**13C/12C Ratio in Methane From the Flooded Amazon Forest**

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Analyses for C2-C4 hydrocarbon concentrations and the 13C/12C ratio in CH4 were performed on two air samples collected in the Amazon jungle (3.5°S, 59°W) after the nearby release of biogenic gas bubbles. The CH4 concentrations of each sample were greatly enhanced (4100 and 310 ppmv) over the background concentration (1.6 ppmv) for remote locations at that latitude and time. The 13C/12C ratio in this biogenic methane is depleted in 13C (−64%) relative to atmospheric CH4 (−47%), as is CH4 from almost all other biogenic sources. Because laboratory measurements to date indicate only a very small 13C/12C isotope effect in the reaction of CH4 with HO, an apparent discrepancy remains between the 13C/12C ratios of the known CH4 sources and that of atmospheric CH4. Five other hydrocarbons (C2H6, C3H8, i-C4H10, n-C4H10) were also found at the 1 to 35 ppbv level in the air sample with 4100 ppmv CH4. These concentrations are not large enough to indicate any major importance for this source in C2-C4 hydrocarbon budgets on either a global or regional basis.

**INTRODUCTION**

The interactions both of methane and of nonmethane hydrocarbons (NMHC) have been of increasing scientific interest as their importance has been recognized relative to such diverse situations as the oxidizing capability of the atmosphere, the greenhouse effect, the reactions of atomic chlorine in the stratosphere, urban smog and other atmospheric chemical problems [NAS, 1984]. The most abundant hydrocarbon in the earth's atmosphere is methane with a worldwide average tropospheric concentration in mid-1985 of 1.65 parts per million by volume (ppmv) [Blake and Rowland, 1985, 1986a]. A very large number of other hydrocarbons ranging from C2 compounds to the terpenes have also been identified in the atmosphere in regions somewhat distant from the probable sources [Greenberg and Zimmerman, 1984]. The observed concentrations of these other compounds have generally been much lower, often in the 0.0001 to 0.01 ppmv range, and are much more variable than that of CH4. Both the lower concentrations and the variability are directly related to their atmospheric lifetimes which are very much shorter than the 10 years estimated for CH4 [Mayer et al., 1982], and the cumulative carbon flux through the atmosphere in these chemical forms may be comparable to, or larger than, the 340 megatons of carbon per year estimated for methane alone.

The concentration of methane in the troposphere has been increasing at a rate of about 0.017 ppmv year over at least the past eight years to its present value [Rasmussen and Khalil, 1981, 1984; Blake et al., 1982; Khalil and Rasmussen, 1983; Blake and Rowland, 1985, 1986a]. Retrospective examination of atmospheric infrared spectra suggest that an increase of about 1% per year in CH4 concentration has been occurring at least since 1951 [Rinsland et al., 1985], while measurements of the composition of air bubbles trapped in ice cores indicate that the concentration of CH4 in the atmosphere may have been only about 0.7 ppmv as recently as two or three hundred years ago [Craig and Chou, 1982; Rasmussen and Khalil, 1984; Stauffer et al., 1985]. This increase in tropospheric methane concentration has raised important questions about the location and strength of the sources of methane and other hydrocarbons being emitted to the atmosphere. The major sources of atmospheric CH4 involve anaerobic biology [Ehnhalt, 1978], including swamps, rice paddies, the rumen of cattle, etc.

Cross comparison of the concentrations of CH4 and CH3CCl3 in air samples collected in or near the Amazon region have shown enhanced CH4, leading to a semiquantitative estimate that as much as 10% of the world's CH4 is emitted in Amazonia [Mayer et al., 1982]. Much more detailed experimental measurements of the magnitude and extent of these source-enhanced concentrations of tropospheric CH4 have been carried out in a NASA-sponsored program during 1985. Measurements have also been made which indicate that NMHC compounds such as ethane have higher concentrations in some tropic regions than are found at similar latitudes elsewhere [Greenberg and Zimmerman, 1984; Greenberg et al., 1984, 1985]. One known source for CH4 in Amazonia is biomass burning [Crutzen et al., 1979, 1985], but quantitative estimates of the strength of this and other sources are both difficult and scarce.

Complementary data bearing on the general atmospheric hydrocarbon problem can be found through consideration of the 13C/12C isotopic composition of CH4, and from the yields of C2-C4 hydrocarbons associated with the CH4 emissions. Various measurements have demonstrated that (1) the 13C/12C isotopic composition of atmospheric CH4 in 1980 was −47.0 ± 0.3% (parts per mil) versus the usual PeeDee belemnite (PDB) carbonate standard [Stevens and Rust, 1982]; (2) the oxidative removal of CH4 from the atmosphere by reaction with HO has been measured to have a 13C/12C kinetic isotope effect of only 1.0028 [Rust and Stevens, 1980], which would require about −49 to −50% in the sources of atmospheric CH4 to leave −47% in the atmospheric burden; and (3) the major northern hemispheric sources emit CH4 with 13C/12C ratios depleted in 13C relative to the atmosphere, i.e.,

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Paper number 6D0517.
0148-0227/87/006D-0517+02.00
more negative than $-50\%$ [Oona and Deevey, 1960; Ossyanin- 
kov and Lebedev, 1967; Silverman, 1971; Schoell, 1980; Rust, 1981; Rice and Claypool, 1981; Stevens and Rust, 1982].

Biomass burning, largely in tropical areas, is an important source of light hydrocarbons, and may be the dominant tropical source for $C_2-C_4$ hydrocarbons [Greenberg et al., 1984]. The $^{13}C/^{12}C$ ratio in the material combusted during most biomass burning contains about -25 to $-30\%$ [Craig, 1953; Bender, 1968, 1971; Troughton et al., 1974] and probably does not undergo substantial isotopic fractionation during combustion. The methane from biomass burning is therefore probably enriched in $^{13}C$ composition relative to the atmosphere, but most estimates of the strength of this source on a global basis do not appear to be large enough to offset the depleted $CH_4$ values, generally in the range from $-50\%$ to $-80\%$, from other known biogenic $CH_4$ sources. Similarly, the fractional contributions of "dead" methane (i.e. no $^{14}CH_4$) to the global total are not large enough to provide an isotopic balance for $^{13}C/^{12}C$ [Ehnhalt and Schmidt, 1978]. Balancing the ratio of $^{13}C/^{12}C$ in atmospheric $CH_4$ appears to require a source enriched in $^{13}C$ (i.e., $^{13}C/^{12}C$ less negative than $-50\%$) in order to combine with and balance the depleted $^{13}C$ sources if agreement is to be found with the observed isotopic atmospheric composition. Stevens and Rust [1982] have suggested that tropical wetlands might be the source of this enriched $CH_4$, but no samples of $CH_4$ from tropical sources have previously been available for measurement.

Measurements have been made earlier of the $C_2-C_4$ hydrocarbon composition of surface air samples collected in the equatorial and southern Atlantic [Rudolph et al., 1982; Ehhalt and Rudolph, 1984; Ehhalt et al., 1985], but very little information is available about the possible quantitative magnitude of such emissions accompanying the release of tropical swamp $CH_4$. Measurements have been made of hydrocarbon emissions from swamp areas in the southeastern United States [Zimmerman, 1977], and of hydrocarbon emissions in general from the tropical rain forest areas [Rasmussen, 1970; Greenberg and Zimmerman, 1984; Greenberg et al., 1984, 1985]. The concentrations of $C_2-C_4$ hydrocarbons have also been measured in air samples from remote regions over the latitude range from 71°N to 47°S during 1983-1985 [Blake and Rowland, 1986].

We report here the analysis of two air samples containing large quantities of methane from Amazonian wetlands, presenting data both on the $^{13}C/^{12}C$ composition of $CH_4$ and on the concentrations of accompanying $C_2-C_4$ hydrocarbons.

**EXPERIMENT**

**Sampling Collection Procedure**

Our routine procedure for collection of tropospheric air samples in remote locations has been described in detail earlier [Makide and Rowland, 1981; Mayer et al., 1982; Blake and Rowland, 1986a]. We use two-liter stainless steel canisters evacuated in the home laboratory, transported to the appropriate sampling site, opened briefly to the ambient atmosphere, and returned to the home laboratory for assay of the trace molecule composition. Seven sets of samples were collected over the whole latitude range of South America between 1978 and 1981. Near the end of such a collection period in June 1981, two additional samples were obtained in a remote region of the flooded Amazon forest. These canisters were filled with air representative of an environment deliber-
enhanced over the 1.6–1.7 ppmv characteristic of the background. The $^{13}$C/$^{12}$C ratios for the two samples are reported in per mil variation relative to the conventional PDB carbonate standard. The working standard in this apparatus was cross-calibrated with that used by C. M. Stevens at Argonne National Laboratory. The value for this standard as measured at NCAR was $-26.7\%$ and at Argonne $-26.8\%$, both relative to PDB carbonate.

Hydrocarbon Analysis

The analyses for CH$_4$ were performed on aliquots of the gaseous samples by standard gas chromatographic methods using flame ionization detection [Blake and Rowland, 1986a]. Aliquots of samples A-1 and A-2 were diluted on the vacuum line with zero air to bring the measured concentrations into the calibrated range for our instrument. The precision and accuracy are reduced to perhaps 2–3% for these samples, rather than the usual $\pm 0.4\%$, but none of the conclusions are dependent upon high accuracy in the data. The trace components volatile from a $-20^\circ$C bath were cryogenically trapped from as much as one-liter STP of air, and then analyzed for C$_2$-C$_4$ compounds on a 3-foot Spherocarb column programmed from $-10^\circ$C to 350$^\circ$C. This procedure provides a sensitivity generally in the 0.1 ppbv range for one-liter STP air samples [Blake and Rowland, 1986b].

RESULTS AND DISCUSSION

C$_2$-C$_4$ Hydrocarbons

The measured concentrations of CH$_4$ and five other hydrocarbons are given in Table 1 for samples A-1 and A-2. The canister (A-1) with the highest concentration of CH$_4$ contained an excess of all five of the C$_2$-C$_4$ hydrocarbons measured in these experiments. The accuracy of the C$_2$-C$_4$ analyses on A-1 and A-2 is judged to be $\pm 5\%$, but the representative nature of these samples is unknown because only two are available. The likely sources for all are the same bubbles which produced the excess methane, and the observations are indicative of the probable formation of such compounds in minor yield by anaerobic biological processes. A third air sample collected in the same area with only minor disturbance of the vegetation contained just 4 ppmv CH$_4$, and a fourth with no disturbance contained 1.7 ppmv CH$_4$. Neither of these latter two samples was retained for later analysis for NMHC compounds.

The C$_1$-C$_4$ analyses for air from three additional samples from the southern tropics are also given in Table 1 for comparison. Two of these air samples were collected on Pacific Islands and one was taken on the Brazilian coast ten days prior to the collection of the jungle samples. The air samples from Nauru and Bora Bora are generally typical of background oceanic air from the southern hemisphere with seasonally-dependent concentrations of CH$_4$ and C$_2$H$_6$ and usually $<0.1$ ppbv of the C$_4$ alkanes [Blake and Rowland, 1986b].

Brazilian “background” air samples, such as B in Table 1, have higher concentrations of CH$_4$, C$_2$H$_6$, and C$_3$H$_8$ than found in samples collected in similar seasons in Pacific Island locations, as in samples C and D, and are presumed to contain additional hydrocarbons from the well-known regional emissions [Greenberg and Zimmerman, 1984; Greenberg et al., 1984, 1985]. The atmospheric lifetime of CH$_4$ in tropical latitudes has been calculated to be no more than two or

| Sample | CH$_4$ | C$_2$H$_4$ | C$_2$H$_6$ | C$_3$H$_8$ | C$_4$H$_{10}$ | n-C$_4$H$_{10}$ |
|--------|-------|---------|---------|---------|-------------|---------------|
| A-1    | 4,100,000 | 15    | 23    | 33    | 8    | 1  |
| A-2    | 310,000   | 1.7   | 2.2   | 1.4   | $<0.1$ | $<0.1$ |
| B      | 1,540     | 2.2   | 2.0   | 0.73  | $<0.1$ | $<0.1$ |
| C      | 1,595     | 0.23  | 0.27  | 0.13  | $<0.1$ | $<0.1$ |
| D      | 1,613     | 0.13  | 0.27  | $<0.05$ | $<0.1$ | $<0.1$ |

Samples are as follows: A, Amazonian wetlands. Gas samples were collected on June 26, 1981, at 3.5$^\circ$S latitude and 59$^\circ$W longitude. Acetylene concentrations were $<0.1$ ppbv in all samples. B, Itapoa (Salvador), Brazil 12.9$^\circ$S, 38.5$^\circ$W, June 16, 1981. C, Nauru, 0.5$^\circ$S, 166.9$^\circ$E, Sept. 24, 1984. D, Bora Bora, 16.5$^\circ$S, 151.8$^\circ$W, June 17, 1985. Parts per billion by volume, 10$^{-9}$.
not an important contribution to the regionally enhanced concentrations of these hydrocarbons found in Amazonia, and are even less important to the global atmospheric release of C$_2$-C$_4$ compounds. These observations are not inconsistent with biomass burning as the major source for C$_2$-C$_4$ compounds in Amazonia [Greenberg et al., 1984].

$^{13}$C/$^{12}$C Isotope Ratio in Methane

The CH$_4$ from sample A-1 had an isotope ratio of $-64.5 \pm 0.3\%_0$, while that from sample A-2 had a ratio of $-63.3 \pm 0.3\%_0$. Correction of the isotope ratio measured for sample A-2 for the presence of 1.7 ppmv of atmospheric CH$_4$ with about $-47\%_0$ would change the measured ratio for the 308 ppmv of CH$_4$ directly emitted from the Amazon wetlands by only 0.1% to $-63.4 \pm 0.3\%_0$. The correction for sample A-1 is even less significant because of the much higher CH$_4$ concentration found in that canister. The $^{13}$C/$^{12}$C ratios in both of these samples indicate substantial depletion in $^{13}$C relative to the atmosphere, i.e., about $-64\%_0$, and therefore do not represent the sought-for missing source of $^{13}$C-enriched methane. It is obvious that many more studies are needed before reasonable extrapolations can be made to the entire Amazon basin. Nevertheless, these first two samples suggest that the resolution of the inconsistency between the $^{13}$C/$^{12}$C ratio in methane sources and in atmospheric methane may well not lie in the tropical emission of $^{13}$C-enriched CH$_4$. With essentially all important biological sources of CH$_4$ depleted in $^{13}$C relative to atmospheric CH$_4$, the physicochemical processes needed to rationalize these respective isotopic ratios remain to be identified.

Acknowledgments: The Brazilian air samples were collected on a trip financed by EPA contract 80535200, and the South Pacific sample collection and the analyses were supported by NASA contract NAGW-452. The $^{13}$C/$^{12}$C analyses were performed at the National Center for Atmospheric Research, Boulder, Colorado.

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(Received March 14, 1986; revised September 2, 1986; accepted September 5, 1986.)