VARIATION OF CONCENTRATION, ^{14}C ACTIVITY AND ^{13}C/^{12}C RATIOS OF CO$_2$ IN AIR SAMPLES FROM KITT PEAK, ARIZONA

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ABSTRACT. Air was sampled with 5L flasks at Kitt Peak (2100m elev) from 1983 through 1984 at approximately monthly intervals, occasionally supplemented with air samples from urban Tucson ca 75km away (760m elev). The Kitt Peak CO$_2$ concentrations, represented by a yield measurement, fluctuated ca 25% over the monitoring period. The δ^{13}C values (uncorrected for N$_2$O) varied from ca -7.6 to -9.0‰, with high values (and low CO$_2$ yields) in the late summer consistent with hemispheric seasonal biosphere effects. Tucson air has lower δ^{13}C values and possibly greater CO$_2$ yield suggesting a local fossil-fuel effect. ^{14}C activity of four Kitt Peak samples range from 1.158±.007 to 1.223±.008 as uncorrected fraction of modern, below free air activity of ca 1.250 for 1984 even after correcting for fractionation. The slightly low ^{14}C activity and δ^{13}C values suggest the Kitt Peak air is not quite 100% clean and there may be a local/regional fossil-fuel contribution, but CO$_2$ concentrations are similar to background atmospheric values.

INTRODUCTION

The ^{13}C/^{12}C ratios and ^{14}C activity of CO$_2$ in air have been used as a measure of the purity of the air with respect to anthropogenic contributions from fossil fuels which are ^{12}C-enriched with no measurable ^{14}C activity (Vogel & Uhlitzsch, 1975; Florkowski & Kuc, 1979; Klouda et al, 1986; Kuc, 1986). Normally, isolated coastal locations such as Mauna Loa, Hawaii, Pt Barrow, Alaska and the South Pole are preferred sites for CO$_2$ concentrations representative of "background" air. Values of CO$_2$ concentrations measured at Kitt Peak, Arizona (LS Waterman, pers commun, 1986), a continental site, seem compatible with those measured in remote coastal locations. We have sampled air at Kitt Peak over a two-year period and measured ^{13}C/^{12}C ratios and ^{14}C activity of the CO$_2$ to determine 1) the variability, 2) relationships of variations to local/regional air movement, and 3) if these parameters also evidence Kitt Peak as a "clean" air site.

METHODS

Arrangements were made in January 1983 to collect air samples on Kitt Peak (2100m elev) in conjunction with a National Oceanic and Atmospheric Administration (NOAA) program for measuring CO$_2$ concentrations at Kitt Peak. Kitt Peak personnel collected air in 5L evacuated glass flasks (usually two) on the same days that they collected samples for NOAA. The sampling dates in 1983 were Feb 1, Feb 23, Mar 20, Apr 27, May 28, Jun 26, Jul 31, Sep 11, Oct 25 and Nov 28; in 1984 the dates were Feb 16, Mar 18, May 29, Aug 28, Sept 18, Oct 29 and Dec 14. Nearly all flask samples (17 of 20) were taken between 1200 and 1500 hours Mountain Standard Time, with the most notable exception being Nov 28, 1983, when one flask was filled at noon and a second at midnight. All samples were taken atop one of the Kitt Peak tele-

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scopes with the exception of May 18, 1984 (1600 hours) which was obtained at ground level. For comparison, we took occasional samples (Jan 24, Aug 23 and Dec 29, 1983) at Tucson, ca 75km east of Kitt Peak, atop the Geology Building (ca 760m elev) of the University of Arizona.

Following cryogenic removal of water vapor with cold ethanol (-80°C) traps, carbon dioxide was collected from the air samples with liquid N_2. A CO_2 yield in moles was determined manometrically, and the CO_2 samples were subsequently analyzed mass spectrometrically to find $\delta^{13}C$ with respect to the PDB standard (Craig, 1957). Because N_2O was not removed from the air samples, there was biasing of mass ratios. According to calculations of Keeling, Mook and Tans (1979), our $\delta^{13}C$ values could be corrected for the N_2O contribution with a factor of ca +0.30‰ for 1983 and 1984. A measure of reproducibility is seen when comparing $\delta^{13}C$ from two flasks when filled on the same date, showing a mean difference of 0.22‰ (1σ=0.15‰).

We chose several samples representing diverse atmospheric conditions for ¹⁴C analysis by tandem accelerator mass spectrometry at the University of Arizona facility. The CO_2 samples from Aug 28, Sep 18 and Oct 29, 1984, were converted from gas to graphite by the catalytic reduction method of Jull *et al* (1986). The sample of Oct 25, 1983, had previously been converted to carbon by magnesium reduction in 1983, so it was recombusted to CO_2 in 1986 and converted to graphite by catalytic reduction. The ¹⁴C activity of all samples was calculated as fraction of modern without a $\delta^{13}C$ correction. Even for the samples converted directly from CO_2 gas which lack a $\delta^{13}C$ correction, however, the similarity of $\delta^{13}C$ values implies the ¹⁴C activities are directly intercomparable. For the sample that had first been Mg-reduced, there is a greater possibility for fractionation because of the added steps.

RESULTS AND DISCUSSION

Figure 1 summarizes the results from our flask sampling program including CO_2 yield, $\delta^{13}C$ (uncorrected for NO_2) and ¹⁴C activity. On many sampling dates, two values of $\delta^{13}C$ and yield are plotted, representing each of the two flasks collecting air. Because one of the flasks had a volume ca 5% larger than the other, one set of yield symbols (open triangles) is consistently higher than the other. After May 1984, only $\delta^{13}C$ was measured. The NOAA Kitt Peak CO_2 concentrations (ppm) determined over the same period are also depicted in Figure 1.

The Tucson flask CO_2 yields of Jan 24, Aug 23 and Dec 29, 1983 are clearly much greater than those at Kitt Peak, but this is likely a result of atmospheric pressure which in a standard atmosphere would be ca 1.18 × greater at Tucson's elevation than at Kitt Peak. The low $\delta^{13}C$ values of the Dec 29 and especially the Jan 24 samples do indicate the likely local contributions of ¹²C-enriched carbon from fossil fuels (and perhaps wood-burning stoves).

The $\delta^{13}C$ mean for all Kitt Peak analyses was -8.5‰. With an N_2O correction of +0.30‰, the $\delta^{13}C$ at Kitt Peak averaged -8.2‰ in 1983 and 1984. Based on extrapolation of $\delta^{13}C$ measurements (Mook, Carter & Keeling, 1983) at La Jolla, California, the same latitude as Tucson, $\delta^{13}C$ of ca -8.0‰ could be expected in 1983 and 1984. Our measurement is within 0.2‰ and
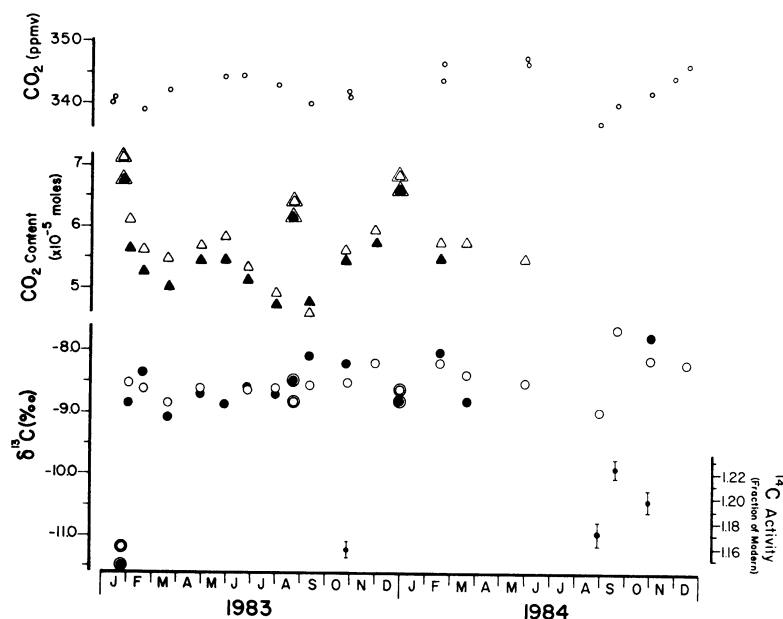
Fig 1. The ^{14}C activity [●] (uncorrected for $\delta^{13}C$), $\delta^{13}C$ [○, ●] (uncorrected for N_2O) and CO_2 yield [△, ▲] from flask samples taken at Kitt Peak, Arizona. The outlined yield and $\delta^{13}C$ values are from flask sampling at Tucson, Arizona. Where two values are plotted on the same sampling date, they represent results from separate flasks. The CO_2 concentrations [○] are results from a NOAA sampling program at Kitt Peak (LS Waterman, pers commun, 1986).

could indicate accuracy errors or continental biosphere or fossil-fuel con-tributions of $^{12}CO_2$. However, whereas the La Jolla $\delta^{13}C$ values show a decrease over the period 1978 to 1981, the Kitt Peak results seem to show increase in 1983 and 1984, contrary to an expected global atmospheric $\delta^{13}C$ decrease.

Sampling was not frequent enough to clearly delineate all seasonal and long-term trends, and some values may represent extremes of diurnal or short-term scatter rather than the mean. There is, however, the appearance in late summer 1983 that CO_2 yields are ca 25% lower while $\delta^{13}C$ is high relative to earlier in the year. This is consistent with the activity of the Northern Hemisphere seasonal biosphere, which effectively reduces atmos-pheric CO_2 concentrations by late summer and has a preference for fixation of $^{12}CO_2$, thus leaving the atmosphere temporarily enriched in $^{13}CO_2$. The Sep and Oct 1984 $\delta^{13}C$ values also seem to show this $^{13}CO_2$ atmospheric enrichment. The apparent seasonal fluctuations of $\delta^{13}C$ of atmospheric CO_2 have an amplitude of ca 0.5 to 1‰, similar to that reported at La Jolla of ca 0.5‰ (Mook, Carter & Keeling, 1983).

The highest ^{14}C activity and $\delta^{13}C$ were on Sep 18, 1984, suggesting exceptionally clean air, although the ^{14}C activity was still somewhat less than the free atmosphere value of ca 1.250 for 1984 cited by Harkness, Harrison and Bacon (1986). Because the free atmosphere value of 1.250 has appa-rently been corrected for isotopic fractionation, valid comparisons require

correction of our Kitt Peak activities. The corrected Kitt Peak ^{14}C activities range from ca 1.14 to 1.20, even more clearly lower than the likely free-air value. On Sep 18, the surface and upper air (500mb) winds were easterly and light (10–20km h^{-1}). The low ^{14}C activity and low $\delta^{13}C$ of air sampled on Aug 28 also occurred on an occasion in which both surface and upper air winds were low (10–20km h^{-1}), but the dominant direction was more southerly. The low ^{14}C activity, but apparently normal $\delta^{13}C$, of Oct 25, 1983 was also accompanied by southerly winds with much greater wind speed (20–40km h^{-1}). The intermediate ^{14}C activity of Oct 29, 1984, was associated with westerly winds. However, these are insufficient data for a high degree of confidence in the low ^{14}C-southerly winds association and the high ^{14}C-easterly winds association.

CONCLUSIONS

Trends of CO_2 (yield) and $\delta^{13}C$ of CO_2 from air at Kitt Peak generally conform to seasonal effects related to biospheric uptake of CO_2 (preferentially $^{12}CO_2$) during the summer and release during the winter. The $\delta^{13}C$ values tended to be slightly ^{12}C-enriched relative to the background values to be expected from air at this latitude, suggesting that the air may contain a CO_2 component from regional fossil-fuel or biospheric contributions, although the ca 0.2‰ enrichment may not be a significant difference. However, the ^{14}C activities of the CO_2 also tend to be slightly low compared to expected background values, lending support to the possibility of a fossil fuel rather than a biospheric regional contribution. This interpretation is still open to question and additional testing because Kitt Peak concentrations measured by NOAA do seem to correspond to expected background values of ca 345 ppmv, rather than showing elevated values from fossil-fuel additions. Finally, there is some evidence of southerly winds related to low CO_2 activity but there is no major fossil-fuel CO_2 source to the south of Kitt Peak. Additional ^{14}C analysis of other samples when air flow was westerly and northwesterly could further refine relationships of ^{14}C activity and air trajectory.

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