data allow consideration of long-term variations of CO_2 in an urban environment and provide a baseline for future monitoring and understanding of these variations. Constraints can also be put on the amount and isotopic composition of the CO_2 introduced locally into the atmosphere.

2. Sampling and Analytical Techniques

2.1. Sampling Locations

[4] The Los Angeles basin is bordered by the Pacific ocean to the south and west, the Transverse ranges (including the San Gabriel mountains) to the north, and the Santa Ana mountains and associated hills to the east (Figure 1). The mountains act as a barrier, trapping pollutants that would otherwise be blown away by the generally westerly wind pattern. The mountains also help to maintain a temperature inversion layer that traps polluted air in the near surface mixed layer in the vicinity of the mountains; closer to the ocean, clean air is generally brought onshore overnight with the marine layer [Lu et al., 1997a, 1997b], which is the moist lowest layer (300–600 m in vertical extent) of the atmosphere, cooled much of the year by the ocean surface [Lu and Turco, 1994]. Indeed, air parcels can cycle through the Los Angeles basin concentrating pollutants in the Pasadena area, owing to the interaction of the inversion layer and the diurnal alternation of onshore and offshore winds [Neiburger, 1969].

[5] The Caltech campus is located in the city of Pasadena, situated in the San Gabriel valley, about 14 km northeast of downtown Los Angeles at an elevation of ~235 m ($34°8'12''N$, $118°7'39''W$). The San Gabriel valley is bounded by the San Gabriel mountains (N), the San Jose hills (E), the Puente hills (S), and the San Rafael hills (W). This location leads to higher pollution levels relative to much of the Los Angeles basin due to enhanced ponding of pollutants in this region.

[6] Air samples were collected at four locations on the Caltech campus within an area of ~1000 m^2 (Figure 1c). Samples were collected from Site 1 in 1972–1973; samples were collected from all four sites in 1998–2003. Site 2 was ~1 m above ground level, whereas the others were 10–15 m above the ground. When changing sampling location, we collected samples at the same time at both old and new sites to verify that the site change did not introduce a bias. No significant differences were observed, with the average differences being 1 ppm CO_2, 0.08‰ $\delta^{13}C$, and 0.09‰ $\delta^{18}O$.

[7] To compare data from our urban location with nominally "clean" environments (unaffected by anthropogenic influences) in the same region, we collected samples from other locations that can be considered characteristic of the local background (Figures 1a and 1b), far removed from industrial sources of CO_2 and from heavy automobile traffic. These samples were collected from Newport Beach (~75 km south of Pasadena; $33°37.2'N$, $117°54.0'W$; 1.5 m elevation); near the top of Mt. Wilson (~11 km north of Pasadena, in the San Gabriel mountains; $34°13.26'N$, $118°3.41'W$; 1716 m elevation); on Santa Catalina island (~40 km off the coast of Los Angeles, ~85 km SSW of Pasadena, above Buttonshell beach; $33°24.45'N$, $118°22.08'W$, 3 and 76 m elevation); near a southwest-facing beach in San Pedro on the Palos Verdes peninsula (~50 km SSW of Pasadena; $33°42.88'N$, $118°18.70'W$; 23 m elevation); at Jawbone canyon in the Mojave desert (~130 km N of Pasadena; $35°20.7'N$, $118°4.9'W$; 3082 m elevation); and at two sites in the Sierra Nevada mountains: along the Kern river (~160 km NNW of Pasadena, in Sequoia National Forest; $35°28.6'N$, $118°43.3'W$; 435 m elevation) and at Wolverton ski area (271 km NNW of Pasadena in Sequoia National Park; $36°34'N$, $118°43'W$; 2200 m elevation). The Newport Beach sample was collected in 1973; all others were collected in 1998–1999.

[8] Several possible anthropogenic sources of CO_2 in Pasadena air were also analyzed: exhaust gases from an automobile; exhaust from a natural gas torch; and breath samples from 3 people. For each of these sample collections, ambient Pasadena air was also collected nearby and close in time, being careful that it was not affected by the specific anthropogenic source being examined.

2.2. Sampling Procedures

[9] Samples were collected 30 May 1972 through 6 August 1973 between 1100 and 1800 local time (LT) into evacuated flasks. A total of 78 samples were collected on 62 different days. From October 1998 until March 2001, air was collected in ~1-L evacuated Pyrex bulbs by manually opening and closing ground-glass stopcocks. During this time period, air was collected in 1–3 flasks within a few of minutes of each other every 1–2 days. Temperature, pressure, and relative humidity were measured at the time of collection using small, portable weather stations (Digital Barometer; VWR Scientific; West Chester, PA).

[10] In March 2001, the sampling procedure changed to an automated system, consisting of a stainless steel vacuum manifold connecting a rough pump to up to 12 Pyrex bulbs (~1 L each) inside the building and 1/4″ Synflex® tubing (an Al tubing with inner polyethylene copolymer coating and high-density polyethylene jacket; Saint-Gobain Performance Plastics, Mantua, OH) extending ~1 m outside the building. Computer-controlled, air-pressure-actuated Varian® valves opened and closed to allow pumping and collection of outside air. The manifold and bulbs were first evacuated for ≥15 min to ~10^{-4} torr; then the Synflex® tubing and manifold were flushed 3 times with fresh air; then air was finally allowed to fill the sample bulbs, filling within 15–20 s and equilibrating for 3 min before a valve closed the bulb. In addition, the CO_2 content and humidity of air were determined continuously (approximately six times a minute) by a CIRAS-SC infrared spectroscopy instrument (PPSystems, UK) with the sampling inlet at this site, which was used to check the accuracy of the manometric method used to determine CO_2 content of the air collected in flasks and reported here. After 28 November
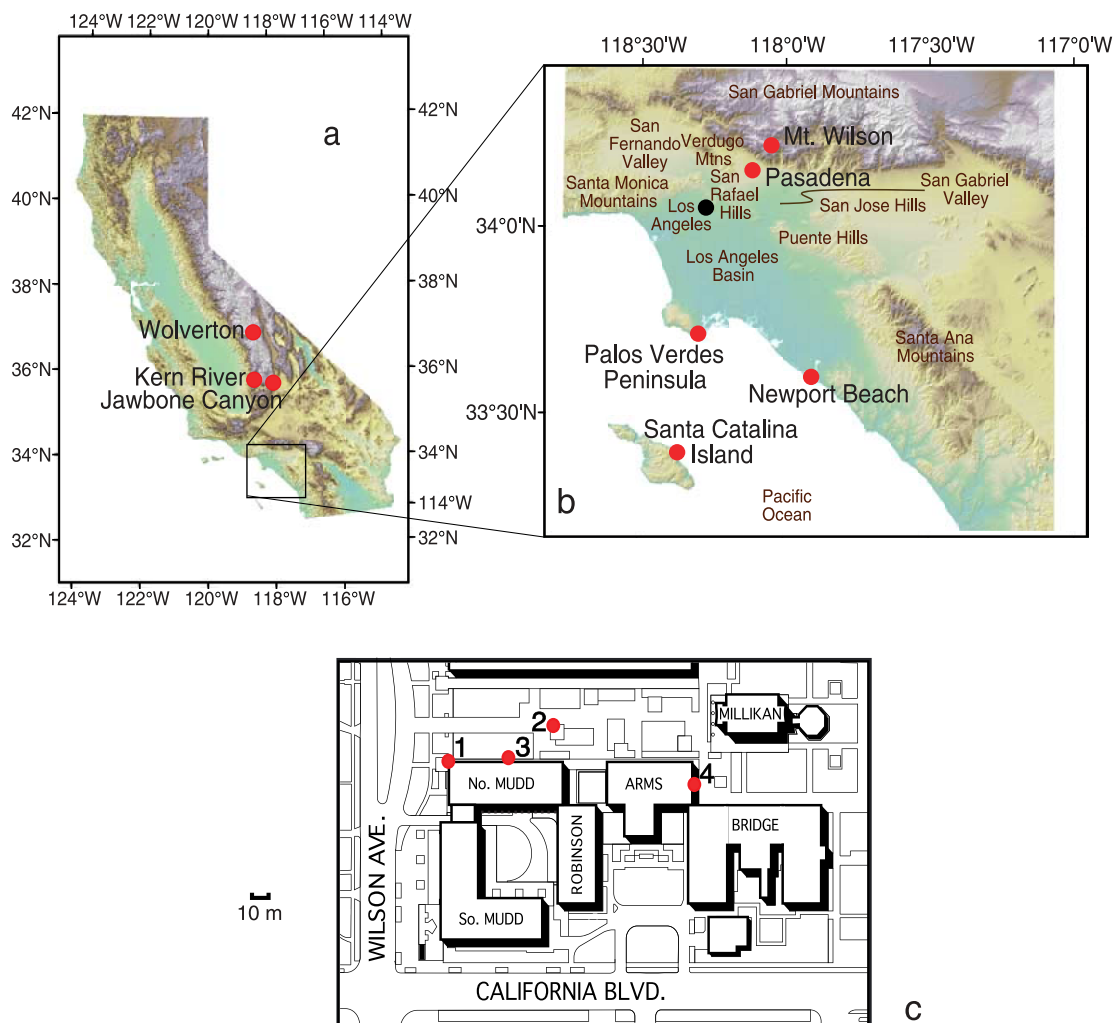
Figure 1. Locations of sampling sites shown as red dots. (a) Physiographic map of California, showing the collection sites for nominally clean air samples obtained in and near the Sierra Nevada mountains. (b) Inset showing the Los Angeles area sampling locations and physiographic features and the location of Pasadena. (c) Map of a portion of the southwest corner of the Caltech campus, showing a projection of the four sampling locations on campus. Numbers adjacent to dots refer to the chronological order of site usage (see text).

2001, all air samples were dried by passing through a trap filled with $Mg(ClO_4)_2$ before entering the flasks. This drying procedure avoids the problem of oxygen isotope exchange between condensed water and carbon dioxide in the bulbs, as discussed by *Gemery et al.* [1996].

[11] Most of the 1114 samples (collected once a day) in the 1998–2003 data set were collected in midafternoon, between 1200 and 1700 LT; one hundred were collected between 1000 and 1200 LT; and sixteen were collected between 1700 and 1900 LT. The data discussed in this paper typically correspond to the time of lowest daily CO_2 content (1200 to 1700 LT; as determined by the CIRAS-SC) and most enriched $\delta^{13}C$ values. Moreover, since there is little variation in CO_2 mixing ratio with time during this midafternoon window, the results are not sensitive to the exact collection time.

2.3. Extraction and Analysis of CO_2

[12] CO_2 was extracted from the air samples on a glass vacuum line by freezing in liquid nitrogen traps and drying

in ethanol-dry ice traps. The amount of released CO_2 and N_2O was then determined by manometry: prior to August 2000, including all of the samples analyzed during 1972 and 1973, a Hg manometer was used; after this date, a Baratron (MKS Instruments; Wilmington, MA; Type 122A absolute Baratron pressure transducer manometer with 10 Torr full scale, calibrated by comparison to the Hg manometer) was used. The average difference between the two measurement techniques was less than 1 ppm.

[13] After the manometric measurement, the CO_2 was frozen into a sample tube and its carbon and oxygen isotopic ratios were determined by dual inlet mass spectrometry. The 1972–1973 samples were analyzed with a custom-built, Nier-type dual-inlet mass spectrometer. The 1998–2003 samples were analyzed with a Finnigan-MAT 252 mass spectrometer in dual inlet mode. The same reference gas was used in both systems. The isotopic ratios for both time periods are reported in per mil (‰) relative to the VPDB standard: $\delta^{13}C$ is reported relative to carbon in
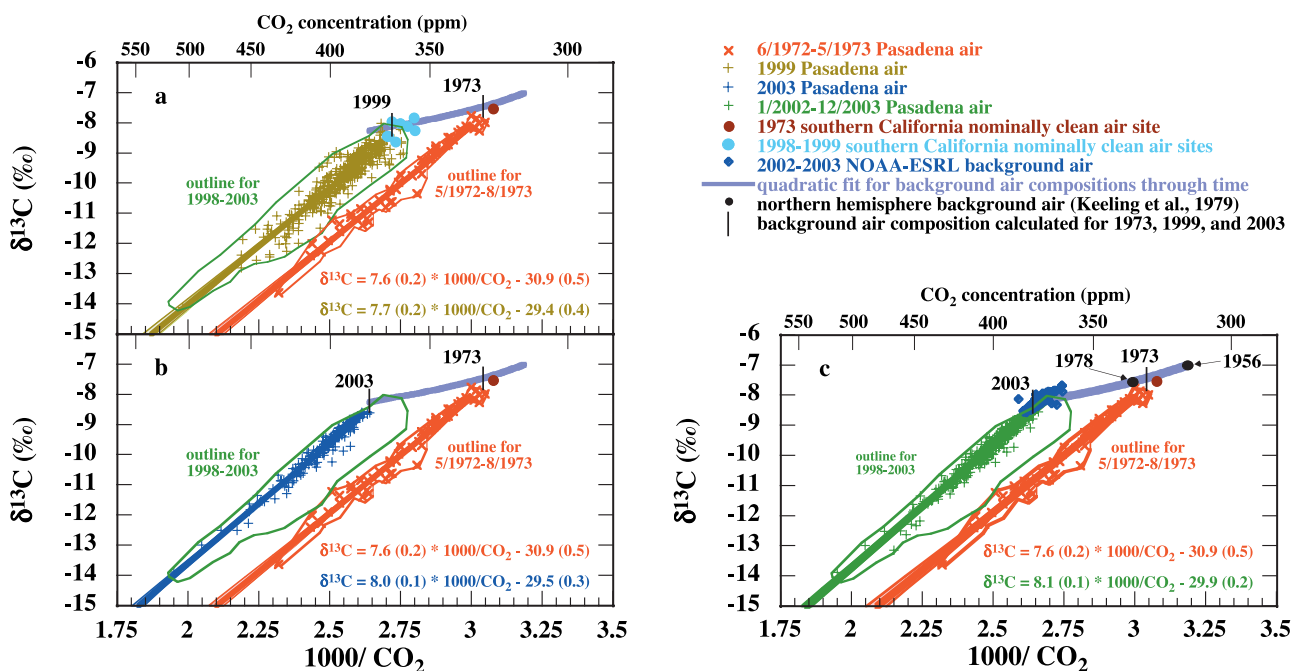
Figure 2. The $\delta^{13}C$ (‰) versus $1000/CO_2$ (ppm^{-1}) May 1972 to May 1973 data set compared with (a) 1999, (b) 2003, and (c) 2002–2003 Pasadena data sets, with simple linear regression lines and 95% confidence bounds for the functions, calculated by Matlab R2006a (The Math Works, Natick, Massachusetts). The red outline indicates the field for the entire May 1972 through August 1973 time period, and the dark green outline indicates the field for the entire October 1998 through December 2003 time period. Also shown are data from California nominally clean-air sites (large dark red dot: Newport Beach, California, collected in 1973; large light blue dots: Santa Catalina island, Mt. Wilson, Jawbone canyon in the Mojave desert, Sequoia National Park, and a location overlooking a southwest-facing beach on Palos Verdes peninsula, all collected in 1998–1999 and shown in Figure 2a) and eight oceanic/coastal NOAA-ESRL background air sites at similar latitudes to Pasadena (25°N–40°N) from 2002 to 2003 (small dark blue diamonds in Figure 2c: the Azores, Bermuda East, Bermuda West, Canary Islands, Key Biscayne (Florida), Pt. Arena (California), and two mid-Pacific sites (25°N and 30°N); data can be found at ftp://ftp.cmdl.noaa.gov/ccg). The thick purple curve is the quadratic regression best fit that represents the changes in the yearly averages for background air from 1956 through 2003: $\delta^{13}C = 1.7877*(1000/CO_2)^2 - 8.2101*(1000/CO_2) + 1.0087$. This was determined by regression of the 1998–2003 yearly averages of the NOAA-ESRL oceanic/coastal sites listed above and the Northern Hemisphere averages for 1956 and 1978 from *Keeling et al.* [1979]. The black vertical tick marks are the background air $\delta^{13}C$ composition calculated from this trend for 1973, 1999, and 2003, respectively. The best fit equations are shown in the colors of the symbols, with 1σ uncertainties in parentheses.

the VPDB standard; $\delta^{18}O$ is reported relative to VPDB-CO₂ [*Gonfiantini et al.*, 1993]. The relative efficiency of measuring mass 44 of N₂O to CO₂ was 0.74 for the Finnigan-MAT 252, similar to that reported in the literature [*Mook and van der Hoek*, 1983; *Sirignano et al.*, 2004]. We therefore applied corrections for the interference by N₂O to the CO₂ isotopic measurements of +0.23‰ to $\delta^{13}C$ values and +0.30‰ to $\delta^{18}O$ values [*Sirignano et al.*, 2004]. These same corrections applied to the 1972–1973 data set result in good consistency between this data set, especially the clean air $\delta^{13}C$ value determined in 1973, and that expected for clean air at the time, based on data from the literature (Figure 2).

2.4. Analytical Uncertainties

[14] The manometric measurements of CO₂ mixing ratios are inferred to be accurate to within ~1 ppm on the basis of duplicate measurements of NIST Standard Reference

Material 1672a (sample number 40-15-B, with a nominal CO₂ mixing ratio of 355.19 ± 0.36 ppm) that gave mixing ratios of 354.2 and 355.4 ppm. Overall reproducibility (1σ) is estimated to be ≤3 ppm for 1972–1973 and ~1 ppm for 1998–2003, on the basis of measurements of air collected simultaneously into two or three bulbs.

[15] Measurements of PDB and Harding Iceland Spar calcite (HIS) in 1972–1973 indicate accuracies of ~0.08‰ for $\delta^{13}C$ and ~0.16‰ for $\delta^{18}O$; measurements of NBS-19, two NOAA air standards, and one standard gas from Oztech Trading Corporation (Safford, AZ) (CALT-1399C) indicate accuracies of ~0.06‰ for $\delta^{13}C$ and ~0.09‰ for $\delta^{18}O$ in 1998–2003, based on the average differences between our measured values and the nominal value of the standards (Table 1). The overall reproducibility of our isotopic measurements of CO₂ in air improved from 1972 to 1973 to 1998–2003: it was 0.12‰ for $\delta^{13}C$ and 0.19‰ for $\delta^{18}O$ in

Table 1. Analyses of Standard Gases[a]

Standard	Nominal $\delta^{13}C_{PDB}$ (‰)	Nominal $\delta^{18}O_{PDB-CO2}$ (‰)	Nominal CO_2 (ppm)	n	Measured $\delta^{13}C_{PDB}$	Measured $\delta^{18}O_{PDB-CO2}$	Measured CO_2 (ppm)	Measured − Nominal $\delta^{13}C$	Measured − Nominal $\delta^{18}O$
PDB[b]	0	10.11		3	−0.03 ± 0.07	10.32 ± 0.15		−0.03	0.21
Harding Iceland spar calcite (HIS)[b]	−4.80	−8.63		7	−4.89 ± 0.03	−8.71 ± 0.14		−0.09	−0.08
CALT-1399C[c] (CO_2 gas)	−3.62	−15.82		2	−3.57 ± 0.01	−15.86 ± 0.02		0.05	−0.05
NBS-19[c] (carbonate)	1.95	−2.20		7	1.84 ± 0.11	−2.21 ± 0.17		−0.11	−0.01
NOAA airCAO5624[c]	−10.67	−6.26	415.25	9	−10.68 ± 0.09	−6.44 ± 0.13	415 ± 1	0.01	−0.18
NOAA airCAO5740[c]	−8.04	−3.48	369.4	5	−8.12 ± 0.08	−3.58 ± 0.23	370 ± 2	−0.08	−0.10

[a]The same solid source material was used to generate the reference gases during the two time periods (HIS). CO_2 gas from solid carbonate standards (PDB, HIS, NBS-19) was evolved at 25°C with 100% phosphoric acid [*Gonfiantini et al.*, 1993].
[b]Analyzed for the 1972–1973 data set.
[c]Analyzed for the 1998–2003 data set; nominal values from the NOAA laboratory.

1972–1973 and 0.07‰ for $\delta^{13}C$ and 0.09‰ for $\delta^{18}O$ in 1998–2003, based on measurements of two or three bulbs collected simultaneously. These values include uncertainties contributed by the collection procedure, the extraction procedure, and the mass spectrometric analysis.

[16] The accuracy of $\delta^{18}O$ measurements has been the source of much concern, because it is easily modified after sample collection by exchange with water that may condense on the inside walls of the sampling flask [*Gemery et al.*, 1996]. As mentioned above, after November 2001, all samples were collected while being dried by passing through $Mg(ClO_4)_2$. Even before that time, during both the 1972–1973 and 1998–2001 collection periods, we do not believe that the oxygen isotopic compositions of the samples were compromised because the CO_2 was extracted immediately after collection, and Pasadena is known to have a semiarid climate, with low atmospheric moisture content.

3. Results

[17] Concentration and isotopic composition results are summarized in Table 2 and Figures 2–5 for Pasadena air,

"nominally" clean air, and possible pollutants. The average CO_2 mixing ratio of midday air in 1972–1973 was 366 ppm, considerably lower than the 1998–2003 average of 397 ppm (1972–1973 range: 328–431 ppm; n = 78; 1998–2003 range: 362–513 ppm; n = 1114). The average $\delta^{13}C$ value in atmospheric CO_2 from the early 1970s, −10.04‰, was within 2σ of that from the more recent time period, −9.82‰, while the extremes of the 1972–1973 range, −13.64 to −7.77‰ (n = 78), were slightly more positive (i.e., more enriched in ^{13}C) than the range in 1998–2003 (−14.12 to −8.02‰; n = 1083). The average $\delta^{18}O$ value from the early 1970s, −1.28‰, was within 2σ of that from the more recent time period ($\delta^{18}O$ = −1.07‰), and the range, −3.56 to +0.21‰ (n = 53), was very similar to that from 1998 to 2003 (−3.99 to +0.45‰; n = 1086; Table 2). The 1972–1973 data set includes data for two summers, making it biased owing to trends associated with seasonal variations, as observed in both background air [*Keeling et al.*, 1984] and urban air [*Pataki et al.*, 2003]. For example, during summer months, air over the Pacific ocean contains less CO_2 with lower $\delta^{13}C$ values than the rest of the year, corresponding to uptake by vegetation during the growing

**Table 2.** Summary of 1972–1973, 2002–2003, and 1998–2003 CO_2 Parameters

	Data for Full Time Period		Data Used in Discussion	
	30 May 1972 Through 6 August 1973	26 October 1998 Through 30 December 2003	June 1972 Through May 1973	January 2002 Through December 2003
Background air CO_2[a] (ppm)	325 ± 2	372 ± 1	325 ± 2	375 ± 1
Background air $\delta^{13}C$[a] (‰)	−7.48 ± 0.03	−8.15 ± 0.02	−7.48 ± 0.03	−8.19 ± 0.02
Background air $\delta^{18}O$[b] (‰)	+0.21 ± 0.09	+0.13 ± 0.04	+0.21 ± 0.09	+0.33 ± 0.04
Pasadena CO_2 range	328–431	362–513	328–431	376–513
average (ppm)	366	397	363	404
Pasadena $\delta^{13}C$ range	−13.64−−7.77	−14.12−−8.02	−13.64−−7.77	−13.88−−8.37
average	−10.04	−9.82	−9.86	−9.84
Pasadena $\delta^{18}O$ range	−3.56−+0.21	−3.99−+0.45	−3.56 − +0.21	−3.70−+0.33
average (‰)	−1.28	−1.07	−1.28	−1.02
Local contribution of CO_2 recorded at Pasadena, CA (ppm)[c]	41 ± 4	25 ± 3	38 ± 4	29 ± 3
Keeling intercept - $\delta^{13}C$ (‰; 1σ errors)	−31.1 ± 0.5	−28.5 ± 0.4	−30.9 ± 0.5	−29.9 ± 0.2
Keeling intercept - $\delta^{18}O$ (‰; 1σ errors)	−15.6 ± 0.8	−13.9 ± 0.3	−15.6 ± 0.8[d]	−13.9 ± 0.5
$\delta^{13}C$ from mass balance from all anthropogenic sources (1σ errors) (Appendix A)			−30.3 ± 0.4	−30.7 ± 0.4

[a]Values for background air CO_2 and $\delta^{13}C$ are from averages for the 25°N–40°N oceanic sites of the NOAA-ESRL network, for 1998–2003 and 2002–2003. The 1972–1973 values for CO_2 and $\delta^{13}C$ were calculated from the quadratic regression trend determined for the 1998–2003 clean air data and the Northern Hemisphere averages for 1956 and 1978 from *Keeling et al.* [1979] (see caption to Figure 2). The original NOAA-ESRL data can be found at ftp://ftp.cmdl.noaa.gov/ccg.
[b]Values for clean air $\delta^{18}O$ for 1998–2003 and 2002–2003 are from the averages of the NOAA-ESRL oceanic/coastal sites.
[c]Calculated as the difference between the average Pasadena CO_2 concentration and the average background air CO_2 concentration.
[d]Since $\delta^{18}O$ data were collected only for 27 November 1972 through 6 August 1973, and not for an entire year, the Keeling intercept for this time period is that reported here.
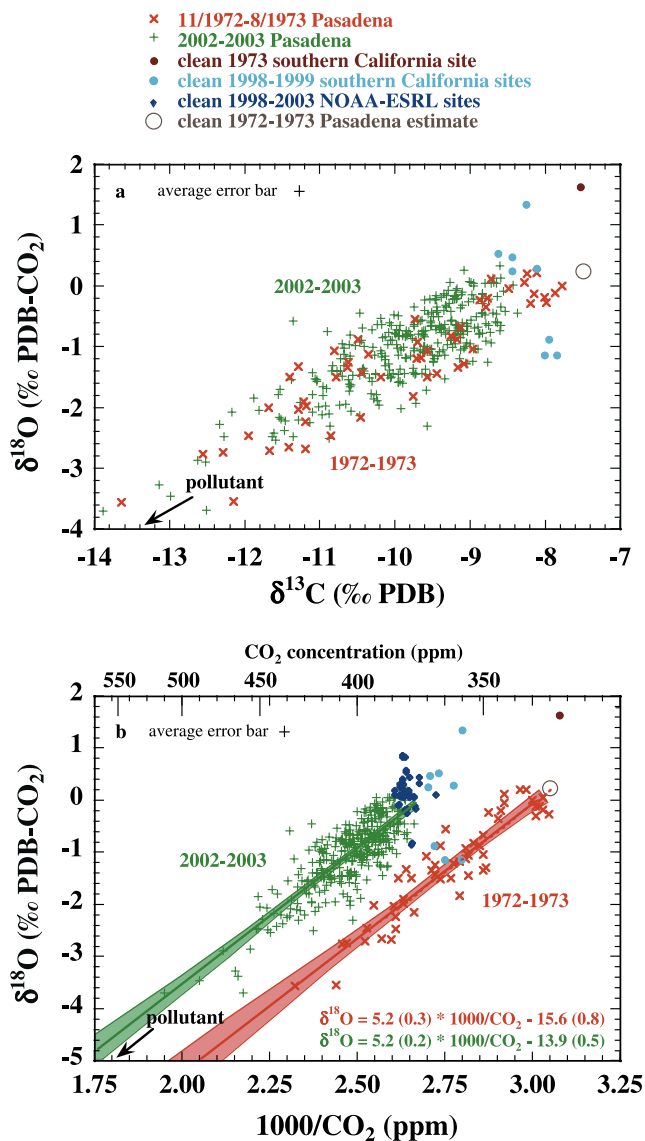
Figure 3. Plots of oxygen isotopic data: (a) δ^{18}O versus δ^{13}C and (b) δ^{18}O versus 1000/CO$_2$ of air in Pasadena for the November 1972 through August 1973 and 2002–2003 time periods, together with linear regression trends. The light brown dot and the light blue dots are the data for the 1973 and 1998–1999 southern California nominally clean air samples, respectively (see caption for Figure 2 and Table 2). The small dark blue diamonds in Figure 3b are the data for the 2002–2003 midday air sampled at the oceanic and coastal NOAA-ESRL sites located between 25°N and 40°N latitude (sites listed in the caption for Figure 2). The open brown circle indicates the composition for background air in 1972–1973: the concentration and δ^{13}C are from Figure 2, and the δ^{18}O was estimated by extrapolating the best fit linear regression line in Figure 3b to the background air concentration for this time period. This extrapolation is indicated by the red dot in the middle of the open brown circle. The best fit equations in Figure 3b are in the colors of the symbols with 1σ uncertainties in parentheses.

season [*Keeling et al.*, 1984; *Keeling and Whorf*, 1985]. Therefore, in the rest of this paper, we limit our discussion to the data for June 1972 through May 1973 for CO$_2$ mixing ratios and δ^{13}C values. The average CO$_2$ mixing ratio for this time period is 363 ppm, and the average δ^{13}C is −9.86‰ (Table 2). The δ^{18}O data are only available for the period of November 1972 through August 1973 and we therefore use this time period for our δ^{18}O comparison.

[18] The δ^{13}C values are frequently observed to vary linearly with 1/CO$_2$ [e.g., *Bakwin et al.*, 1998; *Keeling*, 1958; *Keeling et al.*, 1979; *Miller and Tans*, 2003; *Pataki et al.*, 2003] owing to mixing between background air and a relatively constant CO$_2$-rich source. Figure 2 demonstrates such a relationship for the data sets presented here, with the dark green-outlined field indicating the entire 1998–2003 data set and the red-outlined field indicating the entire May 1972 through August 1973 data set. The major difference between the two arrays, separated in time by roughly 30 years, reflects the increase in the CO$_2$ content of background air over this time period. Indeed, to first order, the data array from 1998 to 2003 is simply displaced to higher CO$_2$ mixing ratios (i.e., to the left) relative to the earlier data (∼30 ppm higher). Figures 2a and 2b, for years 1999 and 2003 respectively, demonstrate that the progressive shift of the data arrays to higher CO$_2$ mixing ratios with similar ranges in δ^{13}C can be distinguished on time periods of 4 years. Although there is very little evidence of the long-term secular trend from one year to the next, there can be unique events (such as forest fires). Therefore we minimize unique year-to-year variations where possible, by combining 2002 and 2003 for the recent time period. Thus, the rest of this discussion focuses on comparing the data for June 1972 through May 1973 to the data for January 2002 through December 2003.

[19] The composition of background air, unaffected by local anthropogenic sources, through time is indicated by the heavy purple curve in Figure 2. This is a quadratic fit to the annual mean values for 1998–2003 collected at eight NOAA-ESRL oceanic and coastal background air sites located between 25 and 40°N (flask data collected at 1100–1800 LT; data shown as blue diamonds in Figure 2c) and the 1956 and 1978 Northern Hemisphere averages reported by *Keeling et al.* [1979] (see caption to Figure 2 for details; this group of sites is hereafter referred to as "the NOAA-ESRL sites"). This trend is consistent with data collected in La Jolla, CA, just ∼200 km south of Pasadena [*Keeling et al.*, 2005]. We have not used the La Jolla data because it is available only for 1978–2002, and therefore covers neither the time period of our earlier data set, nor the latest part of our recent data set. In order to determine the composition of CO$_2$ of background air for specific dates, we calculated δ^{13}C from a linear best fit to the δ^{13}C versus date relationship for the NOAA-ESRL sites and 1956 and 1978 Northern Hemisphere averages reported by *Keeling et al.* [1979]. We then estimated the mixing ratios using the quadratic fit in Figure 2. The data for the background air samples collected during the two time periods (dark red and cyan dots in Figure 2, indicating data for 1973 and 1998–1999, respectively) are consistent with this calculated trend. All δ^{13}C values for Pasadena air from both time periods are lower than those expected for background air, on the basis of the regression curve in Figure 2: in 1972–1973, the highest

data point was −7.77‰, compared with the background air value of −7.48‰ at the beginning of 1973, and the highest 2002–2003 data point was −8.37‰, compared with the background air value −8.17‰ at the beginning of 2003 (Table 2).

[20] Figure 3a shows $\delta^{18}O$ versus $\delta^{13}C$ for Pasadena air during the two time periods. The two data sets overlap, although the November 1972 through August 1973 $\delta^{13}C$ data extend to more positive values. The observation that the 1972–1973 data are not more scattered than the 2002–2003 data is consistent with our assertion above that the dry climate in southern California resulted in little, if any, exchange between CO_2 and H_2O in the sample flasks before analysis (as has been described for humid sites by *Gemery et al.* [1996]). The overlap suggests that the major difference in the CO_2 isotopic compositions between the two time periods is a small decrease in $\delta^{13}C$ over the 30 years between the two data collections. Not surprisingly, given the shift in CO_2 content between 1972 and 1973 and 2002–2003, the two data sets are separated on a plot of $1000/CO_2$ versus $\delta^{18}O$ (Figure 3b). In contrast to the plots of $\delta^{13}C$ versus $1000/CO_2$, for which the yearly data show a progression through time, this is not the case for $\delta^{18}O$, mainly because there has not been a regular, monotonic change in $\delta^{18}O$ through time. Since no background data from the NOAA-ESRL sites or the La Jolla pier site are available to use to estimate the average background air composition for the 1972–1973 time period (ftp://ftp.cmdl.noaa.gov/ccg/co2), we do not have an independent estimate for the oxygen isotopic composition of unambiguously clean air for this earlier time period. The dark red dot is the data point for the one air sample collected in 1973 in Newport Beach, CA, which is a relatively clean, coastal site within the metropolitan Los Angeles region. However, the open brown circle represents an estimate of the value for $\delta^{18}O$ for that time period (+0.21 ± 0.09‰) calculated from the best fit $\delta^{18}O$-$1000/CO_2$ line for the 1972–1973 data shown in Figure 3b using the CO_2 mixing ratio for background air based on the quadratic trend for the $\delta^{13}C$-$1000/CO_2$ relationship for background air (i.e., the purple curve in Figure 2).

[21] The distributions of data are shown in histograms of CO_2 contents and $\delta^{13}C$ and $\delta^{18}O$ values for the 1972–1973 and 2002–2003 time periods (Figure 4). The larger number of measurements in the recent time period and the main points described in the previous paragraphs are apparent in Figure 4: the significant offset in the CO_2 mixing ratio between the two time periods (~40 ppm) and the very similar ranges in $\delta^{13}C$ and $\delta^{18}O$ for the two time periods. The histograms also show a skewing of the 2002–2003 data away from the background air end of the distribution (i.e., the distribution is asymmetric, with the bulk of the compositions falling closer to background air and a tail extending to high CO_2 mixing ratios and more negative $\delta^{13}C$ and $\delta^{18}O$ values). This analysis takes into account the differing number of samples in the two data sets. The distributions of the 1972–1973 data are flatter in $\delta^{13}C$ and $\delta^{18}O$; this may reflect the small number of data points from this time period.

[22] Results of analyses of human breath and exhaust from burning gasoline and natural gas are plotted in Figure 5. $\delta^{13}C$ and $\delta^{18}O$ from exhaust from a gasoline-burning automobile

were −26.0 ± 0.2‰ and −14.2 ± 0.3‰, respectively. The estimated $\delta^{13}C$ values of CO_2 produced by natural gas combustion and human breath exhalation were −40.2 ± 0.5‰ and −20.9 ± 0.4‰, respectively; the $\delta^{18}O$ of CO_2 from natural gas combustion and human exhalation were −21.3 ± 0.4‰ and −5.2 ± 0.3‰, respectively. Although this $\delta^{18}O$ value for human breath is higher than that reported for Paris, France, by *Widory and Javoy* [2003] (−24.5‰), it is similar to that reported by *Epstein and Zeiri* [1988] (−18.7 − −23.5‰) and *Affek and Eiler* [2006] (−22.3 ± 0.2‰) for subjects in the San Gabriel valley and probably reflects a larger proportion of C_4 plants in the Californian diet relative to that in France. Possible relationships of these potential sources of CO_2 to the trends displayed by our analyses of Pasadena air are discussed below.

4. Discussion

4.1. CO₂ Mixing Ratios, $\delta^{13}C$, and $\delta^{18}O$ in 1972–1973 and 2002–2003 Pasadena Air

[23] From 1972 to 1973 to 2002–2003, the average CO_2 mixing ratio in Pasadena air has increased from 363 to 404 ppm but the average $\delta^{13}C$ value has remained almost constant, changing from −9.86 to −9.84‰, as has $\delta^{18}O$, which changed from −1.28 to −1.02‰, within 2σ of each other. As explained in the results section, the CO_2 and $\delta^{13}C$ values for 1972–1973 are for June 1972 through May 1973 and the $\delta^{18}O$ data are for November 1972 through August 1973. In the following discussion, these time periods will be referred to as 1972–1973. The data indicated as 2002–2003 refers to January 2002 through December 2003.

[24] The differences in CO_2 mixing ratio and $\delta^{13}C$ values between average Pasadena CO_2 and those of background air (based on the trend for the eight oceanic and coastal NOAA-ESRL sites and the Northern Hemisphere averages for 1956 and 1978 [*Keeling et al.*, 1979]; Figure 2) were smaller in 2002–2003 than in 1972–1973 (Figure 4). This difference for $\delta^{18}O$ values is insignificant. The skewness (asymmetry) and kurtosis (flatness) statistics associated with these histograms support these observations. The CO_2 mixing ratio histogram is significantly more skewed toward lower concentrations and significantly more peaked in 2002–2003 than in 1972–1973 (skewness of 1.6 ± 0.3 and 0.6 ± 0.6, respectively; kurtosis of 4.4 ± 0.5 and −0.3 ± 1.4, respectively; n = 56 for 1972–1973 and 336 for 2002–2003; errors are twice the standard error) [e.g., *Snedecor and Cochran*, 1967; *White*, 1980]. The $\delta^{13}C$ histogram is significantly sharper, more peaked, in 2002–2003 than in 1972–1973 (kurtosis of 1.8 ± 0.6 and −0.6 ± 1.3, respectively) (Figure 4). The composition of CO_2 was typically further away from that of background air and therefore more polluted in 1972–1973 than in 2002–2003. For neither time period do the data for CO_2 mixing ratio or $\delta^{13}C$ composition overlap the respective average background air value.

4.2. Mixing Relationships

[25] The simplest interpretation of the linear $\delta^{13}C$ versus $1000/CO_2$ relationships (Figure 2) is mixing between a background air end-member (with low CO_2 mixing ratio and high $\delta^{13}C$) and an end-member (or a relatively constant combination of end-members) that reflects a polluted source
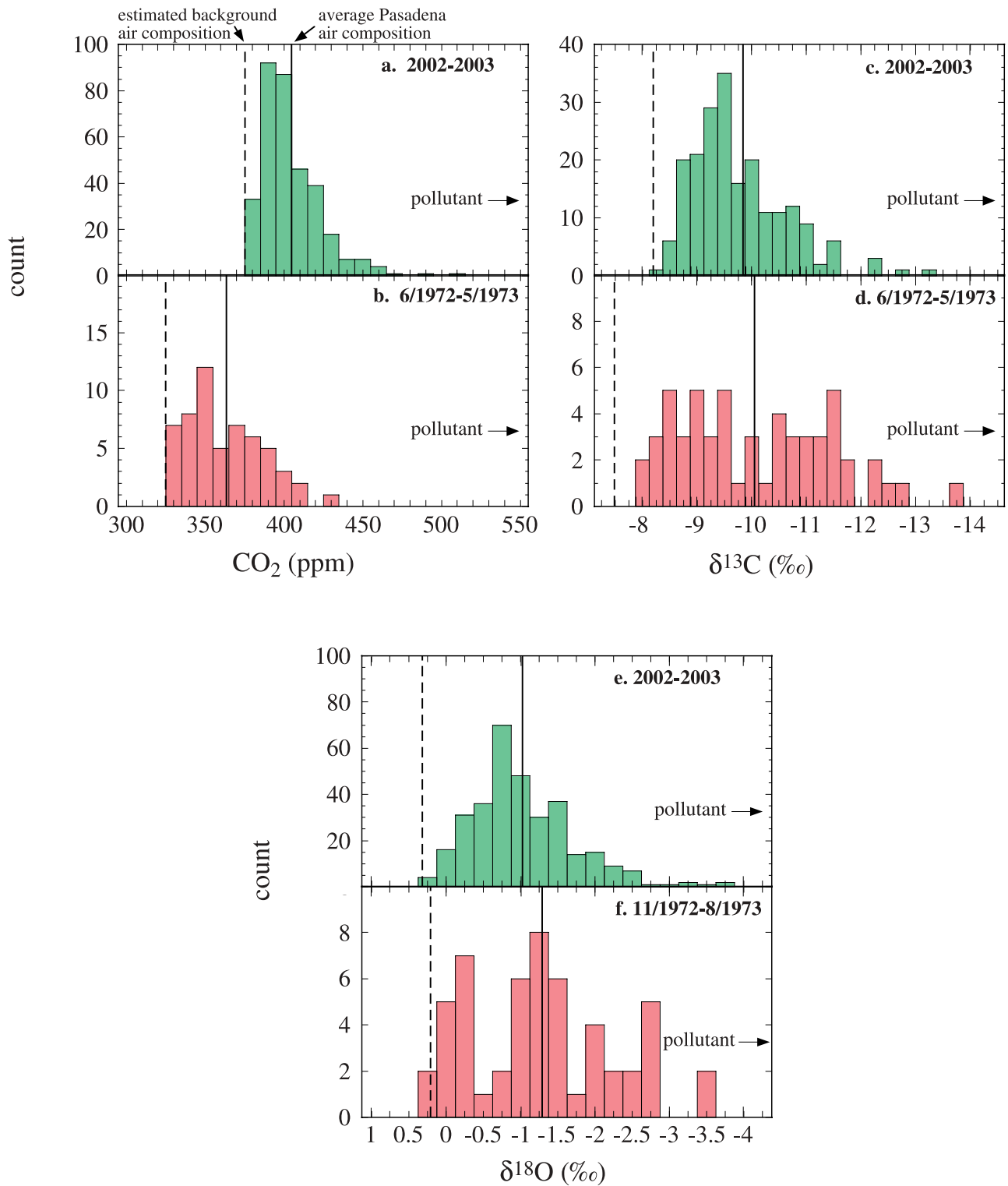
Figure 4. Histograms comparing the distributions of (a, b) CO$_2$ concentration, (c, d) δ^{13}C, and (e, f) δ^{18}O in the two time periods studied here. Also noted are the average compositions for Pasadena (solid vertical lines) and for background air from the average 25–40°N NOAA-ESRL oceanic sites listed in the caption to Figure 2 (vertical dashed lines, labeled "average background air composition" in Figure 4a), except that the clean δ^{18}O value shown for 1972–1973 is that indicated in Figure 3b, estimated by extrapolating the best fit linear regression line in Figure 3b to the background air concentration for this time period.
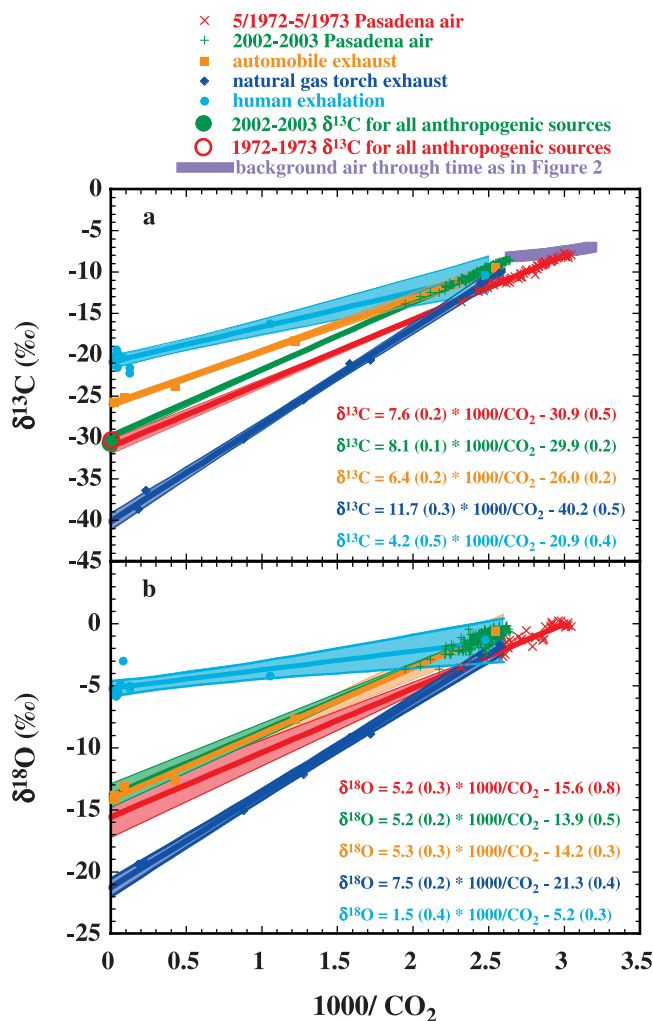
Figure 5. Plots versus $1000/CO_2$ showing (a) $\delta^{13}C$ and (b) $\delta^{18}O$ values of possible pollutants, along with the data for Pasadena, for both the 1972–1973 and 2002–2003 time periods. The lines are the results of simple linear regression and the shaded regions are 95% confidence bounds for the functions of the various data sets. The best fit equations are shown in the same colors as the symbols (1σ errors in parentheses).

(with high CO_2 mixing ratio and low $\delta^{13}C$). In this section, we characterize these end-members.

4.2.1. Isotopic Composition of Clean Air

[26] The $\delta^{13}C$ value of clean air during each time period should be close to the values observed at the low-CO_2 mixing ratio end of the respective data set. Figure 2a compares our Pasadena samples with samples from nominally clean-air sites collected in 1973 and 1998–1999 from background California sites (dark red and cyan dots, respectively, in Figure 2). That the measurements from these nearby sites are indeed representative of "clean" air (as opposed to air that although clean relative to typical Pasadena air is still nonnegligibly influenced by the addition of pollutants) is demonstrated by the observed overlap between them and the trend through time for clean air based on the composition of oceanic and coastal air between latitudes of 25 and 40°N for 1998–2003 and the Northern

Hemisphere averages determined for 1956 and 1978 by *Keeling et al.* [1979] (Figure 2). In addition, the intersections of the best fit lines in Figures 2a, 2b, and 2c with this background air trend differ on average by 0.15‰ from the $\delta^{13}C$ values expected for 1972–1973 on the basis of the trend for background air in Figure 2 (well within the 1σ errors for the best fit lines given in Figure 2, which average 0.23‰). This agreement further demonstrates that our data are consistent with global measurements for background air. Thus, the CO_2 mixing ratio of the background air end-member for the 2002–2003 time period was taken to be 375 ppm, with −8.19‰ for $\delta^{13}C$ (Table 2), the averages for this time period of the midday values for the NOAA-ESRL sites. During 1972–1973, background air contained 325 ppm CO_2 with $\delta^{13}C$ of −7.48‰, calculated from the trends through time for background air for CO_2 mixing ratios and $\delta^{13}C$ values.

[27] The background air composition for $\delta^{18}O$ relevant to Pasadena during 2002–2003 was determined in the same way as that for $\delta^{13}C$: the average compositions of each of the NOAA-ESRL sites were averaged for the time period of interest (Figure 3 and Table 2). As described above, the background air $\delta^{18}O$ value for 1972–1973 was estimated from the linear regression equation for the $\delta^{18}O$-$1000/CO_2$ relationship, using the CO_2 mixing ratio calculated from the background air trend through time. These calculations result in $\delta^{18}O$ background air values of +0.21 ± 0.09‰ and +0.33 ± 0.04‰ for 1972–1973 and 2002–2003, respectively (Table 2).

4.2.2. Isotopic Composition of the Polluted Source End-Member

[28] The CO_2 end-member associated with local sources can be defined by the $\delta^{13}C$ intercepts at $1000/CO_2 = 0$ (pure CO_2) in Figure 2, independent of the composition of background air [*Keeling*, 1958, 1961a]. This end-member, or mixture of end-members, is assumed to be approximately constant over the time period of the data set being plotted. The $\delta^{13}C$ – $1000/CO_2$ correlations were fit to lines using simple linear regression [*Zobitz et al.*, 2006], with 95% confidence bounds (2σ). Fits and their parameters for 1999, 2003, 2002–2003, and 1972–1973 are given in Figure 2. As noted above, there is more scatter in the 1999 than 2003 data, which may be due to enhanced local effects from vegetation close to the ground or exhaust from cars passing by on the road 40 m away from the sampling site (Site 2). Indeed, such very localized exhaust would result in isotopic variability of the high-CO_2 end-member, as observed by *Clarke-Thorne and Yapp* [2003] in Dallas, TX.

[29] On the basis of the fits discussed above, the high-CO_2 (i.e., polluted) end-members in Pasadena air during 1972–1973 and 2002–2003 were characterized by $\delta^{13}C$ of −30.9 ± 0.5‰ and −29.9 ± 0.2‰, respectively (1σ errors), within 2σ of each other (Table 2). These end-members are more depleted in ^{13}C than most pure end-member reservoirs discussed in the literature except for natural gas. For example, *Keeling et al.* [1979] concluded that the values they obtained, −26.97‰ for Inyo mountains, California in 1956 and −26.54‰ for 1978 average Northern Hemisphere, represented the composition of CO_2 contributed by a local air source from plant biological processes and/or the burning of fossil fuels. The average products of biological activity (e.g., plant photosynthesis and ecosystem

respiration) produce CO$_2$ with δ^{13}C of -24.7 ± 0.8‰ [*Bakwin et al.*, 1998]. Production of cement generates CO$_2$ emissions with δ^{13}C of 0.0 ± 0.3‰ [*Tans*, 1981]. Our measurements of human breath and automobile exhaust, at -20.9 ± 0.4‰ and -26.0 ± 0.2‰ (Figure 5), are also more positive than the ^{13}C-depleted end-member in Pasadena. Although some sources of oil used and refined in California are also more enriched in ^{13}C (e.g., average oil pumped from California wells and average foreign oil imported into and refined in California has δ^{13}C of $-23.1 - -30.0$‰) [e.g., *Affek and Eiler*, 2006; *Chung et al.*, 1992, 1994; *Yeh and Epstein*, 1981], Pasadena's local CO$_2$ source is similar to oil from Alaska's north slope (-30.0 ± 0.4‰) [*Chung et al.*, 1992]. On the other hand, the δ^{13}C intercepts of the best fit lines for our data are significantly more positive than that of natural gas (-40.2 ± 0.5‰; Figure 5). Thus a combination of anthropogenic sources (combustion of petroleum from various sources and natural gas and possibly a small contribution from cement production) can explain the δ^{13}C of the ^{13}C-depleted end-member, although some contribution from local biological activity cannot be ruled out.

[30] Given the large number of potential sources of isotopically light carbon that could be contributing to the light CO$_2$ source end-member in Figure 2, we cannot uniquely determine the actual proportions of the sources responsible for this end-member. We can, however, evaluate whether the δ^{13}C value of this intercept can be quantitatively explained by the known consumption of fossil fuels (gasoline and other petroleum products, coal, and natural gas) together with contributions from cement production (similar to the approach taken by *Lowry et al.* [2001] to evaluate sources of methane in London, England).

[31] Although the necessary statistics are not available specifically for the Los Angeles region, relevant information is available for the state of California as a whole, and therefore we assume, as a first approximation, that this statewide information is representative of the Los Angeles region for 2002–2003. Since it is even more difficult to estimate these values for the 1972–1973 time period, we use global statistics. A summary of the parameters and the sources of data are given in the Appendix. According to *Bemis and Allen* [2005], cement production contributed 1.7% of anthropogenic CO$_2$ in the state and fossil fuel combustion contributed the remaining 98.3% during 2002. Comparable worldwide data for 1972–1973 [*Andres et al.*, 2000] indicate that cement production contributed 2.0% of anthropogenic CO$_2$. Records from the Energy Information Administration of the U.S. Department of Energy (see references in Appendix A) indicate that 56% of the state's energy from fossil fuels was produced from petroleum products, 43% from natural gas, and 1% from coal in 1972–1973; and 62% of the state's energy from fossil fuels was produced from petroleum products, 37% from natural gas, and 1% from coal in 2002–2003. Using the δ^{13}C values and uncertainties for each of these sources of CO$_2$, we estimate that the anthropogenic input had a δ^{13}C value of -30.3 ± 0.4‰ in 1972–1973 and -30.7 ± 0.4‰ in 2002–2003 (see Appendix A). These values determined by mass balance agree with the δ^{13}C end-members for Pasadena air (-30.9 ± 0.5‰ in 1972–1973 and -29.9 ± 0.2‰ in 2002–2003), at the 95% confidence level.

[32] Thus, although both the relative proportions of the different types of fossil fuels burned and their origins (which determine their isotopic compositions) changed over the two measurement periods, these differences appear to have canceled each other out, leading to very similar isotopic compositions of the polluted end-member in Pasadena. To illustrate this and to determine whether the proportions or isotopic compositions of the components are more important in determining the overall composition of δ^{13}C value of the polluted source end-member, we have recalculated the 2002–2003 end-member composition by changing the 1972–1973 parameters one at a time. For example, if we recalculate the composition for 2002–2003 by adjusting the isotopic composition of oil for the changing mix of imported petroleum (see Appendix A), while keeping the relative proportions of the different fossil fuels the same as in 1972–1973, the mass balance produces a more negative bulk δ^{13}C value for 2002–2003 (-31.3 ± 0.4‰) than for 1972–1973 (-30.3 ± 0.3‰), opposite to the observed direction of change that is observed in Table 2. Alternatively, if the isotopic compositions of the components were assumed to be the same in the two time periods and only their proportions changed, we would expect a shift of the intercept to slightly less negative values (from -30.3 ± 0.3‰ in 1972–1973 to -29.5 ± 0.3‰ calculated for 2002–2003). The Pasadena intercept did indeed shift to a more positive value (-30.9 ± 0.5‰ to -29.9 ± 0.2‰; Table 2), very similar to this scenario. Therefore, our results support a change in the relative proportions of natural gas and petroleum products burned, a shift to less natural gas and more petroleum, between 1972–1973 and 2002–2003, as indicated by government records (http://www.eia.doe.gov/emeu/states/sep_use/total/use_tot_ca.html). From our perspective, the important point is that the relatively small observed change in the δ^{13}C of the polluted end-member over this 30-year interval is not unexpected given the change in sources of fossils fuels burned; however, understanding the details will likely require better knowledge of the proportions of the components consumed and isotopic compositions (especially of petroleum) used in southern California as functions of time (see Appendix A).

[33] The δ^{18}O composition of the polluted source end-member was determined in a similar fashion from the δ^{18}O–1000/CO$_2$ correlation (Figure 3b). Although there is more scatter in this correlation than in the comparable relationship for δ^{13}C (Figure 2c), there is a dominant mixing relationship between background air with δ^{18}O close to 0‰ ($+0.21 \pm 0.09$‰ and $+0.33 \pm 0.04$‰ for 1972–1973 and 2002–2003, respectively) and a high-CO$_2$ end-member with δ^{18}O $= -15.6 \pm 0.8$‰ for 1972–1973 and -13.9 ± 0.5‰ for 2002–2003 (Figure 5b). These intercept values are heavier than the oxygen isotopic composition of atmospheric O$_2$, -17.0 ± 0.3‰ [*Kroopnick and Craig*, 1972], although the 1972–1973 value overlaps it at the 95% confidence level. The δ^{18}O of CO$_2$ produced by combustion is generally assumed to be the same as that of the atmospheric O$_2$ that is consumed in the combustion process [*Ciais and Meijer*, 1998; *Kroopnick and Craig*, 1972; *Pataki et al.*, 2003; *Zimnoch et al.*, 2004; *Zondervan and Meijer*, 1996]. However, *Affek and Eiler* [2006] found much more ^{18}O-enriched oxygen in CO$_2$ emitted by an automobile burning gasoline (-11.0 ± 0.2‰), even more enriched

Table A1. The $\delta^{13}C$ for Petroleum Products Burned

Oil Sources	$\delta^{13}C^a$ (‰)	Estimated Fraction From Source in 1972−1973[b]	Fraction From Source in 2002−2003[c]
California	−23.5 ± 0.4	0.89	0.452
North Slope, AK	−30.0 ± 0.4	0.042	0.226
Foreign: 1972−1973	−26.8 ± 1.3	0.066	
2002−2003	−26.1 ± 1.3		0.322
Composite $\delta^{13}C$ (‰)		−23.9 ± 0.4	−25.8 ± 0.5

[a]Estimates of $\delta^{13}C$ from *Andrusevich et al.* [2000], *Chung et al.* [1992, 1994], *Hwang et al.* [2002], *Sofer* [1984], *Yeh and Epstein* [1981] and I. Kaplan (personal communication, 2001). For California oil, we used the fraction of oil production by coastal counties and inland counties [*Division of Oil, Gas, & Geothermal Resources*, 2003, 2004] to weight isotopic compositions given by *Sofer* [1984] and *Yeh and Epstein* [1981] for Santa Maria, Los Angeles, and Ventura (coastal) and San Joaquin (inland) oils. Using the isotopic composition of the crude oil to estimate the value for CO_2 released during combustion of refined gasoline can be problematic [*Bush et al.*, 2007; *Widory*, 2006]. However, our analyses of automobile exhaust (Figure 5; −26.0 ± 0.2‰) agree very well with the estimate given above for the 2002−2003 composite $\delta^{13}C$ (−25.8 ± 0.5‰).

[b]Proportions from California, Alaska, and foreign sources for 1972−1973: http://www.eia.doe.gov/emeu/aer/txt/ptb0501.html. This table gives the historical sources of fossil fuels broken down by lower 48 U.S. states, Alaska, and imports. Since California does not have its own records for sources of crude oil prior to 1982, we have applied the ratios for the national crude oil sources between 1972 and 1982 for each source location to the California values for 1982 to calculate California values for 1972. This is a reasonable estimate, since the trends after 1982 are similar (compare http://www.energy.ca.gov/oil/statistics/crude_oil_receipts.html and Figure 11 of http://www.eia.doe.gov/emeu/aer/eh/frame.html).

[c]Proportions from California, Alaska, and foreign sources for 2002−2003: http://www.energy.ca.gov/oil/statistics/crude_oil_receipts.htmlFractions of petroleum from different foreign locations from: http://www.energy.ca.gov/oil/statistics/2002_foreign_crude_sources.html and http://www.energy.ca.gov/oil/statistics/2003_foreign_crude_sources.html.

in $\delta^{18}O$ than the intercept for our gasoline exhaust measurements (−14.2 ± 0.3‰; Figure 5). They attributed this elevated $\delta^{18}O$ (i.e., relative to atmospheric O_2) to exchange equilibration between CO_2 and H_2O (both produced in the combustion process) in the exhaust tail pipe [*Affek and Eiler*, 2006]. The intercept we obtained for CO_2 generated by burning of natural gas (−21.3 ± 0.4‰; Figure 5) also differs from atmospheric O_2, but it is more depleted in ^{18}O than atmospheric O_2. Our result for natural gas combustion is consistent with the suggestion of *Pataki et al.* [2003] that, although oxygen isotope fractionation during the combustion process has not been thoroughly studied, it could result in more negative $\delta^{18}O$ values than normally expected. We do not have corresponding data for combustion of coal, but as discussed above, coal represents a small fraction of the fossil fuels burned in California and therefore is not expected to have a significant impact on the isotopic composition of CO_2 produced by combustion. These values for the local CO_2 source (−15.6‰ for 1972−1973 and −13.9‰ for 2002−2003) are similar to average values observed for plant respiration, ∼−14‰ [e.g., *Farquhar et al.*, 1993a, 1993b; *Flanagan et al.*, 1997]. The 1972−1973 value is similar to and the 2002−2003 value more enriched than the −17‰ estimated for soil respiration in Pasadena [*Affek and Eiler*, 2006]. Given the significant uncertainties in the $\delta^{18}O$ values of CO_2 generated by burning of various fossil fuels and the effects of biological activity, we have not attempted to model the change in the oxygen isotope composition of the polluted end-member through time, and simply note that there has not been a significant change.

4.3. Evaluation of CO₂ Input From Biological Activity

[34] Carbon isotopic compositions may offer some constraints on the relative importance of biogenic and anthropogenic CO_2 sources in the urban air of Pasadena. Although the $\delta^{13}C$ of the local CO_2 source can be explained quantitatively using known amounts of fossil fuel combustion and cement production, we have not accounted for contributions from local biological activity, which is usually considered to be an important contributor to the mass balance of CO_2 and

$\delta^{13}C$ even in urban settings [*Clark-Thorne and Yapp*, 2003; *Farquhar et al.*, 1989; *Keeling*, 1958; *Keeling et al.*, 1979; *Kuc*, 1991; *Pataki et al.*, 2003]. If we assume that photosynthetic/respiration processes contribute CO_2 with $\delta^{13}C$ of −24.7‰ [*Bakwin et al.*, 1998], we can estimate limits to the contribution of this component in the CO_2 budget of Pasadena air. We assume the proportions and isotopic compositions of the various fossil fuels (petroleum products, natural gas, and coal) and cement production given in the preceding section (see Appendix A) and then ask how much CO_2 with a $\delta^{13}C$ value of −24.7‰ can be accommodated given the errors on the best fit $\delta^{13}C$ intercept. The best fit intercept for 1972−1973 is −30.9 ± 0.5‰ and the calculated $\delta^{13}C$ of the anthropogenic component is −30.3 ± 0.4‰. The best fit intercept for 2002−2003 has a $\delta^{13}C$ of −29.9 ± 0.2‰, and the calculated anthropogenic source has a value of −30.7 ± 0.4‰. Using the 2σ error limits of the best fit intercepts and calculated anthropogenic $\delta^{13}C$ values, the range of allowable biological input to the CO_2 inventory in Pasadena for 1972−1973 is 0 − 17% and for 2002−2003 is 0−29%. This range (0 − 29%) for the contribution of plant and soil activity to the local contribution of CO_2 is consistent with other estimates for urban environments: for example, on the basis of ^{14}C measured in a nearby location on the Caltech campus, the daytime biospheric contribution is ∼ 20% of the local carbon source, with 80% being products of the combustion of fossil fuel [*Xu et al.*, 2006]. Similarly, *Pataki et al.* [2003] obtained an average contribution from biological activity in Salt Lake City for 2002 of 23%, with variations from 0 to 60%, depending on the time of year. The larger range in Salt Lake City is due to the greater seasonal variations in weather and plant activity occurring there.

4.4. Amount of Local CO₂ Inventory Resulting From Fossil Fuel Combustion

[35] Having identified the isotopic composition of the local CO_2 source as being dominantly due to combustion of fossil fuels, we can determine how much of the local CO_2 inventory is from this source. The simplest method is to

Table A2. The $\delta^{13}C$ Expected From Fossil Fuels Consumed

Year	Coal[a] (TBtu)	Fraction of Coal Burned	$\delta^{13}C$ of Coal Burned[b] (‰)	Natural Gas[a] (TBtu)	Fraction of Natural Gas Burned	$\delta^{13}C$ of Natural Gas[b] (‰)	All Petroleum Products[a] (TBtu)	Fraction of Petroleum Burned	$\delta^{13}C$ (‰) of Petroleum Products[b]	$\delta^{13}C$ of Fossil Fuels Burned[b] (‰)
1972–1973	57.25	0.011	−24.1 ± 0.3	2228.8	0.429	−40.2 ± 0.5	2912.3	0.560	−23.9 ± 0.4	−30.9 ± 0.3
2002–2003	69.75	0.011	−24.1 ± 0.3	2267.6	0.372	−40.2 ± 0.5	3794.3	0.619	−25.8 ± 0.5	−31.2 ± 0.4

[a]Amount of fuel consumed is taken from http://www.eia.doe.gov/emeu/states/sep_use/total/use_tot_ca.html for 1972, 1973, and 2002; http://www.eia.doe.gov/emeu/states/sep_fuel/html/fuel_use_cl.html, http://www.eia.doe.gov/emeu/states/sep_fuel/html/fuel_use_ng.html, and http://www.eia.doe.gov/emeu/states/sep_fuel/html/csv/use_pet_all_btu.csv for 2003 values of coal, natural gas, and total petroleum products, respectively. Amounts given as 1972–1973 and 2002–2003 are the averages of the values for the 2 years.

[b]Isotopic compositions for petroleum are from Table A1; isotopic composition of natural gas is from this study; isotopic composition of coal is from *Tans* [1981].

assume that all of the CO_2 in the local air in excess of the estimated background mixing ratios is due to combustion of fossil fuels. This is consistent with the conclusions of the previous section: at the 1σ level, no net input from biological sources is necessary to account for the observed isotopic compositions (although up to ~30% is permissible). This suggests an average contribution from the polluted end-member of 38 ± 4 ppm during 1972–1973 and 29 ± 3 ppm during 2002–2003 (1σ errors given; Table 2) and that the amount of CO_2 added during the two time periods to the local atmosphere has decreased. The decrease in CO_2 added between the two time periods is surprising given the known increase in population and number of automobiles in the region that is expected to lead to an increased urban CO_2 source. Indeed, carbon emissions in California have increased ~13% between 1972 and 1973 and 2001, according to *Blasing et al.* [2004]. An increase in the height of the planetary boundary layer (PBL) would lead to an increase in the mixing volume, which could explain this inconsistency [e.g., *Makar et al.*, 2006; *Oke*, 1973; *Sarkar et al.*, 1998]. The PBL could deepen owing to an increased urban heat island resulting from increased anthropogenic heat flux from the increase in population in the greater Los Angeles area (from 9 to 15 million people from 1970 to 2000 in Los Angeles, Riverside, and San Bernardino counties, an increase of 67.5%; http://www.dof.ca.gov/HTML/DEMOGRAP/SDC/documents/1970-1980-1990-2000 Comparability file.xls, accessed 20 May 2008), as well as the increase in housing density and industrial/commercial/transportation land use (from the land use maps for 1992 and 2001 from http://nmviewogc.cr.usgs.gov/viewer.htm, accessed 22 May 2008). Although the direction of these changes is consistent with the apparent inconsistency, unfortunately, data to quantify the PBL depth change are not available. However, in order to explain why the local CO_2 contribution has decreased to 29 ppm instead of increasing 13% to 43 ppm by this mechanism, the height of the daytime PBL must have increased by ~50% between 1972 and 1973 and 2002–2003, which is highly unlikely.

5. Conclusions

[36] The urban environment of Pasadena, California, in the San Gabriel valley of the Los Angeles basin, has created a distinctive pattern of CO_2 mixing ratio and isotopic composition of ambient air through time. We report data for flask samples collected sporadically from late May of 1972 through early August of 1973, and collected every 1 to 2 days from October 1998 through December 2003. CO_2 mixing ratios have increased by 30–40 ppm during the 30-year interval between the two data sets. Although the mixing ratio and isotopic composition of CO_2 in the cleanest air have changed to a similar extent relative to those from the background-air oceanic/coastal sites of the NOAA-ESRL network, the average carbon and oxygen isotopic compositions in Pasadena air have changed very little between 1972 and 73 and 2002–2003. The carbon isotopic composition of the polluting end-member appears to have been very similar 30 years ago to what it is today (2002–2003), owing to compensating changes in the proportions of different fossil fuels burned and in the sources of petroleum used in California. The average

Table A3. The $\delta^{13}C$ for All Anthropogenic Sources

Year	Fraction of CO₂ From Fossil Fuels Burned[a]	$\delta^{13}C$ Fossil Fuels[b] (‰)	Fraction of CO₂ From Cement Production[a]	$\delta^{13}C$ Cement[c] (‰)	$\delta^{13}C$ Expected From All Anthropogenic Sources (‰)
1972–1973	0.980	−30.9 ± 0.3	0.020	0 ± 0.4	−30.3 ± 0.3
2002–2003	0.983	−31.2 ± 0.4	0.017	0 ± 0.4	−30.7 ± 0.4

[a]The fractions of CO₂ from fossil fuels burned and cement production for 1972–1973 are worldwide values from *Andres et al.* [2000]. The fractions for 2002–2003 are for 2002 in California from *Bemis and Allen* [2005].
[b]From Table A2.
[c]From *Tans* [1981].

mixing ratio and carbon isotopic composition of CO₂ in Pasadena air has become more similar to that of clean air during the 30 years between collection of the two data sets.

[37] The polluted source end-member contributed on average 38 ± 4 ppm of the total inventory of CO₂ in Pasadena air in 1972–1973 and 29 ± 3 ppm CO₂ in 2002–2003 on the basis of estimates of the composition of clean air at the same latitude from clean oceanic and coastal sites in the NOAA-ESRL network, in apparent contradiction to the known increase in CO₂ emissions between the two time periods.

[38] There is a large range in both CO₂ mixing ratio and carbon isotopic composition in Pasadena that is consistent with mixing between a ^{13}C-enriched, low-CO₂ background air end-member and a ^{13}C-depleted, high-CO₂ pollutant. The average carbon isotopic compositions of the pollutant for May 1972 to May 1973 ($\delta^{13}C_{VPDB} = -30.9 \pm 0.5‰$) and 2002–2003 ($\delta^{13}C_{VPDB} = -29.9 \pm 0.2‰$) reflect the combustion of approximately equal amounts of gasoline and natural gas, with small contributions from coal burning and cement production. Oxygen isotopic compositions of the pollutant were more enriched (−15.6 ± 0.8‰ and −13.9 ± 0.5‰, in 1972–1973 and 2002–2003, respectively) than that of atmospheric oxygen (−17.0 ± 0.3‰ [*Kroopnick and Craig*, 1972]). This difference may reflect oxygen isotopic fractionations among combustion products during and after combustion and/or the effects of biological contributions (up to ∼30% of the CO₂ in the CO₂-rich end-member could be contributed from biological activity).

[39] The stable isotopic methods employed here illustrate how this type of data can be used to identify anthropogenic sources contributing to the CO₂ inventory. In order to understand global changes, it is important to understand the details of changes in significant regional sources, such as urban metropolitan areas, through time.

Appendix A

[40] Mass balance calculations were performed to estimate the carbon isotopic composition of the fossil fuel mixture that provides the local CO₂ source in southern California (results are given in the text above). These estimates are used in comparison to the compositions determined by the polluted source CO₂ end-member obtained from the intercept of the $\delta^{13}C$ versus 1000/CO₂ plots (Figure 2). The parameters used in the mass balance calculations are given in Tables A1–A3.

References

Affek, H. P., and J. M. Eiler (2006), Abundance of mass 47 CO₂ in urban air, car exhaust and human breath, *Geochim. Cosmochim. Acta*, *70*, 1–12, doi:10.1016/j.gca.2005.08.021.

Andres, R. J., G. Marland, T. A. Boden, and S. Bischof (2000), Carbon dioxide emissions from fossil fuels consumption and cement manufacture, 1751–1991, and an estimate of their isotopic composition and latitudinal distribution, in *The Carbon Cycle*, edited by T. M. L. Wigley and D. S. Schimel, pp. 53–62, Cambridge Univ. Press, New York.

Andrusevich, V. E., M. H. Engel, and J. E. Zumberge (2000), Effects of paleolatitude on the stable isotope composition of crude oils, *Geology*, *28*(9), 847–850, doi:10.1130/0091-7613(2000)28<847:EOPOTS>2.0.CO;2.

Bakwin, P. S., P. P. Tans, J. W. C. White, and R. J. Andres (1998), Determination of the isotopic ($^{13}C/^{12}C$) discrimination of terrestrial biology from a global network of observations, *Global Biogeochem. Cycles*, *12*(3), 555–562, doi:10.1029/98GB02265.

Bemis, G., and J. Allen (2005), Inventory of California greenhouse gas emissions and sinks: 1990 to 2002 update, report, Calif. Energy Comm., Sacramento.

Blasing, T. J., C. T. Broniak, and G. Marland (2004), Estimates of annual fossil-fuel CO₂ emitted for each state in the U.S.A. and the District of Columbia for each year from 1960 through 2001, in *Trends: A Compendium of Data on Global Change*, http://cdiac.ornl.gov/trends/emis_mon/stateemis/emis_state.html, Carbon Dioxide Inf. Anal. Cent., Oak Ridge, Tenn.

Bush, S. E., D. E. Pataki, and J. R. Ehleringer (2007), Sources of variation in delta C-13 of fossil fuel emissions in Salt Lake City, USA, *Appl. Geochem.*, *22*(4), 715–723, doi:10.1016/j.apgeochem.2006.11.001.

Chung, H. M., M. A. Rooney, M. B. Toon, and G. E. Claypool (1992), Carbon isotope composition of marine crude oils, *Am. Assoc. Pet. Geol. Bull.*, *76*(7), 1000–1007.

Chung, H. M., G. E. Claypool, M. A. Rooney, and R. M. Squires (1994), Source characteristics of marine oils as indicated by carbon isotopic ratios of volatile hydrocarbons, *Am. Assoc. Pet. Geol. Bull.*, *78*(3), 396–408.

Ciais, P., and H. A. J. Meijer (1998), The $^{18}O/^{16}O$ isotope ratio of atmospheric CO₂ and its role in global carbon cycle research, in *Stable Isotopes*, edited by H. Griffiths, pp. 409–431, BIOS Sci., Oxford, U. K.

Ciais, P., P. P. Tans, M. Trolier, J. W. C. White, and R. J. Francey (1995), A large northern hemispheric terrestrial CO₂ sink indicated by the $^{13}C/^{12}C$ ratio of atmospheric CO₂, *Science*, *269*, 1098–1102, doi:10.1126/science.269.5227.1098.

Clark-Thorne, S. T., and C. J. Yapp (2003), Stable isotope constraints on mixing and mass balance of CO₂ in an urban atmosphere: Dallas metropolitan area, TX, USA, *Appl. Geochem.*, *18*(1), 75–95, doi:10.1016/S0883-2927(02)00054-9.

Demeny, A., and L. Haszpra (2002), Stable isotope compositions of CO₂ in background air and at polluted sites in Hungary, *Rapid Commun. Mass Spectrom.*, *16*, 797–804, doi:10.1002/rcm.640.

Division of Oil, Gas, & Geothermal Resources (2003), 2002 annual report of the State Oil and Gas Supervisor, Calif. Dep. of Conserv., Sacramento.

Division of Oil, Gas, & Geothermal Resources (2004), 2003 annual report of the State Oil and Gas Supervisor, Calif. Dep. of Conserv., Sacramento.

Epstein, S., and L. Zeiri (1988), Oxygen and carbon isotopic compositions of gases respired by humans, *Proc. Natl. Acad. Sci. U. S. A.*, *85*(6), 1727–1731, doi:10.1073/pnas.85.6.1727.

Farquhar, G. D., J. R. Ehleringer, and K. T. Hubick (1989), Carbon isotope discrimination and photosynthesis, *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, *40*, 503–537, doi:10.1146/annurev.pp.40.060189.002443.

Farquhar, G. D., J. Lloyd, J. A. Taylor, L. B. Flanagan, J. P. Syvertsen, K. T. Hubick, S. C. Wong, and J. R. Ehleringer (1993a), Vegetation effects on the isotope composition of oxygen in atmospheric CO₂, *Nature*, *363*, 439–443.

Farquhar, G. D., J. Lloyd, J. A. Taylor, L. B. Flanagan, J. P. Syvertsen, K. T. Hubick, S. C. Wong, and J. R. Ehleringer (1993b), Vegetation effects on the isotope composition of oxygen in atmospheric CO₂ erratum, *Nature*, *365*, 368.

Flanagan, L. B., J. R. Brooks, G. T. Varney, and J. R. Ehleringer (1997), Discrimination against C¹⁸O¹⁶O during photosynthesis and the oxygen isotope ratio of respired CO₂ in boreal forest ecosystems, *Global Biogeochem. Cycles*, *11*(1), 83–98, doi:10.1029/96GB03941.

Gemery, P., M. Trolier, and J. White (1996), Oxygen isotope exchange between carbon dioxide and water following atmospheric sampling using glass flasks, *J. Geophys. Res.*, *101*, 14,415–14,420, doi:10.1029/96JD00053.

Gonfiantini, R., W. Stichler, and K. Rozanski (1993), Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements, in *Reference and Intercomparison Materials for Stable Isotopes of Light Elements. Proceedings of a Consultants Meeting Held in Vienna, 1–3 December 1993, IAEA-TEC-DOC-825*, pp. 13–29, Int. Atom. Energy Agency, Vienna.

Hwang, R. J., T. Heidrick, B. Mertani, Qivayanti, and M. Li (2002), Correlation and migration studies of North Central Sumatra oils, *Org. Geochem.*, *33*, 1361–1379, doi:10.1016/S0146-6380(02)00104-3.

Keeling, C. D. (1958), The concentration andisotopic abundances of carbon dioxide in rural areas, *Geochim. Cosmochim. Acta*, *13*, 322–334, doi:10.1016/0016-7037(58)90033-4.

Keeling, C. D. (1961a), The concentration and isotopic abundances of carbon dioxide in rural and marine air, *Geochim. Cosmochim. Acta*, *24*, 277–298, doi:10.1016/0016-7037(61)90023-0.

Keeling, C. D. (1961b), A mechanism for cyclic enrichment of carbon-12 by terrestrial plants, *Geochim. Cosmochim. Acta*, *24*, 299–313, doi:10.1016/0016-7037(61)90024-2.

Keeling, C. D., and T. P. Whorf (1985), The concentration of atmospheric carbon dioxide at Ocean Weather Station P from 1961 to 1981, *J. Geophys. Res.*, *90*(D6), 10,511–10,528, doi:10.1029/JD090iD06p10511.

Keeling, C. D., W. G. Mook, and P. P. Tans (1979), Recent trends in the ¹³C/¹²C ratio of atmospheric carbon dioxide, *Nature*, *277*, 121–123, doi:10.1038/277121a0.

Keeling, C. D., A. F. Carter, and W. G. Mook (1984), Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of atmospheric CO₂: 2. Results from oceanographic cruises in the tropical Pacific Ocean, *J. Geophys. Res.*, *89*(D3), 4615–4628, doi:10.1029/JD089iD03p04615.

Keeling, C. D., R. B. Bacastrow, A. F. Carter, S. C. Piper, T. P. Whorf, M. Heimann, W. G. Mook, and H. Roeloffzen (1989), A three-dimensional model of atmospheric CO₂ transport based on observed winds: 1. Analysis of observational data, in *Aspects of Climate Variability in the Pacific and the Western Americas, Geophys. Monogr. Ser.*, vol. 55, pp. 165–236, AGU, Washington, D. C.

Keeling, C. D., T. P. Whorf, M. Wahlen, and J. van der Plicht (1995), Interannual extremes in the rate and rise of atmospheric carbon dioxide since 1980, *Nature*, *375*, 666–670, doi:10.1038/375666a0.

Keeling, C. D., A. F. Bollenbacher, and T. P. Whorf (2005), Monthly atmospheric ¹³C/¹²C isotopic ratios for 10 SIO stations, in *Trends: A Compendium of Data on Global Change*, http://cdiac.ornl.gov/trends/CO2/iso-sio/iso-sio.html, Carbon Dioxide Inf. Anal. Cent., Oak Ridge, Tenn.

Kroopnick, P., and H. Craig (1972), Atmospheric oxygen: Isotopic composition and solubility fractionation, *Science*, *175*, 54–55, doi:10.1126/science.175.4017.54.

Kuc, T. (1986), Carbon isotopes in atmospheric CO₂ of the Krakow region: A two-year record, *Radiocarbon*, *28*(2A), 649–654.

Kuc, T. (1989), Changes of carbon isotopes in atmospheric CO₂ of the Krakow region in the last five years, *Radiocarbon*, *31*(3), 441–447.

Kuc, T. (1991), Concentration and carbon isotopic composition of atmospheric CO₂ in southern Poland, *Tellus, Ser. B*, *43*, 373–378.

Kuc, T., and M. Zimnoch (1998), Changes of the CO₂ sources and sinks in a polluted urban area (southern Poland) over the last decade, derived from the carbon isotope composition, *Radiocarbon*, *40*(1), 417–423.

Kuc, T., K. Rozanski, M. Zimnoch, J. Necki, L. Chmura, and D. Jelen (2007), Two decades of regular observations of (CO₂)-C-14 and (CO₂)-C-13 content in atmospheric carbon dioxide in central Europe: Long-term changes of regional anthropogenic fossil CO₂ emissions, *Radiocarbon*, *49*(2), 807–816.

Levin, I., and B. Kromer (1997), Twenty years of atmospheric ¹⁴CO₂ observations at Schauinsland Station, Germany, *Radiocarbon*, *39*(2), 205–218.

Lowry, D., C. W. Holmes, N. D. Rata, P. O'Brien, and E. G. Nisbet (2001), London methane emissions: Use of diurnal changes in concentration and delta C-13 to identify urban sources and verify inventories, *J. Geophys. Res.*, *106*(D7), 7427–7448, doi:10.1029/2000JD900601.

Lu, R., and R. P. Turco (1994), Air pollutant transport in a coastal environment. Part I: Two-dimensional simulations of sea-breeze and mountain effects, *J. Atmos. Sci.*, *51*(15), 2285–2308, doi:10.1175/1520-0469(1994)051<2285:APTIAC>2.0.CO;2.

Lu, R., R. P. Turco, and M. Z. Jacobson (1997a), An integrated air pollution modeling system for urban and regional scales: 2. Simulations for SCAQS 1987, *J. Geophys. Res.*, *102*(D5), 6081–6098, doi:10.1029/96JD03502.

Lu, R., R. P. Turco, and M. Z. Jacobson (1997b), An integrated air pollution modeling system for urban and regional scales: 1. Structure and performance, *J. Geophys. Res.*, *102*(D5), 6063–6079, doi:10.1029/96JD03501.

Makar, P. A., S. Gravel, V. Chirkov, K. B. Strawbridge, F. Froude, J. Arnold, and J. Brook (2006), Heat flux, urban properties, and regional weather, *Atmos. Environ.*, *40*, 2750–2766, doi:10.1016/j.atmosenv.2005.11.061.

Miller, J. B., and P. P. Tans (2003), Calculating isotopic fractionation from atmospheric measurements at various scales, *Tellus, Ser. B*, *55*, 207–214.

Mook, W. G., and S. van der Hoek (1983), The N₂O correction in the carbon and oxygen isotopic analysis of atmospheric CO₂, *Isot. Geosci.*, *1*, 237–242.

Mook, W. G., M. Koopmans, A. F. Carter, and C. D. Keeling (1983), Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of atmospheric carbon dioxide: 1. Results from land stations, *J. Geophys. Res.*, *88*(C15), 10,915–10,933, doi:10.1029/JC088iC15p10915.

Neiburger, M. (1969), The role of meteorology in the study and control of air pollution, *Bull. Am. Meteorol. Soc.*, *50*, 957–965.

Oke, T. R. (1973), City size and the urban heat island, *Atmos. Environ.*, *7*, 769–779, doi:10.1016/0004-6981(73)90140-6.

Park, R., and S. Epstein (1960), Carbon isotope fractionation during photosynthesis, *Geochim. Cosmochim. Acta*, *21*, 110–126, doi:10.1016/S0016-7037(60)80006-3.

Pataki, D., D. R. Bowling, and J. R. Ehleringer (2003), Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: Anthropogenic and biogenic effects, *J. Geophys. Res.*, *108*(D23), 4735, doi:10.1029/2003JD003865.

Pataki, D., D. R. Bowling, J. R. Ehleringer, and J. M. Zobitz (2006), High resolution atmospheric monitoring of carbon dioxide sources, *Geophys. Res. Lett.*, *33*, L03813, doi:10.1029/2005GL024822.

Pataki, D. E., T. Xu, Y. Q. Luo, and J. R. Ehleringer (2007), Inferring biogenic and anthropogenic carbon dioxide sources across an urban to rural gradient, *Oecologia*, *152*(2), 307–322, doi:10.1007/s00442-006-0656-0.

Sarkar, A., R. S. Saraswat, and A. Chandrasekar (1998), Numerical study of the effects of urban heat island on the characteristic features of the sea breeze circulation, *Proc. Indian Acad. Sci., Earth Planet. Sci.*, *107*(2), 127–137.

Sirignano, C., R. E. M. Neubert, and H. A. J. Meijer (2004), N₂O influence on isotopic measurements of atmospheric CO₂, *Rapid Commun. Mass Spectrom.*, *18*, 1839–1846, doi:10.1002/rcm.1559.

Snedecor, G. W., and W. G. Cochran (1967), *Statistical Methods*, 5th ed., Iowa State Univ. Press, Ames.

Sofer, Z. (1984), Stable carbon isotopic compositions of crude oils: Application to source depositional environments and petroleum alteration, *Am. Assoc. Pet. Geol. Bull.*, *68*(1), 31–49.

Tans, P. P. (1981), ¹³C/¹²C of industrial CO₂, in *Carbon Cycle Modelling*, edited by B. Bolin, pp. 127–129, John Wiley, Chichester, U. K.

Tans, P. P., I. Y. Fung, and T. Takahashi (1990), Observational constraints on the global atmospheric CO₂, *Science*, *247*, 1431–1438, doi:10.1126/science.247.4949.1431.

White, G. H. (1980), Skewness, kurtosis and extreme values of Northern Hemisphere geopotential heights, *Mon. Weather Rev.*, *108*, 1446–1455, doi:10.1175/1520-0493(1980)108<1446:SKAEVO>2.0.CO;2.

Widory, D. (2006), Combustibles, fuels and their combustion products: A view through carbon isotopes, *Combust. Theory Modell.*, *10*(5), 831–841, doi:10.1080/13647830600720264.

Widory, D., and M. Javoy (2003), The carbon isotope composition of atmospheric CO₂ in Paris, *Earth Planet. Sci. Lett.*, *215*(1–2), 289–298, doi:10.1016/S0012-821X(03)00397-2.

Xu, X., H. P. Affek, and S. Trumbore (2006), Delta-¹⁴C of atmospheric CO₂ in urban air, *Eos Trans. AGU*, *87*(36), West. Pac. Geophys. Meet. Suppl., Abstract A44A–0042.

Yeh, H. W., and S. Epstein (1981), Hydrogen and carbon isotopes of petroleum and related organic-matter, *Geochim. Cosmochim. Acta*, *45*, 753–762, doi:10.1016/0016-7037(81)90046-6.

Zimnoch, M., T. Florkowski, J. M. Necki, and R. E. M. Neubert (2004), Diurnal variability of δ^{13}C and δ^{18}O of atmospheric CO$_2$ in the urban atmosphere of Krakow, Poland, *Isot. Environ. Health Stud.*, *40*(2), 129–143, doi:10.1080/10256010410001670989.

Zobitz, J. M., J. P. Keener, H. Schnyder, and D. R. Bowling (2006), Sensitivity analysis and quantification of uncertainty for isotopic mixing relationships in carbon cycle research, *Agric. For. Meteorol.*, *136*, 56–75, doi:10.1016/j.agrformet.2006.01.003.

Zondervan, A., and H. Meijer (1996), Isotopic characterisation of CO$_2$ sources during regional pollution events using isotopic and radiocarbon analysis, *Tellus, Ser. B*, *48*, 601–612, doi:10.1034/j.1600-0889.1996.00013.x.

_____

H. P. Affek, Department of Geology and Geophysics, Yale University, New Haven, CT 06520-8109, USA.

S. Newman and E. Stolper, California Institute of Technology, Mail Code 170-25, Pasadena, CA 91125, USA. (sally@gps.caltech.edu)

X. Xu, Earth System Science, University of California, Irvine, CA 92612, USA.