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Atmospheric methane measurements in central New England: An analysis of the long-term trend and the seasonal and diurnal cycles

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Abstract. We have compiled a unique high-resolution ambient-air methane data set consisting of approximately 125,000 independently measured data points for the years 1991–1995 that have been collected at a site in the northeastern United States. The annual median mixing ratio of methane for all measurements was 1808 ppbv in 1992, increasing at a variable rate to 1837 ppbv in 1995. The lower 10–30% of the data from each month were defined as representative of background air and were compared with the global Climate Monitoring and Diagnostics Laboratory (CMDL) data set. The background data exhibit a variable upward trend of 5.5 ± 2 ppbv/yr during the 4-year time period, with most of the increase observed during 1993 and 1994. The seasonal cycle for the background data set is similar to what is observed by CMDL stations and varies from 24 to 35 ppbv. The amplitude of the seasonal cycle for the full data set was larger, ranging from 35 to 44 ppbv. Differences between the full and background mixing ratios vary on a seasonal basis and are largest in the winter and smallest in the summer. These differences appear to be controlled by changes in atmospheric stability and changes in emissions from local and regional sources throughout the year. Diurnal cycles exist in the data, with the magnitude and timing of maximum and minimum values being controlled by inputs from local sources and atmospheric stability. Nearby wetlands contribute to an overnight buildup of methane in the late spring and summer. The magnitude of the daily cycle is largest in July and August (~23 ppbv), when inputs from wetlands are large and wind speed is generally low. In April, the daily cycle is smallest (~6 ppbv), when inputs from local sources are low and more vigorous atmospheric mixing limits pollution buildup.

1. Introduction

In 1993 the United States released a climate action plan proposing to return U.S. greenhouse gas emissions to the 1990 level by the year 2000. The largest contributor to the potential of global warming is carbon dioxide (CO_2), followed by methane (CH_4). Stabilizing the atmospheric burden of CO_2 will require a reduction in emissions of 60–80%. This is unlikely in the near future given industrial societies' strong dependence on fuels coupled with the 200-year lifetime of CO_2. In comparison, CH_4 emissions need to be reduced only 10–15% to stabilize its global concentration, and the 11-year lifetime of CH_4 means the effects of mitigation strategies may be observed within several decades.

A critical factor in determining if mitigation strategies are working is the paucity of quantitative measurements of CH_4 at local to regional scales in which changes in emissions over long time periods may be verified. To address this problem, automated high-frequency (8–11 min) CH_4 measurements have been made by Patrick M. Crill from the University of New Hampshire at the Harvard Forest (HF) research site since 1992. The proximity of this site to numerous industrial/urban areas presents the opportunity to sample from known CH_4 sources on a regular and repeatable basis and to characterize the chemical signature of the sampling location and assess its sensitivity to both local and regional sources.

This paper examines the long-term trend and seasonal and diurnal cycles of CH_4 at the HF research site. Key questions that are addressed include the following: How does the long-term trend at this site, which is located in a heavily industrialized region, compare with the observed trends for clean-air sites in the northern hemisphere? How is the timing and amplitude of the seasonal cycle altered by air pollution events? What is the amplitude and timing of the daily cycle, and how does it relate to changes in local sources of CH_4 and atmospheric stability throughout the year?

2. Background

A series of reports by the *Intergovernmental Panel on Climate Change (IPCC)*, [1990, 1992, 1995] provide a comprehensive assessment of global sources and sinks of atmospheric CH_4. Individual articles and references contained in the IPCC documents suggest that human activities are now responsible for approximately 70% of the global CH_4 sources. Anthropogenic inputs of CH_4 are associated with energy production and use, landfills, domestic sewage, rice agriculture, domestic ruminants, and animal wastes. Natural sources include wetlands, termites, lakes, and coastal waters.

Future growth in CH_4 sources has been estimated by the IPCC, with the largest growth expected to occur in emissions from land-

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fills, energy production and use, and animal production/waste systems. Sources with modest expected growth are biomass burning and rice agriculture. In the United States the largest anthropogenic sources of CH_4 are from landfills, which account for about 25% of total emissions [*Environmental Protection Agency (EPA)*, 1994].

While the yearly rate of increase in the mixing ratios of CH_4 is variable [*Steele et al.*, 1992; *Harris et al.*, 1992; *Khalil and Rasmussen*, 1993; *Conway et al.*, 1994; *Dlugokencky et al.*, 1994a; *Keeling et al.*, 1995], over the past two centuries they have approximately doubled [*Etheridge et al.*, 1992; *Thompson et al.*, 1993; *Khalil and Rasmussen*, 1994]. On a geologic timescale, ice-core records show the current mixing ratios of CH_4 to be 2–3 times higher than have been observed during the past 160,000 years [*Chappellaz et al.*, 1990], with the doubling over the past two centuries representing an unprecedented rise of CH_4.

Since 1983, CH_4 measurements have been made at approximately weekly time intervals at an increasing number of stations around the globe by the National Oceanic and Atmospheric Administrations's Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) [*Lang et al.*, 1990a, b; *Steele et al.*, 1992]. This extensive worldwide network collects background, clean-air measurements of CH_4 which provide insight into the complex temporal cycles that compose the changing global CH_4 signal [*Steele et al.*, 1987; *Blake and Rowland*, 1988; *Conway et al.*, 1994; *Dlugokencky et al.*, 1994a].

3. Site Description and Instrument Methodology

The 1200-ha HF research site is located in Petersham, Massachusetts (42.48° N, –72.18° W; elevation 340 m) is ideally located to sample air from numerous anthropogenic CH_4 sources, and is subjected to pollution events on a year-round basis. The micrometeorological tower from which the samples are taken is 30 m high and is situated within a 60-year-old mixed hardwood forest typical of the transition hardwood-white pine-hemlock forests in much of the region. There is a highway approximately 5 km to the north and a secondary road 2 km to the west. A dirt road leads to the site and has very limited vehicular traffic. Depending on the prevailing wind speed and direction, the instruments on the tower generally sample air with trajectories from industrial/urban environments to the south and southwest and from rural landscapes to the west and north.

The automatic CH_4 analysis system was designed and is maintained by Patrick M. Crill from the University of New Hampshire and is built around a Shimadzu Mini-2 gas chromatograph equipped with a flame ionization detector. Ambient air is continuously sampled from an inlet 20 m above the ground surface (a few meters above the forest canopy) through 1/4" OD plastic-coated aluminum tubing (Dekoron 041943-1 tubing) with an electric diaphragm pump at a rate of 25 L/min. This flow is sampled every 8–11 min with a Valco stream select valve and dried across a 1-m Perma Pure nafion drier, and, after sample loop pressure is allowed to relax to atmospheric pressure, 1 mL is injected into the carrier gas stream of the chromatograph by another Valco electrically actuated valve. The sampling procedure yields an independent measurement of ambient CH_4 every 8–11 min. CH_4 is separated on a 2-m by 3.2-mm OD stainless steel column packed with HayeSep Q at 40° C. Detector temperature is 125° C. Valve timing, analog-to-digital conversion of the detector output, and signal integration are controlled by a Hewlett-Packard HP3395A series II integrator with an HP19405A event controller. Raw data and integration reports are transferred to and stored on a personal computer until the data are transferred to the University of New Hampshire in Durham via modem every 3 days. (Hourly averaged data are available from io.harvard.edu/pub/nigec/UNH_Crill via anonymous ftp.)

During operation a field calibration sample is processed with each ambient air sample. The field standard are cylinders of breathing air containing near-ambient mixing ratios of CH_4 that have been calibrated with Niwot Ridge air standards prepared by NOAA/CMDL in Boulder, Colorado. Over the course of a day, the standard response of the gas chromatograph varies about 1% due to diel heating and cooling, since the standard is kept in an unheated pump room in order to mimic the temperature of the outside air sample. Therefore, to evaluate the precision of the CH_4 measurements, the responses of an individual analysis of the standard are compared with the 24-min running average of the standard response. The coefficient of variation (CV) (the standard deviation/mean) expressed as the percent variation from the 24-minute running mean ranged annually from 0.18 to 0.29%. If this CV represents the sum of errors in the system measurement (an assumption not entirely true since the standard does not flow through the sampling pump), then the precision of the analysis would be considered to 3.6 ± 0.4 ppbv CH_4. Additionally, all data points were filtered for instrument response by calculating the difference between each standard response and its average with the two points on either side. This difference was then divided by the sample standard deviation for these same five points. The resulting number was then compared with the mixing ratios obtained by the Grubbs test for outliers at a significance level of 95% [*Sokal and Rohlf*, 1981] and removed if it exceeded that value. No data were removed in 1992 and 1993, 1.4% were removed in 1994, and 1.55% were removed in 1995.

4. Statistical Methods and Data Representation

Analysis of the time series for these data presents challenging problems. First, the data must be considered nonuniformly sampled due to variable length data gaps, some of which are several weeks in duration. This precludes standard time series analysis techniques, which assume evenly spaced data. Second, the series is a nonstationary process in that the underlying global and regional sources and sinks of CH_4 are changing and changing at different rates over time. As a consequence, robust statistical techniques resistant to outliers are used in the analysis of the full data set [*Meeker et al.*, 1995; *Khalil and Moraes*, 1993; *McRae et al.*, 1979].

A subset of these data is used to examine the long-term trend and seasonal cycle in background, clean-air conditions comparable to those observed by the global CMDL network. Following work by *Goldstein et al.* [1995], the lower 10–30% of CH_4 mixing ratios from each month are considered to be representative of a background air mass. While the full data set is skewed by pollution events and is nonnormally distributed, the lower 10–30% of the data have a near normal frequency distribution, as would be expected when extreme values are removed [*Gaines and Denny*, 1993]. Elimination of the lowest 10% of CH_4 mixing ratios removes low values that may be associated with either diluted stratospheric or aged tropical air which is not representative of surface background conditions at the HF site.

The frequency distribution of mixing ratios for January and June, 1993, is shown in Figure 1. In January, the lower 10–30% of mixing ratios range from 1796 to 1810 ppbv, eliminating several severe pollution events that occurred during the month. Likewise,

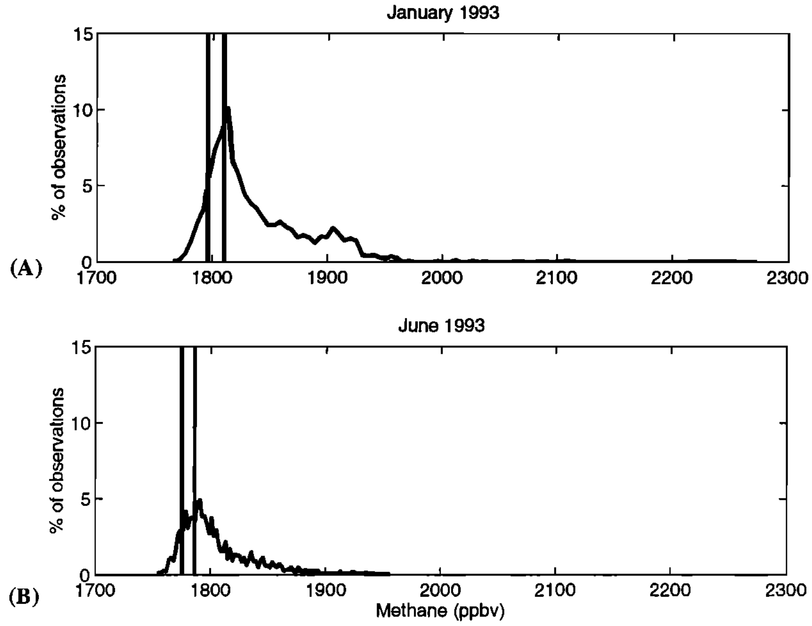

Figure 1. Frequency distribution of methane mixing ratios for (a) January 1993 and (b) June 1993. Solid lines bracket the lower 10–30% of the data range. Both high and occasional low events are separated from the background data.

the data envelope for June bounds mixing ratios from 1775 to 1786 ppbv, again eliminating high episodes of CH_4 associated with pollution and/or stagnation events.

The mixing ratio for the HF background data for 1993 is compared with the CMDL data network in Figure 2. The background annual average mixing ratio of 1796 ppbv at HF is similar to CMDL sites near this same latitude. The mean HF mixing ratio using the full database is 1828 ppbv, an enhancement of 32 ppbv. For the remainder of this discussion the term "full" will refer to the entire database, while "background" will refer to the subset of the monthly data that uses the lower 10–30% of the data.

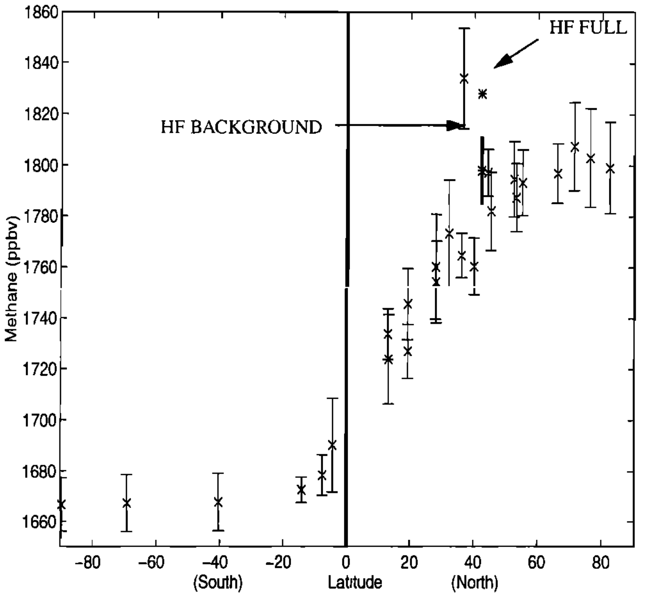

Figure 2. Concentrations of methane for the global Climate Monitoring and Diagnostics Laboratory (CMDL) network and Harvard Forest (HF). Crosses are the means with bar lengths being ±1 standard deviation.

The background data were adjusted in order to derive the long-term trend and yearly seasonal cycles. The data were detrended by subtracting a 12 month running mean from the original data, leaving cycles of 12 months or less. The data were then deseasonalized by subtracting the mean seasonal cycle of the 4-year time period from the original data, leaving the long-term trend. Finally, the background data were analyzed by a least squares algorithm to see if expected yearly and seasonal cycles existed as well as to determine if other unknown cycles were present [*Lomb,* 1976; *Meeker et al.,* 1995]. Figure 3 is the spectrum from the Lomb analysis, which shows a yearly cycle of 364 days and a seasonal periodicity of 191 days. Other weak signals, especially the one centered around 260 days, appear to be the result of interannual variability, as time of maximum and minimum CH_4 mixing ratios varies by several months from year to year.

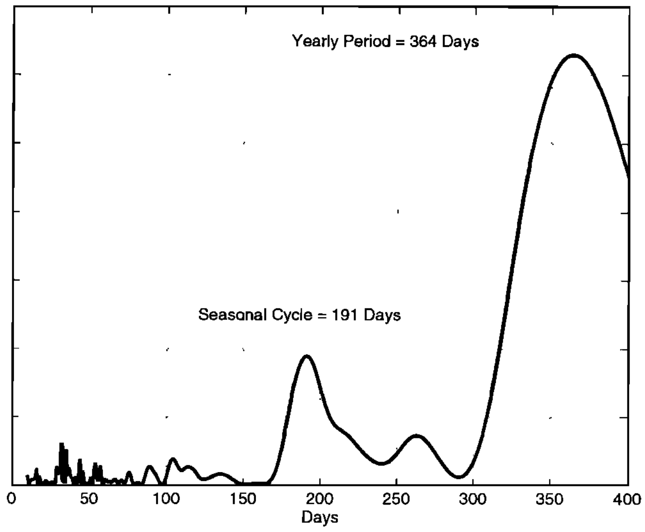

Figure 3. Least squares frequency analysis of methane mixing ratios at Harvard Forest for 1992–1995.

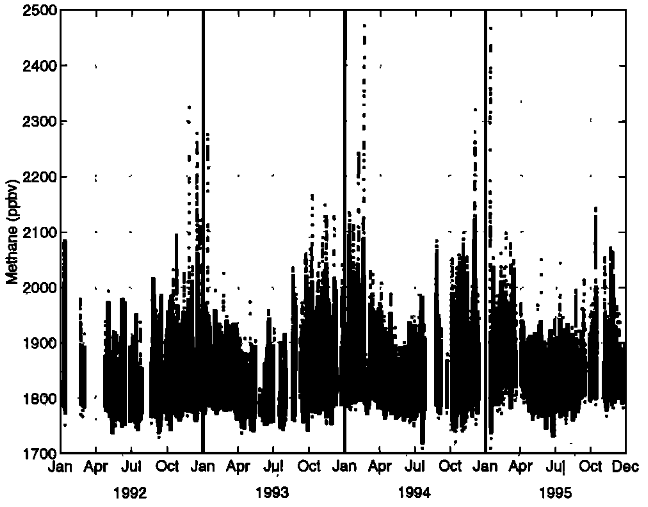

Figure 4. The atmospheric mixing ratios of methane at Harvard Forest between 1992 and 1995. These data show a variable upward trend, seasonal cycles, and the many pollution events that affect the site.

The diurnal cycles were obtained by taking the mean of all recorded data values centered at ±30 min of each hour for each day in the 4-year time period. The resulting monthly figures of the daily cycle are a composite of the 4 years of data and represent highly averaged conditions.

5. Long-Term Trend and Seasonal and Diurnal Cycles

For the 4-year time period from 1992 to 1995, approximately 125,000 individual CH_4 samples have been collected. Raw CH_4 mixing ratios are shown in Figure 4, while Tables 1–4 present monthly and seasonal summary statistics. The data shown in Figure 4 and the associated tables depict a variety of trends and systematic variations including a variable upward long-term trend; interannual variability; seasonal cycles; and a daily cycle, which are all discussed below. In addition and perhaps most noticeable are the numerous elevated CH_4 episodes, which will be discussed in a future publication [*Shipham et al.,* 1998].

5.1. Long-Term Trend

The long-term trend of CH_4 was calculated using the background data and is due to changes in global sources and sinks. The monthly median and median absolute deviation (MAD) for the full and background CH_4 mixing ratios are shown in Figure 5. From 1992 through 1995 a variable, upward trend of 5.5 ± 2 ppbv/yr is observed. However, from 1992 to mid-1993 the growth of CH_4 was slightly negative, with a decrease of −1 ± .3 ppbv/yr for 1992. This corresponds to a time period when *Dlugokencky et al.* [1994b] also noted a sharp decrease in the growth rate of the global mixing ratios of CH_4. During the summer of 1993 the variable upward trend again resumed. On an annual basis, increases of 8 ± 2 ppbv/yr, 9 ± 3 ppbv/yr, and 3 ± 1 ppbv/yr were observed for the years 1993, 1994, and 1995, respectively.

In the full data set, the annual median increased from 1808 to 1837 ppbv, an increase of 29 ppbv. The annual mean increased from 1826 to 1845 ppbv, increasing 19 ppbv. Differences between the mean and median values reflect the skewed distributions in the full data set. For the background data, the median increased from 1791 to 1811 ppbv, a difference of 20 ppbv, while the mean increased from 1790 to 1811 ppbv, a difference of 21 ppbv. Mean annual differences between the full and background data sets for each year are about 36, 30, 40, and 34 ppbv. Any significant increase or decrease in these values over time could indicate changes in the nature of pollution events reaching the site. Within this current four 4-time frame, no discernible trend was evident.

Table 1. Monthly and Seasonal Summary Statistics of Methane for 1992

	Median, ppbv	Median Absolute Deviation	Mean, ppbv	Standard Deviation	Measurement Maximum, ppbv	Measurement Minimum, ppbv	Number of Measurements
Jan.	1830	30	1870	84	2084	1752	1186
Feb.	1827	11	1834	27	1979	1767	934
March	1823	13	1828	23	1916	1784	260
April	1813	11	1817	20	1938	1779	1001
May	1803	12	1812	32	1993	1738	4994
June	1806	23	1823	45	1978	1750	2881
July	1797	14	1804	30	1951	1743	2835
Aug.	1817	29	1838	60	2015	1755	2194
Sep.	1801	18	1816	43	1985	1729	5076
Oct.	1812	25	1834	60	2094	1743	3915
Nov.	1821	28	1838	55	2324	1761	2808
Dec.	1812	24	1845	77	2278	1760	3484
Winter	1826	46	1851	65	2084	1752	2380
Spring	1805	26	1816	36	1993	1738	8876
Summer	1802	34	1817	46	2015	1729	10105
Fall	1815	47	1839	65	2324	1743	10207
Annual	1808	38	1826	54	2324	1729	31568

Table 2. Monthly and Seasonal Summary Statistics of Methane for 1993

	Median, ppbv	Median Absolute Deviation	Mean, ppbv	Standard Deviation	Measurement Maximum, ppbv	Measurement Minimum, ppbv	Number of Measurements
Jan.	1823	22	1840	51	2275	1764	3121
Feb.	1817	15	1825	30	2025	1772	3531
March	1814	16	1826	34	1947	1762	3487
April	1804	12	1808	23	1908	1737	3469
May	1800	14	1805	26	1973	1741	2124
June	1796	16	1805	32	1957	1753	2407
July	1788	16	1797	31	1924	1743	2226
Aug.	1815	24	1831	50	2034	1759	1682
Sep.	1825	26	1838	50	2060	1742	2261
Oct.	1818	18	1839	53	2165	1766	3659
Nov.	1837	33	1857	62	2148	1754	2959
Dec.	1838	18	1850	41	2127	1786	2360
Winter	1818	29	1830	39	2275	1762	10139
Spring	1801	20	1806	27	1973	1737	8000
Summer	1809	36	1822	48	2060	1742	6169
Fall	1829	41	1848	54	2165	1754	8978
Annual	1815	33	1828	46	2275	1737	33286

5.2. Seasonal Cycles

In the northern hemisphere, seasonal differences of CH_4 of 25–30 ppbv are related to changes in the oxidizing capacity of the atmosphere [*Khalil et al.,* 1993]. On a regional scale, seasonal differences at HF are enhanced due to a complex interaction between local sources and sinks, as well as meteorological patterns that advect CH_4 to the site from regional urban sources. Using monthly mean background data (with trend removed), a seasonal amplitude of about 26, 24, 26, and 36 ppbv/yr for the years 1992–1995 is observed (Figure 6). The seasonal cycles for the full data set have amplitudes of about 39, 36, 36, and 44 ppbv/yr for the same time period (Figure 7). In both cases, the maximum mixing ratios occur near midwinter and minimum ratios occur around midsummer, differing by up to several months from year to year.

Subtracting the background values (as shown in Figure 6) from the full data set values (as shown in Figure 7) leaves a seasonally varying residual, which is shown in Figure 8. This residual

Table 3. Monthly and Seasonal Summary Statistics of Methane for 1994

	Median, ppbv	Median Absolute Deviation	Mean, ppbv	Standard Deviation	Measurement Maximum, ppbv	Measurement Minimum, ppbv	Number of Measurements
Jan.	1838	25	1861	61	2134	1778	3887
Feb.	1840	24	1867	75	2471	1772	3206
March	1835	18	1848	38	2028	1782	3471
April	1823	18	1831	32	2007	1764	3699
May	1802	10	1812	32	1987	1763	1957
June	1811	20	1820	33	1945	1749	3041
July	1832	24	1836	39	1986	1709	2930
Aug.	1859	37	1873	59	2083	1787	842
Sep.	1811	13	1819	30	1948	1764	1426
Oct.	1850	35	1859	56	2058	1721	3097
Nov.	1843	28	1859	60	2098	1741	2799
Dec.	1860	29	1888	79	2320	1752	1736
Winter	1837	43	1858	60	2471	1772	10564
Spring	1813	26	1823	33	2007	1749	8697
Summer	1827	33	1837	45	2083	1709	5198
Fall	1850	48	1866	64	2320	1721	7632
Annual	1832	40	1847	56	2471	1709	32091

Table 4. Monthly and Seasonal Summary Statistics of Methane for 1995

	Median, ppbv	Median Absolute Deviation	Mean, ppbv	Standard Deviation	Measurement Maximum, ppbv	Measurement Minimum, ppbv	Number of Measurements
Jan.	1841	22	1864	86	2467	1709	1682
Feb.	1863	22	1873	40	2097	1772	2466
March	1860	18	1873	44	2079	1783	2281
April	1845	18	1845	27	1970	1776	2184
May	1810	15	1820	32	2050	1761	2468
June	1810	18	1817	33	1941	1732	2860
July	1824	17	1830	31	2044	1755	3137
Aug.	1825	21	1833	35	1995	1761	2505
Sep.	1843	21	1852	38	2013	1793	509
Oct.	1846	20	1864	52	2142	1788	1694
Nov.	1838	19	1854	51	2072	1768	2474
Dec.	1833	17	1840	30	1985	1783	2833
Winter	1857	37	1870	57	2467	1709	6429
Spring	1820	27	1826	33	2050	1732	7512
Summer	1826	26	1833	34	2044	1755	6151
Fall	1838	31	1851	45	2142	1768	7001
Annual	1837	32	1845	46	2467	1709	27525

between the full and background data is largest during the winter (15–21 ppbv) and smallest during the summer (11–13 ppbv) season. This pattern indicates that the effects of pollution are more pronounced in the winter than the summer. This is significant, as the contribution by natural local sources (wetlands) is lowest in the winter, suggesting that boundary layer dynamics are the dominant controlling process over the seasons. Changes in the seasonal differences between the full and background data over a longer time frame could be an indication of changes in CH_4 emissions.

5.3. Diurnal Cycles

The mean diurnal cycle during the 4-year time period for each month is shown in Figures 9a–91. Although the samples were taken during all meteorological conditions and represent highly averaged CH_4 mixing ratios, the figures show cycles that change in timing and magnitude through the year. The daily maximum and minimum mixing ratios of CH_4 and differences between them (both magnitude and time) are controlled by a number of factors, which

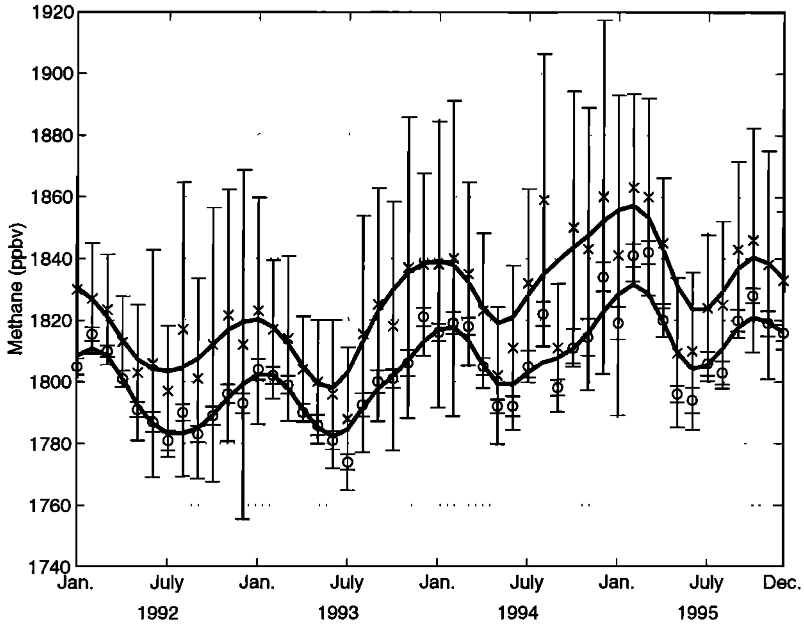

Figure 5. Monthly median and median absolute deviation of mixing ratios of methane for 1992–1995. The crosses (all data) and circles (background data) represent the median mixing ratios overlain by an error of ±1 median absolute deviation. The curves are generated by a robust spline fitting algorithm using the monthly data.

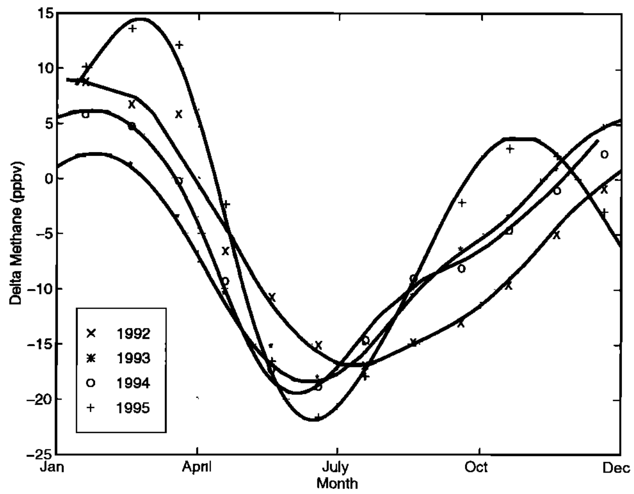

Figure 6. Background data seasonal cycles for 1992–1995. Symbols for each year are the monthly mean mixing ratios. Curves are generated by a robust spline fitting algorithm.

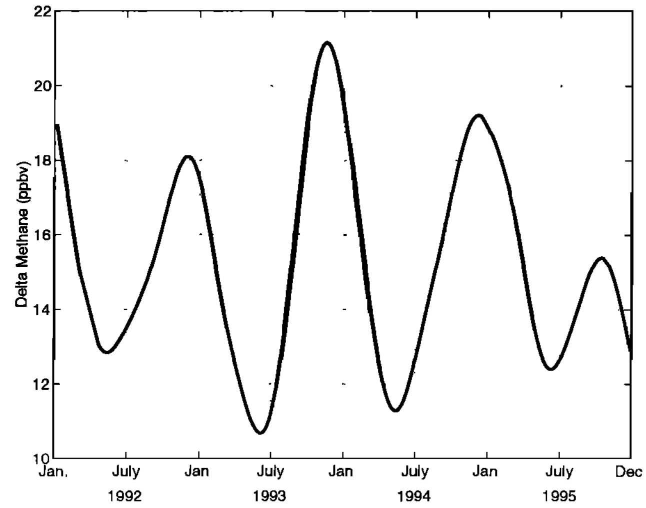

Figure 8. Residuals representing the monthly means of the full minus monthly means of the background data. The residuals are largest in the winter and smallest in the summer.

vary in importance on a seasonal basis. The most important factors include changes in oxidation rates, changes in the amount of emissions from sources, the amount of solar radiation, and the extent of atmospheric stability and mixing.

From December through February (Figures 9a–9c), limited vertical mixing and inputs from local sources appear to be the most important factors. Minimum values occur around 1500 LT, with a gradual buildup until around midnight, when values begin to decrease again. Approximately 6 hours elapse between the minimum concentration and the overnight maximum. The average amplitude of the daily cycle for these months is about 17 ppbv. Sources of CH_4 during the winter would be primarily from local and regional landfills, whose emissions continue on a year-round basis [*Czepiel et al.,* 1996a, b]. Although considered a small source, localized emissions from wood burning in association with home heating could also contribute to CH_4 buildup during the overnight hours [*Piccot et al.,* 1996; *Blaha et al.,* 1998]. With the ground frozen and generally snow covered, emissions from local wetlands are negligible during the winter season [*Melloh and Crill,* 1996].

March and April (Figures 9d and 9e) are a time of transition as solar radiation increases, temperatures begin to warm, the winter snowpack melts, and the frequency of strong nighttime temperature inversions decrease [*Holzworth,* 1967]. Inputs from nearby natural sources, mainly wetlands, however, remain low, and wood burning for home heating decreases. The resulting diurnal signal is very weak, with April amplitudes being the smallest during the year, around 6 ppbv.

From May through July (Figures 9f–9h) a pronounced diurnal cycle is observed. Increasing oxidation of species by OH and emissions from nearby local sources, wetlands and landfills, become the most important factors. Minimum concentrations occur around 1700 LT and begin increasing prior to sunset with the collapse of the turbulent mixed layer and continue to increase through the night, reaching a maximum near sunrise at 0600 LT. The period between maximum and minimum is about 12 hours, twice the wintertime length. Minimum values occur during the late afternoon, when the strongest vertical mixing occurs and the OH sink is large. July and August have the largest differences between maximum and minimum values, about 23 ppbv. The overnight increase in mixing ratios suggests that local sources, perhaps the nearby wetlands, are contributing to the increase.

August and September (Figures 9i and 9j) represent a second transitional time period when the amount of solar input is decreasing and vertical mixing is becoming less vigorous. For both months the minimum values occur around 1500 LT. During August, values increase until about midnight, when they begin to fall. The amplitude of the diurnal change decreases by about half (from 25 to 12 ppbv) from August to September, suggesting decreasing inputs from nearby wetlands. Finally, cycles in October and November (Figures 9k and 9l) reflect the shorter day length and reduced local inputs from wetlands, as a weak diurnal signal is observed. At this time of year the ground is still relatively warm and unfrozen, but the emissions from wetlands are decreasing and emissions from woodstoves are just beginning.

On a yearly basis the change in the diurnal cycle from month to month is for the most part gradual. However, a relatively large decrease in CH_4 is observed from March to April each year and may be due to increased oxidation by OH as longer days ensue and temperatures increase (Figure 10). By April, on average, the snow has melted and the waterlogged ground is drying, allowing inputs from local wetlands to contribute to the strong diurnal cycle discussed above. Emissions from local wetlands are acting to increase

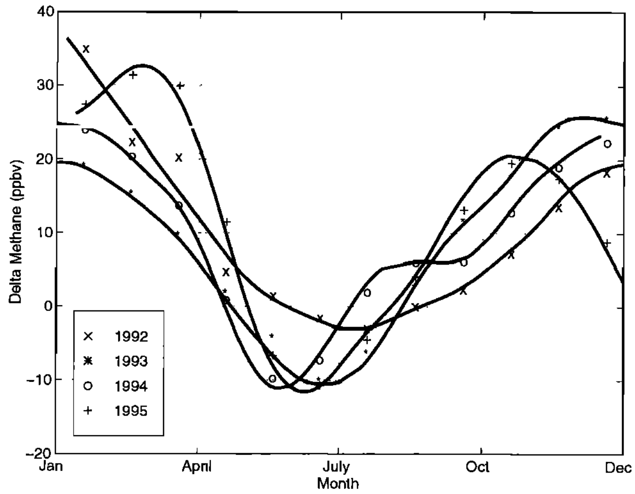

Figure 7. Full data set seasonal cycles for 1992–1995.

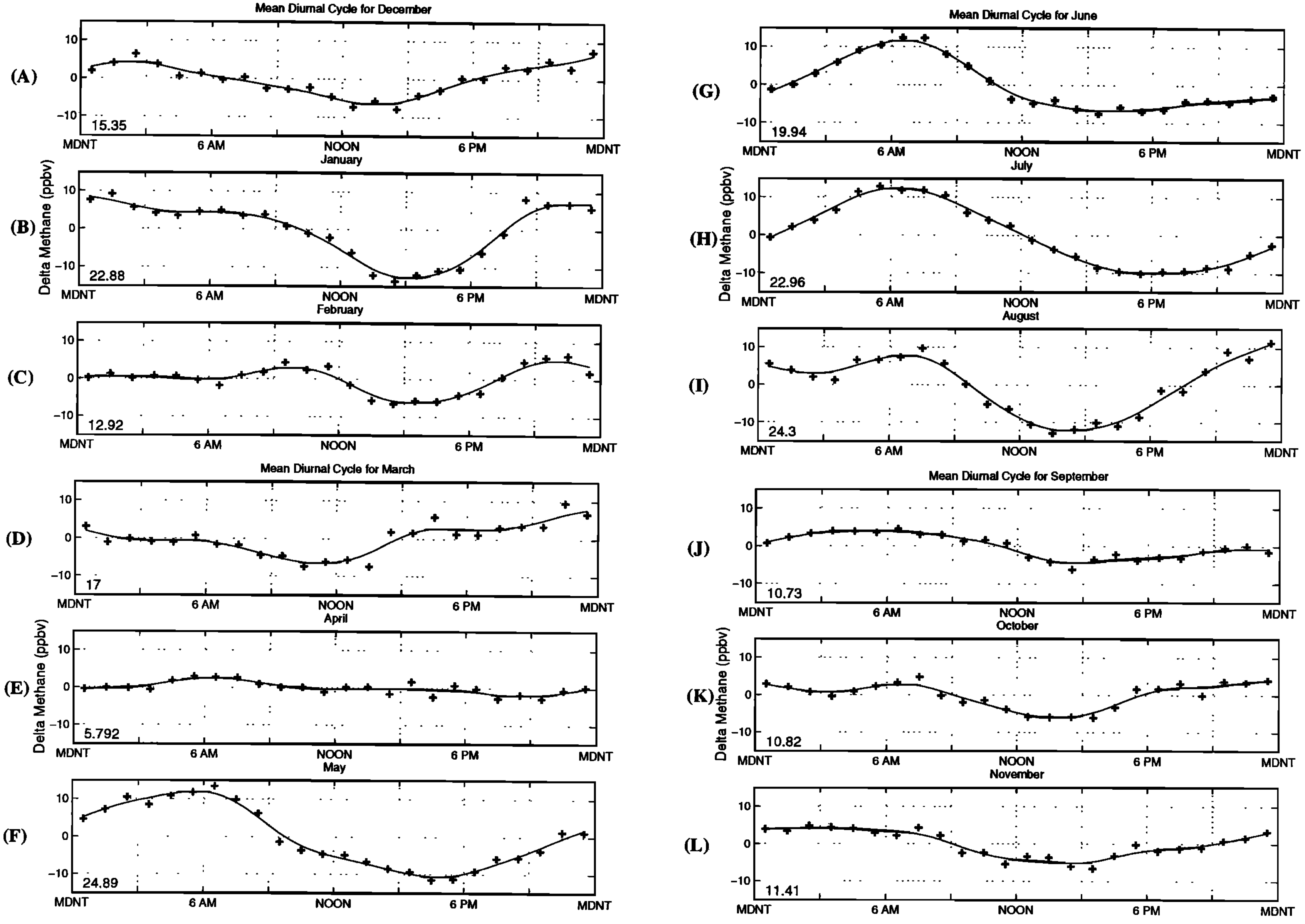

Figure 9. Mean diurnal cycle observed for each month, December through November. Number in the lower left-hand corner of each panel is maximum-minimum hourly mixing ratio.

the amount of CH_4 in the atmosphere at a time when removal by OH is increasing.

Opposite the spring effect, a large increase in CH_4 occurs between July and August (Figure 11), which is linked to decreasing OH oxidation. In August the diurnal cycle including overnight build up continues, but by September the emissions from nearby wetlands have diminished. Similar patterns were observed for the other years.

6. Conclusions

For the years 1992–1995, approximately 125,000 individually measured CH_4 mixing ratios were obtained at the HF research site. Over the 4-year period a variable upward trend of 5.5 ± 2 ppbv/yr was observed in the background data. Comparison of changes in the full and background data sets suggest that there has been little change in anthropogenic CH_4 inputs at the sampling site during the 4-year time period.

The trend and seasonal cycle were found to be similar to the global data set when the effects of pollution were minimized by analyzing a subset of the data. This is significant, as the global behavior of CH_4 is based on data that have been collected in remote regions carefully chosen to avoid the effects of pollution. Future sites could be located in more accessible and cost-effective locations and can serve a dual purpose in characterizing both changes in the composition of clean, background air and changes in the number and severity of pollution events on a regional scale.

The seasonal cycle reaches a maximum in midwinter and a minimum in early summer. In the background data, seasonal differences are around 25 ppbv, similar to those found for the global data set. Pollution events exaggerate the full data set seasonal cycle, especially during the winter when stable atmospheric conditions appear to contribute to longer and more severe pollution events.

A daily cycle is observed in which maximum mixing ratios are observed just prior to sunrise and minimum mixing ratios are observed in the afternoon near the time of maximum atmospheric mixing. Cycles vary between seasons, having the largest amplitudes in late spring and early summer when local wetlands may contribute to the signal and again in the winter when emissions from wood burning for home heating may impact the site. Smallest changes are in the spring and fall when inputs from both wetlands and wood burning are low.

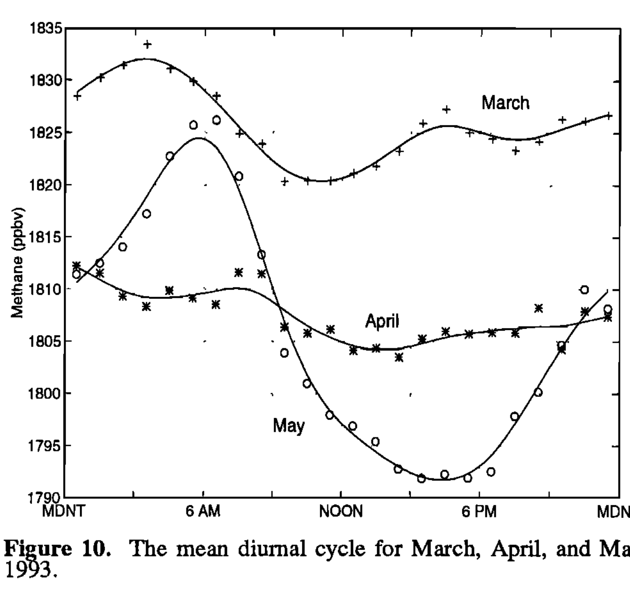

Figure 10. The mean diurnal cycle for March, April, and May, 1993.

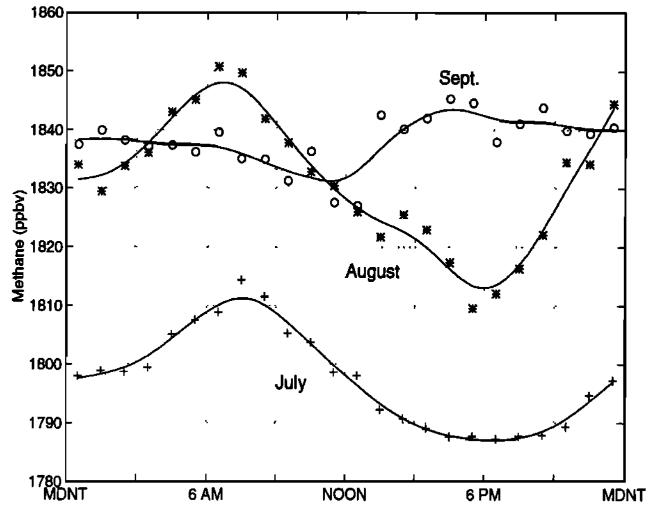

Figure 11. The mean diurnal cycle for July, August, and September, 1993.

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