ATMOSPHERIC METHANE, RECORD FROM A GREENLAND ICE CORE OVER THE LAST 1000 YEAR

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Abstract: The atmospheric methane concentration in ancient times can be reconstructed by analysing air entrapped in bubbles of polar ice sheets. We present results from an ice core from Central Greenland (Eurocore) covering the last 1000 years. We observe variations of about 70 ppbv around the mean pre-industrial level, which is confirmed at about 700 ppbv on a global average According to our data, the beginning of the anthropogenic methane increase can be set between 1750 and 1800 Changes in the oxidizing capacity of the atmosphere may contribute significantly to the pre-industrial methane concentration variations, but changes in methane emissions probably play a dominant role. Since methane release depends on a host of influences it is difficult to specify clearly the reasons for these emission changes. Methane concentrations correlate only partially with proxy-data of climatic factors which influence the wetland release (the main source in pre-industrial times). A good correlation between our data and a population record from China suggests that man may already have influenced the CH_4-cycle significantly before industrialisation.

Introduction

Methane is a radiatively and chemically active trace gas of the earth's atmosphere. Its atmospheric concentration has been measured continuously and directly since 1978 and shows an average increase of 0 8 to 1% per year [Blake and Rowland, 1988] with a slow-down during the most recent years [Steele et al., 1992]. There is strong evidence that the increase is caused by the increasing agricultural and industrial activities of the growing human population. Future trends of atmospheric CH_4 depend on the strength of the anthropogenic sources, the sinks as well as on the potential natural feedbacks of the greenhouse warming on the CH_4 cycle. One can learn about natural feedbacks by looking at the past variations of the atmospheric CH_4 and their links with natural climatic changes. At present, the most reliable means to investigate the evolution of the atmospheric trace gases in the past is the analysis of air entrapped in the bubbles of polar ice sheets. Previous ice core studies which focused on the past atmospheric CH_4 trend have revealed that over the last 1000 years, the CH_4 background was mostly around 700 ppbv, that is only about 40% of its present-day level [Rasmussen and Khalil, 1984; Stauffer et al., 1985; Raynaud et al., 1988; Etheridge et al., 1992]. Only during the last 200-300 years did the CH_4 mixing ratio increase to its present-day level of about 1700 ppbv. Fluctuations of up to 50 ppbv around the 700 ppbv "natural" level were suggested [Khalil and

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Rasmussen, 1989] but were not clearly resolved due to the large scatter of the data and problems in dating the air samples. This paper presents new results from two laboratories with an analytical precision and time resolution which allow the observation of features not seen before on the time scale of the last 1000 years.

In the framework of the Eurocore project, in 1989, an ice core of 304 meters was drilled electromechanically at Summit in Central Greenland (72.58°N, 37.64°W; mean annual temperature: -32°C, mean accumulation rate: 209 kg/m²/yr). The absence of any drilling fluid and the low temperature make the core suitable for gas measurements. The core was dated with an accuracy of ± 2 years by combining seasonal variations of δD and $\delta^{18}O$ with electric conductivity measurements and chemical data. Acid layers of volcanic eruptions were used as timemarkers for cross-checking. The age difference between the ice and the mean age of the enclosed air is about 210 years. Due to the diffusive mixing in the firn the air in the bubbles has not a discrete age but an age distribution with a standard deviation of about 7 years [Schwander et al., 1993].

Experiments

Since methane does not interact chemically with water, both dry and melt extraction methods are applicable. The measurements presented were carried out in two laboratories In Grenoble a melt extraction technique was used and in Bern the gas was extracted with a dry extraction method.

For the melt extraction method an ice sample of about 40 g is placed in a glass vessel sealed with vacuum grease. The air surrounding the sample is evacuated, then the ice is melted. After that, the meltwater is slowly refrozen from the bottom, expelling close to 100% of the dissolved air. After refreezing, the extracted gas is expanded in an extraction line and injected in a gas chromatograph (GC) (Varian 3300) equipped with a flame ionization detector (FID). The extracted air is used for three injections. The measured methane concentrations have to be corrected due to a contamination in the extraction chamber The correction is determined by calibration with standard gas added to gas-free ice. The overall accuracy estimated from calibration analyses (95% confidence interval, excluded the uncertainty due to the standard gas) is ± 40 ppbv [Raynaud et al. 1988]. The system is calibrated using an air standard (Air Liquide) containing 1200 ± 100 ppbv of CH_4.

The dry extractions have been performed with a newly developed milling device [Fuchs et al., 1993]. 10 to 15 g of ice are sealed in the extraction chamber which is continuously flushed with helium. When the air in the chamber is entirely replaced by helium, the ice is milled with a rotary cutter. The helium carries the gases escaping from the opened bubbles to a cryofocusing device (Porapack Q column, cooled to below -170 °C by liquid nitrogen) where they are stored until the injection into the GC (Hewlett Packard 5880 A, equipped with a FID) through thermal desorption. For calibration a standard gas with 980 ± 30 ppbv (Messer Griessheim) of

CH$_4$ is used. To estimate the analytical accuracy we carried out a calibration series by introducing standard gas into the mill in order to approximate a real extraction. From this series the 95% confidence interval for an analyses is ± 28 ppbv (excluding the uncertainty due to the standard gas).

An independent check of the above-mentioned precision estimates is to look at the reproducibility of measurements performed at the same depth level in the ice. Samples on a given depth level are separated at most by 55 cm, corresponding to a difference of age of about 2 years and hence a negligible difference in composition of the air-bubbles. In both laboratories, generally two samples were analysed at each depth level (Table 1). From the variance of the results we calculate mean 95% confidence intervals for single data points from each laboratory. We find ± 40 ppbv for Grenoble and ± 20 ppbv for Bern. This is within the statistical variation in good agreement with the analytical precision indicated above.

TABLE 1: Methane concentrations versus depth and gas age:

Depth [m]	Gas age yr AD	Bern CH$_4$ [ppbv]			Depth [m]	Gas age yr AD	Grenoble CH$_4$ [ppbv]	
		C1	C2	C3			K1	K2
89.2	1907	996	991	980	89.6	1905	1030	968
99.3	1864	870	862		99.1	1865	859	896
110.1	1817	808	798		104.5	1842	812	818
118 9	1775	803	796		110.5	1815	764	754
128.8	1734	753	763		119.2	1774	755	765
138.7	1691	738	773		129	1733	729	726
148.8	1651	740	766		139	1690	770	774
158.4	1605	730	743		148.6	1652	714	750
168.8	1555	763	760		158.8	1603	690	722
178.2	1510	761	726		168 4	1557	760	781
188.4	1466	690	710		178.6	1508	740	728
216.1	1335	692	678		188.2	1467	724	727
233.5	1254	694	703		211.5	1357	700	688
242.9	1210	743	729		219.2	1320	714	749
252.4	1165	763	756		222.7	1304	703	733
263	1114	738	727		233.7	1253	693	656
272 3	1075	711	725		243	1210	710	774
283	1025	722	717		251.9	1168	811	752
292.6	974	714	695					

Depth: Meters below the surface of 1989. Each of the sets C1-C3 and K1, K2 consists of results from neighbouring samples. While each of C1-C3 are results from single gaschromatographic analysis of the extracted gas, K1 and K2 are mean values from three analyses

Fig. 1: Methane results obtained at the same depth levels: Comparision between Grenoble and Bern. Solid line: Linear regression. Dashed lines: Limits for the 95% confidence interval for the regression.

The comparison between the two laboratories was carried out by measurements at the same depth levels and by inter-calibrating the standard gases. For each depth level analysed by both laboratories, the mean result from Grenoble is plotted against the mean result from Bern in Figure 1. The linear regression with a slope of 1.03 ± 0.09 and the mean difference between data pairs (Bern minus Grenoble values) of 7 ± 6 ppbv demonstrate that the equipment in Bern and in Grenoble lead to the same results within the statistical variations. The intercalibration of the standard gases used by the two laboratories reveals an agreement better than ± 5 ppbv. We assume therefore that the absolute uncertainty of the standard gases used in Bern and in Grenoble corresponds to the lower one of those indicated by the two suppliers, that is ± 30 ppbv.

Results

A total of 36 samples at 18 depth levels and 39 samples at 19 depth levels have been analysed in Grenoble and Bern, respectively (Table 1). The samples were spaced at age intervals ranging from 15 to 109 years with an average of 42 years. The composite record from both laboratories is plotted against the mean gas age in Figure 2. The characteristics of the records obtained in the two laboratories are very similar. To illustrate the tendencies more clearly we fit a smoothed spline curve through the combined Bern/Grenoble data set. The very general shape of the CH$_4$ record is consistent with previously published data, with a roughly stable level before 1750 AD and a large increase starting at the beginning of the nineteenth century. On the average, a concentration of 730 ppbv is obtained in the time interval 1000-1750 AD. Considering a pre-industrial interhemispheric gradient of 70 ppbv [Rasmussen & Khalil, 1984], this results in a mean global pre-industrial CH$_4$ concentration of 700 ppbv. Apart from this general trend, the present record reveals CH$_4$ variations up to 70 ppbv during pre-industrial times. A concentration maximum occurred around 1150 AD, followed by lower CH$_4$ concentrations between 1250 and 1500 AD. Around 1500 AD the concentration increased again to remain relatively constant till 1750 AD. According to our data, the beginning of the large and recent anthropogenic methane increase can be set between 1750 and 1800 AD.

Rasmussen and Khalil [1984] have published the most complete CH$_4$ record covering the same time interval as ours based on ice core data from Greenland and Antarctica. To compare their record with our results, we reconsidered their record and recalculated the age of the enclosed air by using newer results concerning the enclosure process [Schwander and Stauffer, 1984]. We have increased the data from Antarctica by 10% in order to account for the interhemispheric gradient [Rasmussen and Khalil, 1984]. A couple of data suspected of being contaminated were eliminated [Khalil and Rasmussen, 1989]. The general trend was extracted by moving averages over each successive 9 data points, following the approach of Khalil and Rasmussen [1989], though there are few results in the period 1200-1500 AD which makes the appropriateness of the running mean approximation questionable. The mean pre-industrial value is the same within the error limits, but the characteristics of the two records are quite different (Figure 2). We consider our record as more reliable because (1) we got more results over the entire interval, (2) the scatter of our results is smaller, and (3) our two
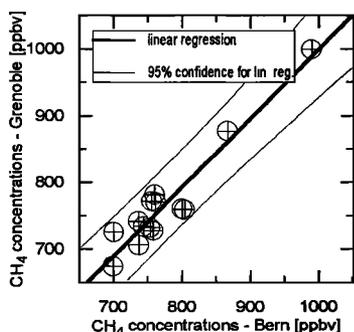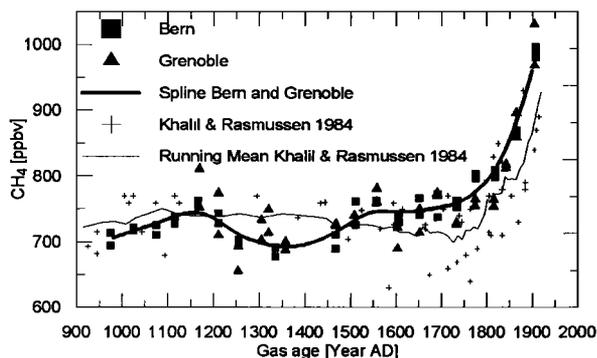
Fig. 2: Methane records versus the mean gas age. Squares and triangles from this study (squares: results from Bern; triangles: results from Grenoble) Thick solid line: Smoothed spline through the Bern and Grenoble data. Crosses: Results from various ice cores [Khalil and Rasmussen, 1984] corrected to Greenland concentration level The mean gas age was recalculated after Schwander and Stauffer [1984]. Thin solid line: Running Mean of 9 data points.

laboratories obtained the same characteristics using different analytical methods. We are therefore confident that the detailed pre-industrial trend revealed by our record is significant and reflects variations of the atmospheric CH_4 concentration.

Discussion

In this section we discuss possible causes for the concentration fluctuations observed at Summit in the pre-industrial period between 900 and 1700 AD. The methane concentration of the air in the ice reflects changes on a global scale with a higher influence from the northern hemisphere where the majority of the sources is situated. Regional sources are small and thus of minor importance for the air composition in Central Greenland. The difference of 70 ppbv between maximum and minimum CH_4 levels corresponds to a 10% change of the atmospheric burden, that is 190 Tg. Assuming steady state conditions, this change (C) is related to the emission change (S) by the equation: $C = S \tau$, where τ is the atmospheric residence time of CH_4. Therefore the 70 ppbv variation can be the consequence of a 10% change of either the sources or the residence time, or a combination of both. The pre-industrial range for τ is 8-11 years and the CH_4 emissions amounted to about 200 Tg/year [Chappellaz et al., 1993].

The main sink (about 95%) for methane is the reaction with OH-radicals in the atmosphere. Photochemical models taking into account climate and trace-gas concentration changes suggest a 10 to 30% decrease of the OH concentration from the Last Glacial Maximum to the Pre-Industrial Holocene [Thompson, 1992]. The pre-industrial changes in climatic parameters (temperature, trace gases) amount to about one fifth of the shift from glacial to interglacial conditions. Assuming an approximately linear response of the OH concentration to climate changes, the pre-industrial variations would give rise to 2 to 6% change of the CH_4 lifetime, explaining 20 to 60% of the 70 ppbv methane concentration change. The remaining 40 to 80% would have to be explained by changes in the source intensity.

Methane emissions can vary by natural causes or by changes in man-made emissions. According to pre-industrial

budget estimates the main natural sources are wetlands which may cause as much as 75% of the natural emissions during pre-industrial times [Chappellaz et al., 1993]. A 15% change of the pre-industrial wetland emission would explain the concentration change of 70 ppbv. Wetland emissions of CH_4 depend on many parameters including temperature and water table elevation. The extent of wetlands itself depends essentially on the hydrological balance (precipitation minus evaporation and run off). Therefore climatic fluctuations will have an impact on the wetland source strength both through precipitation and temperature.

Since 75% of the wetland release [Chappellaz et al, 1993] originates from the northern hemisphere we restrict the following comparison to northern hemispheric temperature records. The majority of the available temperature records [Bradley and Jones, 1992] is quite similar, but there exist also a few records showing a quite different picture. Representative of the general trend, two temperature records, one from lake sediments in Michigan (USA) [Bernabo, 1981] and a chronicle record from Central England [Lamb, 1977] are plotted together with our methane data in Figure 3. One remarkable feature is the correspondence between the high CH_4 concentrations and the temperature records at the end of the 12th century, corresponding to the Medieval Warm Époque. However, this climatic event is for instance not observed in northern Sweden [Briffa et al. 1990]. The following climatic event, the Little Ice Age, is clearly seen in the two temperature records of Figure 3. While at its beginning there is a parallel decrease in methane, the latter rises already around 1500, much before the end of the Little Ice Age. Although there is some indication of a correlation between temperature and CH_4 concentration, the lack of a global coverage and the broad regional scatter of temperature data preclude detailed conclusions. Data related to the hydrological balance are even more scanty and will not be discussed here.

The magnitude of anthropogenic CH_4 sources is in a first approximation related to the global human population, primarily through the increase of the rice cultivation area and the number of domestic ruminants which may be responsible for around 50% of the concentration change from pre-industrial times to the present [Khalil et al., 1993]. When comparing the pre-industrial methane record with the development
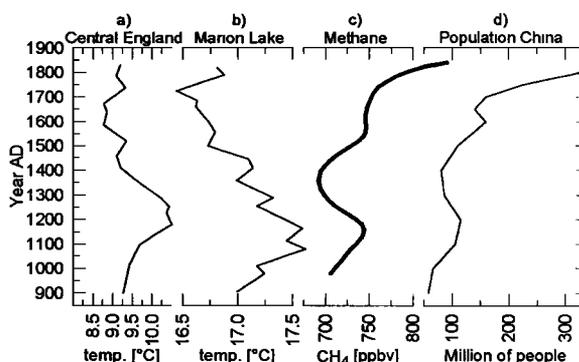

Fig. 3: Comparison between our data and historical records. a) Mean annual temperature of Central England [Lamb, 1977]. b) Growing season temperature from Marion Lake, Michigan [Bernabo, 1981]. c) Methane smoothed spline, this study. d) Population of China [McEvendy and Jones, 1979].

of the human population in China, one of the main rice cultivating areas (Figure 3) [McEvendy and Jones, 1979], one can observe that the CH_4 concentration variations are surprisingly well correlated with the population fluctuations. The relationship between population and methane emissions from rice cultivation depends on agricultural practices. For the beginning of this century Khalil et al. [1993] report a value of about 35 Tg/year/billion people. Assuming this relation to be valid also for the beginning of the millenium the Chinese population variations alone could explain up to 10% of a 20 Tg change in the global emissions between 1200 and 1300 AD. Although data on population and on rice cultivating areas and cultivation practices in ancient times are not very reliable, we think that rice cultivation is likely to contribute to the observed atmospheric concentration change. If so, we have to go further back in time to investigate atmospheric methane concentrations which are totally undisturbed by human.

Conclusion

Investigations of the atmospheric CH_4 changes over the last 1000 years from the Summit ice core confirm the mean pre-industrial level of about 700 ppbv and the recent anthropogenic increase. In addition, we see pre-industrial concentration variations in the range of 70 ppbv. 20 to 60% of these variations can be explained by changes in the oxidizing capacity of the atmosphere. The larger contribution stems from changes in methane emission. Since methane release depends on a host of influences it is difficult to assign reasons for the 70 ppbv pre-industrial variations. Climatic fluctuations on this time scale have probably impacted the largest natural sources, i.e. the wetlands, but the lack of climate proxy data on a global scale preclude a quantitative estimate of this impact. Finally, the role of the pre-industrial anthropogenic sources may have been significant but cannot account for the full amplitude of CH_4 variations. Further investigations on historic and proxy climate records are necessary to elaborate a more satisfying scenario describing the interaction of climate, man and the CH_4-cycle in the pre-industrial period of this millennium.

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