Observation of CH4 in the Stratosphere and Troposphere in the California and Colorado Regions for Summer 1996

Jennifer Price
Significant Opportunities in Atmospheric Research and Science (S.O.A.R.S.)
National Center for Atmospheric Research
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Jennifer Price, Bethune-Cookman College/Florida A&M University
Significant Opportunities in Atmospheric Research and Science
National Center for Atmospheric Research, Boulder, CO
Atmospheric Chemistry Division
Elliot Atlas, Scientific Mentor

Abstract

Whole-air samples have been collected from the stratosphere and troposphere from two different aircraft. The National Oceanic and Atmospheric Administration (NOAA) P3 aircraft took samples from the Denver, Colorado area, while the National Aeronautics and Space Administration (NASA) ER-2 took samples from the Moffett Field area in California. All samples were brought to the Stratospheric/Tropospheric Measurements Laboratory at the National Center for Atmospheric Research (NCAR) for analysis by gas chromatography. Calculations for each aircraft were compiled into two data sets. The concentration of CH$_4$ in each air sample was measured. Correlations were made between CH$_4$ concentrations and altitude for both sets of data. Further relationships between CH$_4$ and other hydrocarbons were observed. Overall results show that the concentration of CH$_4$ varies with altitude. Strong relationships between CH$_4$ and each ethane, ethene, i-butane, and acetylene are also shown. Results from these correlations point towards a variation in the sources of CH$_4$ concentrations in the areas.
1. Introduction

Methane (CH$_4$) in the upper atmosphere is recognized as the most prevalent trace gas involved in man-made climate change, second only to carbon dioxide in its global warming capabilities (Khalil, 1993). Since it is a reactive greenhouse gas, CH$_4$ also has an effect on the oxidizing capacity of the atmosphere by controlling tropospheric OH radicals. In the stratosphere CH$_4$ contributes to the water vapor present by removing chlorine atoms (Khalil, 1993). Evidently CH$_4$ has a profound effect on the lifetimes and reactions of other trace gases, and is important in the study of the chemistry of the atmosphere.

Though the changing of the atmosphere is a partly natural process, anthropogenic sources, too, play a major role in this alteration. Trace gases emitted from human activities are the cause for increases in the concentrations of certain greenhouse gases. The sources of these gases consist of the burning of fossil fuels including coal mines, natural gas, the petroleum industry, and coal combustion; waste management systems such as landfills, animal waste, and domestic sewage treatment; as well as enteric fermentation, biomass burning, and rice paddy cultivation (Sanhueza, 1994). Some natural sources include wetlands, termites, the ocean and freshwater ecosystems, as well as volcanoes, hydrothermal activities, and hydrates (Judd et al., 1993; Lacroix, 1993; Sanhueza, 1994).

Sinks for CH$_4$ concentrations also exist. More than 90% of the CH$_4$ released into the atmosphere each year was removed mostly by the oxidation of CH$_4$ in the troposphere (Khalil and Rasmussen, 1993). However, the oxidation of CH$_4$ in the troposphere depends heavily upon the concentration of OH, and thus it relies on latitudinal and longitudinal locations (Khalil and Rasmussen, 1993). It has also been calculated that 64% of the oxidation of CH$_4$ takes place in the mid-latitudes (Khalil and Rasmussen, 1993). Concentrations of CH$_4$ are also depleted in soil microbial communities (Reebrugh et al., 1994) by methane-oxidizing bacteria.

A sudden increase in greenhouse gas concentrations is an indication that warming, though on a time scale of a decade or more, will occur on the surface of the earth (Trenberth, 1988). Harriss (1988) reported that the concentration of
CH$_4$ has increased by nearly 1,000 parts per billion by volume (ppbv) over the 200-year period from 1788 to 1988; this increase is thought to be directly related to the growth of human population and industrial societies in the Northern Hemisphere (Matsueda and Inoue, 1995). However, the growth rate of CH$_4$ has declined steadily (Steele et al., 1992; Khalil and Rasmussen, 1993; Khalil et al., 1993; Dlugokencky et al., 1994b; Sanhueza, 1994) and has done so more rapidly in the 30°-90°N semi-hemisphere than in the other semi-hemisphere (Dlugokencky et al., 1994b). This occurrence is unexpected since more industrialized societies are more numerous in the northernmost of the two semi-hemispheres. This global decline in CH$_4$ growth rate can be the outcome of a series of global changes including changing in natural gas emissions from fossil fuels in a large part of Asia (Dlugokencky et al., 1994b) or from biomass burning in the tropics (Lowe et al., 1994). However, paleo records of atmospheric CH$_4$ concentrations show that its growth rate has not always been monotonic (Etheridge et al., 1992; Dlugokencky et al., 1994a; Sanhueza, 1994).

As evident from past research, the concentration level of CH$_4$ is increasing but the rate of its growth is declining. This could be an implication that CH$_4$ concentrations are leveling on their own (Khalil, 1993). Another theory is that this stabilization can result because certain CH$_4$ emission sources are meeting their production limits while contributors to the CH$_4$ sinks are increasing (Khalil, 1993). If this is the explanation, there is a possibility that CH$_4$ concentrations will recur and increase to an unpredictable level (Khalil, 1993).

The trends in the growth rate and concentration of CH$_4$ exist on a global basis and are useful in defining global climate change. However, understanding the dynamics of the atmosphere in more specific locations can help us to better understand changes in local climate. The purpose of this study is to measure CH$_4$ concentrations in the California and Colorado regions. I will present concentrations of atmospheric CH$_4$ in the California and Colorado regions as well as discuss the relationship of CH$_4$ with altitude and other hydrocarbons in the atmosphere. Finally I will target the major sources of CH$_4$ emissions in the region and present future research interests.

2. Methods and Procedures
2.1 Whole-Air Sampling

The whole-air samples for my study are collected from the atmosphere from two different aircraft. Air samples collected on the National Oceanic and Atmospheric Administration (NOAA) P3 aircraft are taken at tropospheric altitudes. For these summer missions, as a part of the Stratosphere/Troposphere Experiment: Radiation, Aerosols, Ozone (STEREO-A) Program, the P3 flew from Buckley Field, near Denver, Colorado. Samples collected on the National Aeronautics and Space Administration (NASA) ER-2 aircraft are taken at stratospheric and upper-tropospheric altitudes. ER-2 flights (Fig. 1) are based at the NASA Ames Research Center at Moffett Field, California.

All air samples are collected in stainless steel canisters. On the ER-2, up to 29 canisters, each 1.5 L, are connected to an electronically controlled manifold (Fig. 2a). In this way, a valve is opened automatically and the cans are filled with air sample. The canisters on the ER-2 are pressurized near 40 psi. On the P3, between four to eight canisters are loaded at once, each 2.6 L. On this aircraft, the pressure in each can varies, and the valves are opened manually. During the sampling process flight altitudes, start and finishing can fill times, and pressure are recorded for future reference. Once the canisters are filled, the valves are closed. Samples are then ready to be tested for several compounds. For my research, a total of 29 cans from a single ER-2 flight and nearly 63 cans from a total of 11 P3 flights were analyzed.

2.2 The Chromatographic Process

The Hewlett Packard 5890A gas chromatograph in the Stratospheric and Tropospheric Measurements Laboratory at the National Center for Atmospheric Research is specifically set up to measure the amount of CH$_4$ in any whole-air sample (Fig. 2b). A small amount of the air sample to be analyzed and a small amount of a primary standard gas are introduced into the column. Primary standards, a mix of gases formulated in a laboratory, are used since their composition is known both quantitatively and qualitatively. The purpose of using a standard when testing for CH$_4$ and other trace gases is to be able to compare the results of an unknown air sample to one that is known. The primary CH$_4$
standard used, which is prepared by the National Institute of Standards and Technology (NIST), contains 0.913 ppmv of CH$_4$. This standard is compared to a second NIST standard as well as a whole-air standard measured at NOAA's Climate Monitoring and Diagnostics Laboratory.

The combination of air sample and standard gas is introduced into the column, which acts as the separation device of the chromatograph system. Contained in a temperature-controlled oven, the sample-gas mixture within the column is heated. The many different components travel through the column at differing rates. These different times, called retention times, are recorded by a flame ionization detector and are used to classify the various compounds found in the samples. The entire gas chromatography process, from the initial injection time to the production of a chromatograph report, takes approximately 20 minutes for two injections each of the air sample and standard.

2.3 Acquiring Data

The data obtained from the chromatograph system is transferred to a printer (Fig. 3) and a computer where a chromatograph of the data is formed by peak integration. From peak integration the retention times, peak areas, and peak heights are recorded on the chromatograph report. The data from the chromatograph reports is transferred to data files on Microsoft Excel, version 5.0. This same information is transferred to KaleidaGraph for Windows, version 3.0, where graphic results are produced. The graphic results obtained are used as the basis for analysis.

3. Results and Observations

3.1 Methane Concentrations

The concentrations of atmospheric CH$_4$ for both P3 data and ER-2 data were compared to other data from the same flights. The ER-2 collects a vertical profile of the atmosphere and covers a broad range of altitudes. For the ER-2 flights, a comparison between the manifold position of the canisters and the average altitude in meters was made. Figure 4a shows that as the manifold
position increases, average altitude decreases. Since the canisters are filled in succession beginning at lower-stratospheric altitudes, the average CH$_4$ content begins at lower concentrations. Thus the manifold position and average CH$_4$ concentrations versus manifold position and altitude (figure 4b) are inversely related. These figures also show that near 15 km the average altitude begins to noticeably decrease. At the same time, the CH$_4$ concentrations become markedly constant in the troposphere with an extreme decrease once stratospheric altitudes are approached. This demonstrates the distribution of CH$_4$ throughout the levels of the atmosphere.

The concentration of CH$_4$ was next compared to the concentrations of other hydrocarbons. The first comparison shows the relationship between CH$_4$ and ethane (Fig. 5a). In comparison to the same relationship observed in a winter study (Fig. 5b), the concentrations of the two hydrocarbons are similar. However, in my research I found that instead of a steady decrease in CH$_4$ concentrations between 1750 and 1700 ppbv, there was a slight increase. The reason for this difference in behavior is not fully known at this time. The final correlation involving ER-2 data was made between ethane and i-butane (Fig. 6). The relationship between these two hydrocarbons shows that i-butane appears to disperse from the atmosphere more quickly than does ethane. It also illustrates that the concentration of i-butane in the upper atmosphere is less than the concentration of ethane.

Since the P3 collects air samples from the troposphere, a representation of CH$_4$ concentration (Fig. 7) versus the altitude shows a wide scatter of data. There is, however, a slight trend; as the concentrations approach stratospheric altitudes they begin to decrease. This is an example of how CH$_4$ is distributed in the troposphere. The CH$_4$ concentrations from the P3 data were also compared to the concentrations of other hydrocarbons. Comparing CH$_4$ concentrations to ethane (Fig. 8) shows a moderate relationship. Though some of the data points seem scattered, there is a modest similarity between their behavior as altitudes increase. Ethene presents a near identical situation (Fig. 9a). The trend between CH$_4$ and ethene is more noticeable than with ethane. As shown in figure 9b, after removal of five data points with unusually low ethene concentrations, the correlation between the two compounds becomes even more profound. The five data points that were removed were results from the same
flight date. The reason for this outcome is not yet known. Finally, the concentrations of CH₄ and both i-butane and acetylene, too, show a positive correlation (Fig. 10a,b).

To observe the patterns of the hydrocarbons between the ER-2 and P3 flights a plot comparing the CH₄ and ethane concentrations for all data was produced. Figure 11 shows that ethane is more dense in the troposphere and seems to die out quickly in the stratosphere as shown by the ER-2 data. This is probably because the troposphere is a more dynamic layer of the atmosphere and therefore mixing ratios are higher. The final relationship was made to compare the CH₄ concentrations to the estimated global average (Fig. 12). The global average of CH₄ concentration appears to grow approximately 25 ppb per year. In my study, the present global average was estimated to be near 1,750 ppb. Therefore, the tropospheric CH₄ concentrations for the ER-2 flight average near 1,730 ppb, while the average for all 11 of the P3 flights is 1.441 ppb (Fig. 13). The average standard deviation of these values is approximately 5.36 ppb.

3.2 Possible Sources of CH₄

After correlating CH₄ concentrations with those of other hydrocarbons, some assumptions can be made about the sources for the CH₄ concentrations in the regions of study. Figure 14 lists the sources for emissions of several hydrocarbons. A positive correlation between CH₄ and each ethane and i-butane implies that the source for the ER-2 flights is most likely natural gas emissions, oceans, or biomass burning. P3 flights showed a moderate relationship between CH₄ and ethane, which could imply a natural gas, biomass burning, or ocean source. However, correlations between CH₄ and i-butane make the presence of these sources more feasible. Stronger correlations with ethene and acetylene point towards fuel combustion, and biomass burning.

4. Summary and Future Work

To observe the relationships between CH₄ concentrations and other factors, whole-air samples were analyzed for their CH₄ content. These values were next compared to the range of altitudes for each flight to show the distribution of CH₄ between the stratosphere and troposphere. The
concentrations were also compared to the concentrations of other hydrocarbons that were analyzed by other chromatograph systems in the laboratory. Results from the correlations for each region point towards a variation in the sources for the CH$_4$ concentrations in the areas. On a whole, the CH$_4$ concentrations of the California and Colorado regions are consistent with that of the probable global average. However, specifics concerning the decline in the growth rate of CH$_4$ have not yet been established.

It would be useful to observe the factors that affect the decline of the growth rate of CH$_4$. Examining the several hypotheses that surround the phenomenon could lead to some highly probable solutions for this trend.
5. References


Figure 1. The NASA ER-2, one of the aircraft used for whole-air sampling, flies at lower-stratospheric to upper-tropospheric altitudes.
Figure 2. The canister configuration (A) on the ER-2. A total of 29 canisters, each 2.6 L and with motor driven valves are connected to a manifold to be filled with air sample. After filling is complete, the canisters are ready for the analysis. Samples are loaded onto the gas chromatography system (B) to be tested for various trace gases.
Figure 3. Contents of the air sample are analyzed by peak integration. Retention times, peak areas, and peak heights are recorded.
Figure 4. For the ER-2 data, a vertical profile is taken. As the manifold position increases, the average altitude decreases (A). There is an inverse relationship between manifold position and CH₄ concentration (B).
Figure 5. Data from the ER-2 flight (A) was compared to the same type of data from a winter flight (B) and shows an inverse relation.
Figure 6. Ethane and i-butane relationships show that i-butane dissipates from the atmosphere more quickly than ethane.
Figure 7. Air samples from the P3 are taken at tropospheric altitudes. A slight trend illustrates the behavior of CH$_4$ in the atmosphere; as altitudes approach the lower-stratosphere, CH$_4$ concentrations decrease.
Figure 8. Ethane and CH$_4$ show a moderate correlation between the two, as altitude increases.
Figure 9. Ethene and CH₄ show a more similar correlation (A); after removal of a few data points (blackened points) the correlation (B) is even more profound.
Figure 10. Concentrations of CH₄ as compared to i-butane (A) and acetylene (B) show extremely positive correlations between the hydrocarbons.
Figure 11. A comparison between ethane and CH$_4$ for both sets of data shows ethane's distribution in the atmosphere as it relates to CH$_4$. Apparently, ethane dies out in the stratosphere as does CH$_4$ and is more dense in the troposphere.
Figure 12. An estimate of the global average for CH$_4$ concentrations was approximated to be near 1750 ppb for 1996 in this study.
Figure 13. An average of 1741 ppb was calculated for the CH$_4$ concentration from all P3 flights; 1730 ppb is the average for the ER-2 flight.
Global sources of individual NMEC species (adapted from Singh and Zimmerman, 1992)

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Emission, Tg/yr</th>
<th>Major Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>10-15</td>
<td>natural gas emissions, biomass burning, oceans, vegetation</td>
</tr>
<tr>
<td>n-hexene</td>
<td>20-45</td>
<td>fuel combustion, biomass, terrestrial ecosystems</td>
</tr>
<tr>
<td>isoprene</td>
<td>3-6</td>
<td>fuel combustion, biomass burning</td>
</tr>
<tr>
<td>isobutane</td>
<td>15-20</td>
<td>natural gas, biomass burning, oceans, vegetation emissions</td>
</tr>
<tr>
<td>isopropene</td>
<td>7-12</td>
<td>fuel combustion, biomass burning, oceans</td>
</tr>
<tr>
<td>isobutane</td>
<td>1-2</td>
<td>fuel combustion, natural gas, biomass burning, oceans</td>
</tr>
<tr>
<td>isoctane</td>
<td>1-2</td>
<td>fuel combustion, natural gas, biomass burning, oceans</td>
</tr>
<tr>
<td>isonitriles</td>
<td>2-3</td>
<td>fuel combustion, biomass burning, oceans</td>
</tr>
<tr>
<td>1-pentane</td>
<td>1-2</td>
<td>fuel combustion, natural gas, biomass burning</td>
</tr>
<tr>
<td>2-pentene</td>
<td>2-3</td>
<td>fuel combustion, natural gas, biomass burning</td>
</tr>
<tr>
<td>benzene</td>
<td>4-5</td>
<td>fuel combustion, biomass burning</td>
</tr>
<tr>
<td>toluene</td>
<td>4-5</td>
<td>fuel combustion, biomass burning, solvents</td>
</tr>
<tr>
<td>xylenes (m, p, o)</td>
<td>2-3</td>
<td>fuel combustion, biomass burning, solvents</td>
</tr>
<tr>
<td>styrene</td>
<td>350-450</td>
<td>forest/plant emission</td>
</tr>
<tr>
<td>mono-terpenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>and other biogenic</td>
<td>400-500</td>
<td>forest/plant emission</td>
</tr>
</tbody>
</table>

**Figure 14.** A list of global sources of emissions of hydrocarbons.