

VI. ANTHROPOGENIC VARIATIONS

URBAN ATMOSPHERIC ^{14}C O AND ^{14}C CH₄ MEASUREMENTS BY ACCELERATOR MASS SPECTROMETRY*

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ABSTRACT. Atmospheric gas samples (0.1m³) were collected at ground level during January/February 1984 in Las Vegas, Nevada for $^{14}\text{C}/^{13}\text{C}$ accelerator mass spectrometry and total abundance measurements of CO and CH₄. During winter months in this locale, CO concentrations can occur at 10 to 100 times background, occasionally exceeding the National Ambient Air Quality Standard (NAAQS). Methane concentrations show a slight enhancement (~24%) above the background (non-urban troposphere) level. A comparison of CO and CH₄ concentrations shows a good linear correlation which may indicate a common source. Preliminary $^{14}\text{C}/^{13}\text{C}$ results of the two species suggest that fossil emissions are the predominant source of excess CO and CH₄ in the samples taken. Estimates of anthropogenic CO and CH₄ are important for source apportionment of combustion emissions. In addition, this information is valuable for understanding the global CO and CH₄ cycles and, therefore, human impact on climate and the stratospheric ozone layer.

INTRODUCTION

During the winter months in the Central Valley area of Las Vegas, Nevada, carbon monoxide levels often exceed the 9ppm, 8 hour NAAQS. These periods of high CO, which are accompanied by elevated levels of total suspended particulate matter, occur on calm, clear evenings when the air temperatures drop rapidly in the late afternoon. Coincident with these observations is a brown-gray haze believed to be a result of primary emissions from urban activity. An inventory of local combustion sources suggests that residential wood burning and vehicle emissions are the major probable combustion sources responsible for the excess CO concentrations (Naylor, 1985).

The objective of this study was to estimate the impact of residential wood burning and vehicle emissions on Las Vegas, Nevada by 1) measuring the $^{14}\text{C}/^{13}\text{C}$ ratio in CO and CH₄ extracted from 0.1m³ whole air samples, and 2) measuring the CO and CH₄ concentrations in the same samples. The ^{14}C abundances in these two species relative to current living (contemporary) carbon gives a quantitative estimate of fossil/biogenic source contributions, *ie*, vehicle *vs* wood-burning sources. Ambient CO and CH₄ concentrations yield estimates for the amount of each species in excess of their 1984 background levels, ≈0.14ppm CO (at 45°N Lat, Khalil & Rasmussen, 1984) and ≈1.71ppm CH₄ (latitude band from 30°N–39°N, Blake & Rowland, *in press*), due to local sources. The determination of $^{14}\text{C}/^{13}\text{C}$ in CH₄ was expected to be more difficult since less carbon as CH₄ (at 2ppm, ~100μg-C) in contrast to CO (at 10ppm, ~500μg-C) would be available in 0.1m³ polluted air samples. Also, more precise $^{14}\text{C}/^{13}\text{C}$ measurements, ~3% relative standard error, are required for source discrimination since urban concentrations of CH₄ are only slightly in excess (~24%) of the background.

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EXPERIMENTAL METHODS

The experimental procedures include 1) ambient sampling, 2) CO and CH₄ concentration measurements, 3) extraction of CO and CH₄ fractions for carbon isotope measurements, 4) preparation of Fe-C alloy targets from extracted fractions for accelerator mass spectrometry (AMS) ¹⁴C/¹³C ratio measurements, and 5) measurements of ¹⁴C/¹³C ratios at the NSF-University of Arizona tandem accelerator mass spectrometer.

Ambient Sampling

Six samples of whole air were collected in the Las Vegas area by pumping air into evacuated 35L stainless steel cylinders to a pressure of ~303kPa absolute (45psia). Additional sampling details are listed in Table 1.

CO and CH₄ Concentration Measurements

Gas chromatographic (GC) separation of CO and CH₄ was performed on sample aliquots using a 5Å molecular sieve column at 105°C with N₂ carrier gas. A methanation system at the exit of the column consisted of a 350°C bed of Ni catalyst loaded on fire brick in an H₂ atmosphere and was used to convert the CO to CH₄. The CH₄ and CO converted to CH₄ were measured by a flame ionization detector. National Bureau of Standards (NBS) Standard Reference Material (SRM) gas mixtures; SRM 2612 (9.91ppm by mole(m) CO), SRM 2613 (17.9ppm(m) CO), SRM 1658 (0.97ppm(m) CH₄), and SRM 1660 (3.88ppm(m) CH₄), were used for GC calibration. Standard calibration curves for CO and CH₄ were obtained from the peak heights fit to the known concentrations. Sample concentrations were calculated from these curves based on their peak heights. The ambient sample concentrations are important in assuring quality control for the complete separation of these two species from the air sample. In addition, the degree of correlation between CO and CH₄ concentrations may provide information regarding source contributions. These results will be discussed below.

CO and CH₄ Extraction System

Gas samples were individually processed through a gas manifold (Fig 2) consisting of cryogenic traps and molecular sieve columns to remove CO₂, H₂O, and NO_x; and selective oxidizers for oxidation of CO and CH₄ (*cf*

TABLE 1
Ranges of sampling conditions: Las Vegas Valley, Nevada
(see Fig 1)

| |
|--|
| Dates: Jan 20–Feb 1, 1984 |
| Locations: East Charleston—elev 567m, Onyx—elev 628m (3 samples from each site) |
| Period: 1825 to 2005 |
| Duration: 10 to 20 min |
| Temperature: 10 to 13°C, except sample L1 at 3°C |
| Wind direction and speed: 230 to 270°, 10 to 16kmh ⁻¹ |
| Barometric pressure: 93 to 94kPa (701 to 711mm Hg) |

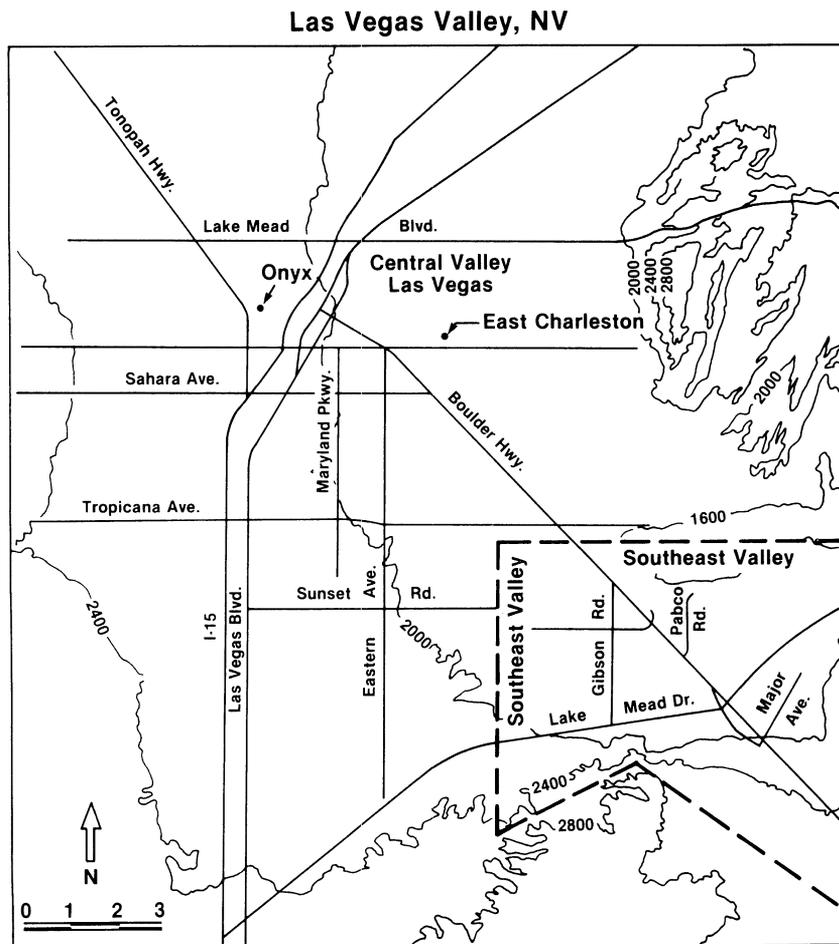


Fig 1. Map of Las Vegas Valley, Nevada

Stevens & Krout, 1972; Stevens & Rust, 1982). Liquid nitrogen (LN_2) trap #1 removed the bulk of sample atmospheric CO_2 , H_2O , and NO_x . Traces of these species not removed by LN_2 trap #1 and the two 13X molecular sieve columns were condensed in LN_2 trap #2. The Schutze Reagent, diiodine pentoxide impregnated in silica gel, oxidizes CO to CO_2 at room temperature and Hopcalite[®] at 480°C oxidized CH_4 to CO_2 . Carbon dioxide originating from CO was condensed in LN_2 capillary trap #3 and CO_2 originating from CH_4 was condensed in LN_2 capillary trap #4. The system was calibrated by processing several reference samples (Table 2) under identical conditions.

¹ Hopcalite[®] is a product of Mine Safety Appliances Co, Pittsburgh, Pennsylvania. This catalyst is primarily a blend of manganese and copper oxides.

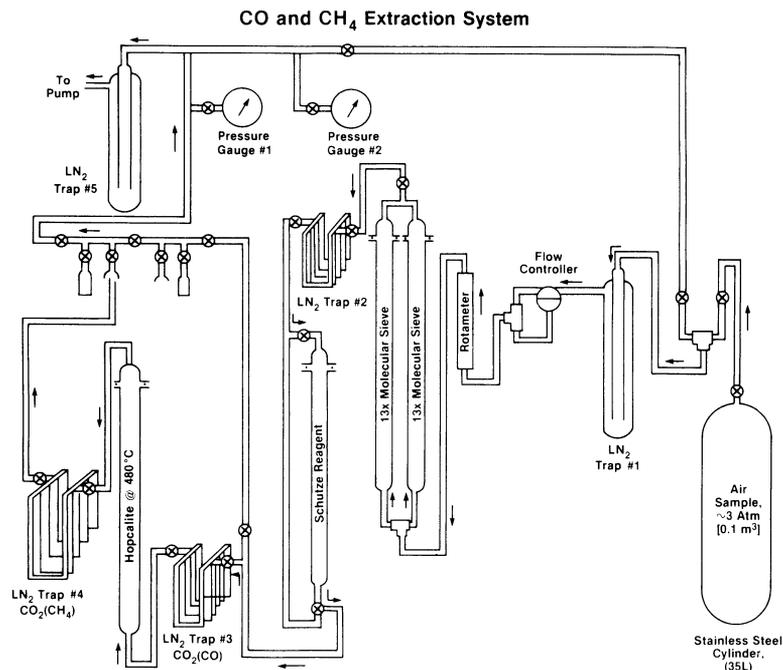


Fig 2. Schematic diagram of vacuum manifold for the extraction of CO and CH₄. CO oxidized by I₂O₅ (Schutze Reagent) to CO₂ is condensed in LN₂ trap #3. CH₄, oxidized by Hopcalite® catalyst to CO₂, is condensed in LN₂ trap #4.

Sample Processing

The preparation of the system required an initial baking out of the 13X molecular sieve columns at ~200°C and Hopcalite® at ~480°C. The latter was purged with He while heated, until virtually all adsorbed gases were removed. After bake-out procedures, the entire system generally reached a

TABLE 2
Concentrations of reference samples for characterization of
CO and CH₄ extraction system*

| Reference** sample | [CO] (SE, n) ppm (m) | [CH ₄] (SE, n) ppm (m) | [CO ₂] (SE, n) ppm (m) |
|-----------------------|-------------------------|---------------------------------------|---------------------------------------|
| 1 Blank | 0.02 (0.01, 3) | 0.02 (0.01, 2) | 0.20 (0.04, 3) |
| 2 Blank | 0.26 (0.01, 2) | 0.02 (0.01, 3) | 0.20 (0.04, 3) |
| 3 CO Ref Std | 10.25 (0.02, 4) | 0.02 (0.01, 3) | 249 (1, 3) |
| 4 CO Ref Std | 10.22 (0.02, 3) | 0.02 (0.01, 3) | 1.8 (0.1, 3) |
| 5 Air | 0.25 (0.02, 7) | 1.75 (0.02, 3) | 359 (2, 3) |
| 6 Air | 0.18 (0.01, 2) | 1.75 (0.02, 3) | 393 (2, 3) |

* All concentrations are in ppm by mole. The standard error and number of replicates are designated as (SE, n).

** Reference samples are described as follows: 1) Air Products (AP) He, ultra-pure carrier grade, 2) AP Air, zero grade 3) and 4) secondary CO reference standards produced by diluting NBS SRM 2620, 1% CO₂, and SRM 1681, 0.1% CO with AP air, zero grade, 5) AP breathing quality air, and 6) ambient laboratory air.

vacuum of 13Pa (0.1 mm Hg). Repeated processing of reference samples #1 and #2 (Table 2) yielded $\sim 30\mu\text{g}$ carbon blanks (total CO_2 condensed in LN_2 trap #4) for CH_4 oxidation and isolation. This constant blank remained even after extensive baking and purging of the catalyst. No leaks in the system were evident. Thus, blank runs, using He (ultra-pure carrier grade), were interspersed between sample runs to obtain enough CO_2 from the CH_4 blanks to measure ^{14}C . $^{14}\text{C}/^{13}\text{C}$ measurements of CH_4 fractions were then corrected for this blank contribution.

An air sample was first introduced into the evacuated system until a back pressure of 27kPa was reached. Valves at the source and before the vacuum pump were then regulated such that a flow of $\sim 1\text{Lmin}^{-1}$ and a pressure of 20 to 27kPa were observed. These conditions were maintained throughout the 6-hour processing period after which all but $\sim 0.7\text{kPa}$ remained unprocessed in the gas cylinder. The two isolated fractions, CO_2 originating from atmospheric CO (in LN_2 trap #3) and CO_2 originating from atmospheric CH_4 (in LN_2 trap #4), were then cryopumped at -196°C to remove any condensed oxygen, distilled at -78°C to remove H_2O , and transferred to ampules for subsequent sealing and storage until AMS target preparation.

The processing of blanks, CO reference samples and CH_4 reference samples (Table 2), yielded limits for system blanks, cross-contamination, and oxidation/recovery efficiencies. The system blanks and yields for separation and selective oxidation of CO and CH_4 were obtained by fitting a linear curve to the observed CO_2 recovered from oxidation *vs* the amount of CO_2 expected for each species. The intercept of each curve was an estimate of the blank and the slope was an estimate of the yield.

AMS Target Preparation and $^{14}\text{C}/^{13}\text{C}$ Measurement

Iron-carbon alloy targets of the CO and CH_4 fractions were prepared for AMS $^{14}\text{C}/^{13}\text{C}$ measurements by a method which involves 1) reducing sample CO_2 to C over hot Mg, 2) removing Mg and MgO by acid dissolution from the reduced carbon, and 3) fusing a mixture of iron powder and reduced sample carbon in an approximate ratio of 20:1 by weight at $\sim 1800^\circ\text{C}$ (Klouda *et al*, 1984). Slight modifications to this method of microgram target preparation were made in an attempt to reduce the background.²

Sample targets were measured for $^{14}\text{C}/^{13}\text{C}$ ratios four times each on the NSF-University of Arizona tandem accelerator mass spectrometer. Each run represented alternate measurements between ^{13}C (10s) and ^{14}C (50s) for 5 cycles (5min/run). Results are expressed as the fraction of "modern carbon," f_M , defined by the ratio of the sample $^{14}\text{C}/^{13}\text{C}$ signal to the $^{14}\text{C}/^{13}\text{C}$ signal for $0.95 \times \text{NBS SRM 4990B}$ oxalic acid. The fraction of contemporary (biogenic) carbon, f_C , is the adjustment of f_M to account for man's isotopic perturbations to atmospheric CO_2 .

²Mg powder was heated in an inert atmosphere to de-gas adsorbed atmospheric CO_2 contamination before the reduction step. Microcentrifugation was used to isolate the reduced carbon after the acid digestion step.

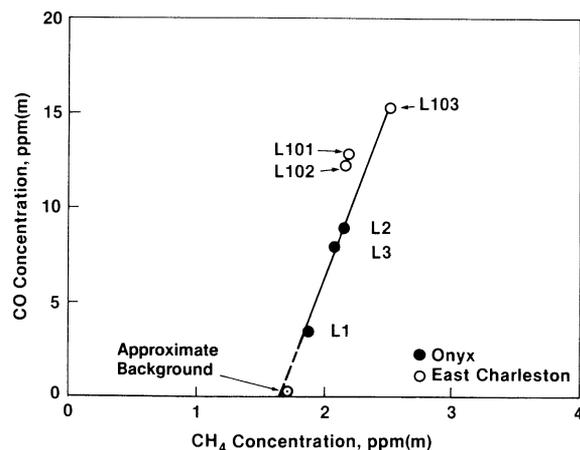


Fig 3. Ambient CO and CH₄ concentrations in ppm by mole. The standard errors, from sample CO measurements in quadruplicate, ranged from 0.01 to 0.07 with a median of 0.06 ppm(m). Standard errors for CH₄ measurements were 0.01 ppm(m). The line shown is a best fit to the four data points and is represented by the following equation: $y = (-30.4 \pm 1.9) + (18.3 \pm 0.9)x$, where y = CO concentration in ppm(m) and x = CH₄ concentration in ppm(m). "o" defines the approximate coordinate location for the background concentrations of the two species (Khalil & Rasmussen, 1984; Blake & Rowland, in press).

RESULTS AND DISCUSSION

Six samples of whole air were collected during Jan/Feb 1984 in Las Vegas (East Charleston and Onyx sites). Four of the 6 samples showed a good correlation ($r^2 = 0.995$, vs $r^2 = 0.841$ for all 6) between ambient CO and CH₄ concentrations (Fig 3) when fit to a linear curve. The goodness of fit resulting from this correlation suggests a common source for the excess of each species above background. An extrapolation of this curve to the approximate CO background concentration (~ 0.14 ppm, Khalil & Rasmussen, 1984) results in a CH₄ concentration of 1.66 ± 0.13 ppm(m), which is consistent with the background abundance of CH₄ cited earlier. Samples L101 and L102 are slightly displaced from this curve which may suggest an additional source input. An independent analysis of the CO and CH₄ concentrations by R A Rasmussen revealed a similar trend (Naylor, 1985, pers commun).

The procedure described for extraction of CO and CH₄ from air samples for ¹⁴C measurements was greater than $99.9928 \pm 0.0080\%$ efficient for removal of sample atmospheric CO₂ from the air stream. This estimate is defined by the equation $[1 - (m_1/m_2)] \times 100$ where m_1 is the total amount of condensable carbonaceous gases in LN₂ trap #2 and m_2 is the total amount of CO₂ processed from a 0.1 m³ reference sample containing the approximate ambient concentration of CO₂. Estimates of the system blanks (contamination) for CO and CH₄ extraction are 16 ± 8 and 33 ± 8 μg carbon. The oxidation/recovery efficiencies for CO and CH₄ were 97% and 76%, respectively. The equations which best describe the calibration of the

system for extraction of CO and CH_4 are the following:

$$\text{CO calibration;} \\ y = (1.30 \pm 0.68) + (0.97 \pm 0.02)x, \quad (n = 14) \quad (1)$$

$$\text{CH}_4 \text{ calibration;} \\ y = (2.72 \pm 0.65) + (0.76 \pm 0.10)x, \quad (n = 13) \quad (2)$$

where $y = \mu\text{moles}$ of carbon recovered as CO_2 from the oxidation and $x = \mu\text{moles}$ of carbon as CO_2 expected from the oxidation of the total amount of each species. CO and CH_4 fractions from samples L101, $605\mu\text{g-C}$ CO and $108\mu\text{g-C}$ CH_4 recovered, and L3, $409\mu\text{g-C}$ CO and $116\mu\text{g-C}$ CH_4 recovered, were prepared in the form of iron-carbon alloy targets for $^{14}\text{C}/^{13}\text{C}$ measurements. The target prepared from the CO fraction of sample L3 failed to produce a suitable ($>0.1\mu\text{Amp}$) $^{12}\text{C}^-$ beam, therefore, the $^{14}\text{C}/^{13}\text{C}$ ratio could not be measured on this (CO) fraction.

^{14}C Results and Model Calculations

The ^{14}C result for sample L101, f_c (fraction of biogenic carbon) = 0.01 (SE = 0.03) (*ie*, 99% fossil carbon), is consistent with a dominant fossil source for urban CO in these Las Vegas (East Charleston site) area samples. The $^{14}\text{CH}_4$ results for samples L101 and L3 (Onyx site) are $f_c = 0.58$ (SE = 0.11) and 0.64 (SE = 0.09), respectively. The CH_4 f_c values have been corrected for a $33\mu\text{g-C}$ blank with an $f_c = 0.82$ (SE = 0.06). Since there exists a good correlation between the ambient CO and CH_4 concentrations, one might assume that the ambient excess CH_4 is also a result of fossil emissions. This assumption can be tested by the following expression:

$$f_c(\text{calc}) = \phi_{\text{bkg}}(f_c = 0.77) + \phi_{\text{exc}}(f_c = 0.0). \quad (3)$$

The fraction of background CH_4 , $\phi_{\text{bkg}} = 0.81 \pm 0.03$, is calculated from the background of CH_4 , $1.71 \pm 0.01\text{ppm}$ for the appropriate date and latitude zone (Blake & Rowland, *in press*), and the median CH_4 concentration of samples L101 and L3 ($2.12 \pm 0.06\text{ppm}$) measured in this work. The fraction of excess CH_4 (ϕ_{exc}) is, therefore, 0.19 ± 0.03 and assumed to be of fossil origin ($f_c = 0.0$). The value of f_c for background CH_4 is taken to be 0.77 (SE = 0.02) (Table 3, ref 2, N11). This $^{14}\text{CH}_4$ result from sample N11 was chosen to represent the background, since excess CH_4 due to local vehicle emissions was estimated to be small, $\sim 2\%^3$. The calculated fraction of biogenic carbon, $f_c(\text{calc})$, is then 0.62 ± 0.03 , which is consistent with the 0.61 (SE = 0.08) weighted average fraction of biogenic CH_4 observed from this work.⁴ The overall imprecision of these preliminary $^{14}\text{CH}_4$ results is

³The estimated vehicle contribution for sample N11 is an upper limit assuming an average CH_4 concentration of 1.83 ppm during peak traffic hours ($\sim 4\text{h/day}$) and a background of $1.62 \pm 0.01\text{ppm}$ CH_4 for June 1980 at 39°N latitude (interpolated from data of Blake & Rowland, *in press*).

⁴Using the *observed* average f_c , 0.61 ± 0.08 , in Eq (3), however, we obtain $\hat{f}_c \text{ excess} = -0.074 \pm 0.44_8$. That is, the estimated value indicates a fossil source; but the large uncertainty would accommodate up to $\sim 66\%$ of the *excess* CH_4 coming from a contemporary source.

TABLE 3
Urban atmospheric $^{14}\text{CH}_4$ *

| Id# | Date | Sampling location | f_M (SE) | f_C (SE) | Ref** |
|------|------------|-------------------|-------------|-------------|-------|
| L101 | Feb 1984 | Las Vegas, NV† | 0.76 (0.11) | 0.64 (0.09) | 1 |
| L3 | Jan 1984 | Las Vegas, NV† | 0.69 (0.14) | 0.58 (0.11) | 1 |
| A9 | July 1980 | Murray Hill, NJ | 1.02 (0.04) | 0.82 (0.03) | 2 |
| N11 | June 1980 | Gaithersburg, MD | 0.96 (0.02) | 0.77 (0.02) | 2 |
| N1 | June 1980 | Gaithersburg, MD | 1.01 (0.09) | 0.81 (0.07) | 3 |
| | Jan 1960 | Gary, IN | 0.75 (0.01) | 0.60 (0.01) | 4 |
| | Oct 1950 | Tonawanda, NY | 1.02 (0.03) | 1.02 (0.03) | 5 |
| | April 1950 | Wembley, England | 0.69 (0.02) | 0.69 (0.02) | 5 |
| | Dec 1949 | Wembley, England | 0.75 (0.02) | 0.75 (0.02) | 5 |

* f_M is the fraction of "modern carbon." The standard error, SE, is 1σ -Poisson. f_C is the fraction of contemporary (biogenic) carbon resulting from the adjustment of f_M for human isotopic perturbations to atmospheric CO_2 (see text).

** Refs: 1) This work; 2) Klouda *et al.*, 1984; 3) Currie & Klouda (unpub data); 4) Bainbridge, Suess, & Friedman 1961; and 5) Libby (unpub data, cited in Ehhalt, 1967). Samples A9 and N1 were one week collections. Sample N11 was a 24-hour collection. Ambient CH_4 concentration, measured in Gaithersburg, MD on a weekday in June 1980 from 0815–0845 hr, was 1.83ppm by mole (m) (SE = 0.01, $n = 6$) and, from 1600–1800 hr, was 1.67ppm(m) (SE = 0.01, $n = 7$).

† The results of these two samples have been corrected for a $33\mu\text{g-C}$ system blank with an $f_C = 0.82$ (SE = 0.06).

largely due to the uncertainty in the system blank for CH_4 extraction. Steps are in progress to resolve this blank problem.

CONCLUSIONS

The ^{14}CO measurement for sample L101 reflects a fossil origin and suggests that vehicle emissions may contribute substantially to the urban (CO) pollution in the Central Valley (East Charleston site) of Las Vegas, Nevada. ^{14}CO measurements from the remaining samples will indicate whether wood burning emissions contribute significantly to ambient CO concentrations on other days. The conclusion based on this preliminary result is further supported by a good correlation between ambient CO and CH_4 concentrations for 4 of the 6 samples collected. A result from a simple model calculation, assuming that excess CH_4 originates from fossil emissions, is consistent with the fraction of biogenic CH_4 observed. Error amplification, due to the relatively small CH_4 excess, however, yields an upper limit (95%, 1-sided) of 66% contemporary carbon in the excess methane.

At present, a minimum concentration of $\sim 2\text{ppm CO}$ is required for ^{14}C measurements from a 0.1m^3 air sample. Future, more precise estimates of anthropogenic CH_4 will be valuable for understanding the CH_4 cycle and human impact on the stratospheric ozone layer which may influence climatic change.

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REFERENCES

- Bainbridge, A E, Suess, H E, and Friedman, I, 1961, Isotopic composition of atmospheric hydrogen and methane: *Nature*, v 192, p 648–649.
- Blake, D R and Rowland, F S, in press, World-wide increase in tropospheric methane, 1978–1983: *Jour Atmospheric Chemistry*.
- Ehhalt, D H, 1967, Methane in the atmosphere: *Air Pollution Control Assoc Jour*, v 17, no. 8, p 518–519.
- Khalil, M A K and Rasmussen, R A, 1984, Carbon monoxide in the earth's atmosphere: Increasing trend: *Science*, v 224, p 54–56.
- Kloda, G A, Currie, L A, Donahue, D J, Jull, A J T and Zabel, T H, 1984, Accelerator mass spectrometry sample preparation: methods for ¹⁴C in 50–1000 microgram samples: *Nuclear Instruments & Methods*, v 233, p 265–271.
- Naylor, M H (ms), 1985, Air pollution from fireplaces in Las Vegas, Nevada: Paper presented at 78th ann mtg, Air Pollution Control Assoc, Detroit, Michigan, June 16–21.
- Stevens, C M and Krout, L, 1972, Method for the determination of the concentration and of the carbon and oxygen isotopic composition of atmospheric carbon monoxide: *Internatl Jour Mass Spectrometry Ion Physics*, v 8, p 265–275.
- Stevens, C M and Rust, F E, 1982, The carbon isotopic composition of atmospheric methane: *Jour Geophys Research*, v 87, no. c7, p 4879–4882.