Methane in the northern Atlantic controlled by microbial oxidation and atmospheric history

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Abstract. During May - August, 1997, the distributions of dissolved methane and CCl_3F (CFC11) were measured in the Atlantic between 50° and 60°N. In surface waters throughout the region, methane was observed to be close to equilibrium with the atmospheric mixing ratio, implying that surface ocean methane is tracking its atmospheric history in regions of North Atlantic Deep Water formation. Despite the different atmospheric history and ocean chemistry of CH_4 and CFC11, their spatial distribution patterns in the water column are remarkably similar. One-dimensional distributions have been simulated with an advection-diffusion model forced by the atmospheric histories. The results suggest that the similar patterns result from the increasing input of CH_4 and CFC11 to newly formed deep waters over time, combined with the effect of horizontal mixing and the oxidation of methane on a 50 year time scale.

Introduction

In the deep ocean, methane is generally undersaturated with respect to the present atmospheric mixing ratio, apparently due to its oxidative consumption. Earlier data from the North Atlantic indicated that methane decreases to a background concentration of about 15% of saturation during the first 100 years after deep water formation, after which the consumption virtually ceases [*Scranton and Brewer*, 1978]. Since the atmospheric methane concentration has almost doubled during the last 100 years (Fig. 1), it is possible that part of the apparent undersaturation is due to lower concentrations implanted in deep waters formed in the past. This would occur if the methane concentration in their surface water sources tracks the atmospheric history.

The only pathway for the chlorofluoromethanes to enter the ocean is by air-sea exchange. CFC11 has been released into the atmosphere since the 1940s, increasing monotonically to a contemporary value of 265pptv (Fig. 1). The CFC11 concentration in surface waters has followed this increase in the atmosphere. In regions of deep water formation, the surface CFC11 signal is introduced into the deep ocean, and thus newly formed deep water is tagged with a higher CFC11 signal than deep water formed earlier. CFC's behave in the ocean like a noble gas; their distribution is of a transient nature and en-

tirely controlled by deep water circulation and mixing. Owing to this behavior, the CFC's are often used to estimate the time scales of deep water spreading and to study the various spreading pathways [*Fine*, 1995; *Rhein et al.*, 1995].

Analogous to CFC11, the rise in atmospheric CH_4 should affect the temporal evolution of the deep water CH_4 concentration. In the northern North Atlantic, deep water is formed in areas of the Labrador and Greenland seas. Hence, conversion of former surface water to deep water should account in part for the CH_4 undersaturation relative to the present atmospheric CH_4 partial pressure observed in the deep ocean. Both trace gases are influenced by lateral circulation and mixing, but unlike CFC11, methane is consumed in deep water by microbial oxidation; thus, it is not a conservative tracer.

It appears that the oxidation rate of methane varies widely with environmental conditions in the sea. Radiocarbon incubation experiments and combined $CH_4/^{222}Rn$ measurements indicate very rapid rates in hydrothermal plumes [*De Angelis et al.*, 1993; *Kadko et al.*, 1990] and much slower rates in "normal" seawater with low particle/substrate concentration. *Scranton and Brewer's* (1978) early estimate of 0.15 nmol l^{-1}
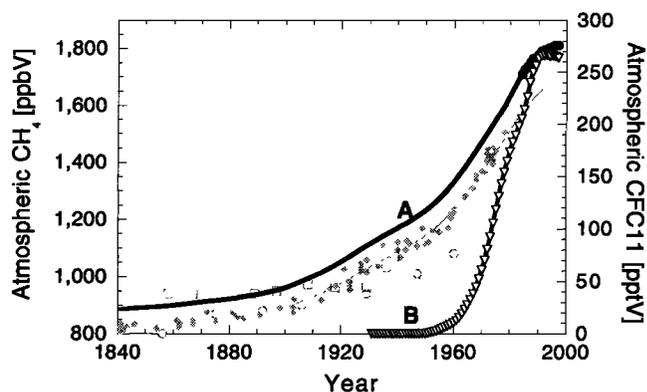
Figure 1. Atmospheric concentrations of CH_4 and CFC11 over the last 150 years. (♦): CH_4 concentrations for the southern hemisphere from 1841 to 1978 derived from the Antarctic ice core DE 08 [Etheridge et al., 1992]. Also shown are the data from the Mt. Logan (Yukon) ( ) and 2OD ( ) (Greenland) ice cores [Dibb et al., 1993] in the northern hemisphere. To estimate the atmospheric history in the northern hemisphere, the best fit to the data from DE 08 was multiplied with the factor 1.076 to account for the interhemispheric gradient [Dlugokencky et al., 1994; Nakazawa et al., 1993]. **A.** Estimated atmospheric CH_4 concentrations from 1841 to 1878 (——), and methane concentrations at Station M (66° N, 2° E) from 1984 to 1997 (●) [Dlugokencky et al., 1994]. **B.** (▼): Atmospheric CFC11 concentrations on the northern hemisphere were calculated from Chemical Manufacturers Association (CMA) CFC11 release figures from 1931 to 1981, and measured CFC11 concentrations are shown from 1981 to 1997 [Cunnold et al., 1994].
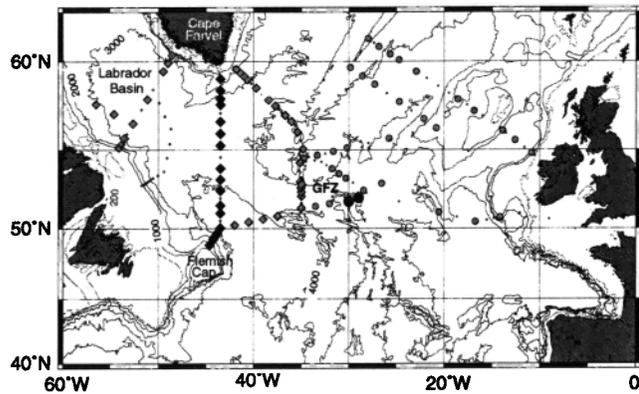
Figure 2. Bathymetry of the northern North Atlantic and station locations of the CH_4 and CFC11 survey. (●): Stations sampled in May-June 1997 during METEOR cruise 39/2; (●): Stations with enhanced CH_4 concentrations in the lower water column at the eastern end of the Gibbs Fracture Zone (GFZ); (◆): Stations sampled in July-August 1997 during METEOR cruise 39/4; (◆): Stations used for the CH_4 and CFC11 section from Cape Farvel to the Flemish Cap shown in Figure 3.

yr^{-1} in northern components of North Atlantic Deep Water (NADW) corresponds to an average residence time of about 14 years. In this report, we compare the distributions of dissolved CH_4 and CFC11, and we deduce from this comparison that the time scale of methane oxidation in NADW components is about 50 years.

Methods

During METEOR cruises 39/2 and 39/4 (Fig. 2), methane and chlorofluorocarbons were measured on discrete samples from the water column, and CH_4 in surface waters was continuously surveyed along the cruise track using an equilibration system [*Rehder*, 1996]. For CH_4 analysis on the discrete samples, a modification of the vacuum degassing method described by *Lammers and Suess* [1994] was used. The modification involved sampling of 400 ml of seawater using a large glass syringe and injecting the sample into pre-evacuated 600 ml glass bottles. The air and water phases were equilibrated by shaking for at least 30 min. The gas phase was subsequently recompressed to atmospheric pressure and the CH_4 mole fraction of the extracted gas was determined by gas chromatography using flame ionization detection. The total gas content of the sample was calculated from the measured dissolved oxygen concentration and assuming that N_2 and Argon were 100% saturated relative to their atmospheric partial pressures [*Weiss*, 1970]. The dissolved methane concentration was calculated as the product of the mole fraction in the extracted gas phase and the amount of total gas (STP) in the sample. For calibration, mixtures of 1.936ppm ±0.003 ppm and 9.854 ±0.006 ppm in synthetic air (Deuste Steininger, calibrated against NOAA/CMDL standards at the Institute for Environmental Physics, Heidelberg) were used. The average deviation of duplicate samples was 3%. The mean saturation of all discrete surface water samples (<15m) during the surveys (101.5±4.2%) is in good agreement with the results from the continuous survey (see following section).

CFC11 was analysed on board using a gas chromatographic technique similar to that of *Bullister and Weiss* [1988]. The gas standard (273.1pptV, SIO93 scale) was kindly provided by D. Wallace (now IFM Kiel). Analysis of duplicates on about 10% of all samples gave a precision of ±0.8%. About 1450 water samples for CH_4 and 2600 for CFC11 were measured.

Methane on air samples was measured every 40 minutes, and the average value agrees well with the mean value for the period of May to September at Station M (66°N), i.e. 1.797 ppmV [ftp://ftp.cmdl.noaa.gov/ccg/ch4/flask/month]. The atmospheric mole fraction of CFC11 was measured once a week (mean 265 pptV; σ= 5pptV) and is in agreement with the mean value of 263 pptV for the period from May to September at Mace Head, Ireland [http://cdiac.esd.ornl.gov/ftp/ale_gage_Agage/Agage].

CH_4-Equilibrium in Surface Waters

The surface waters of the subpolar North Atlantic appear to be almost exactly in equilibrium with the atmospheric partial pressure for CH_4, similar to CFCs. The mean saturation for CH_4 was +101.1% (σ = 1.4%) for all equilibrator measurements along the cruise track. This is in contrast to the greater oversaturation of surface waters often found in lower latitudes, which is caused by the production of methane in anoxic microenvironments in the upper water column [*Karl and Tilbrook*, 1994]. However, surface waters of the northern Pacific are also in equilibrium with atmospheric methane, and the latitudinal gradient of CH_4 oversaturation appears to result from upwelling processes and the seasonal cycle of sea surface temperature [*Bates et al.*, 1996]. Low sea surface temperatures might also be a reason for a small CH_4 production in high latitudes, as lower temperatures generally tend to depress methanogenesis. *Bates et al.* [1996] have shown that the methane concentration in surface waters of the North Pacific has followed the atmospheric increase over a 7 year time period, and this coupling of atmospheric and surface ocean methane is predicted in the box model of *Bange et al.* [1994]. Thus, it seems very likely that the methane concentration in the North Atlantic has also been tracking the atmospheric CH_4 content.

CH_4 and CFC11 Distributions

In order to compare the distribution patterns of CH_4 and CFC11 in the water column, we calculate their percentage of saturation relative to equilibrium with the present atmospheric mole fractions in the northern hemisphere (1,800 ppbV and 265 pptV, respectively). This approach eliminates differences due to the temperature dependence of the trace gas solubilities in seawater [*Wiesenburg and Guinasso*, 1979; *Warner and Weiss*, 1985]. As illustrated by the section from Cape Farvel to the Flemish Cap (Fig. 3), the distributions of CH_4 and CFC11 percent saturations were found to be remarkably similar. The highest percent saturations below the thermocline are found in the Labrador Sea Water (LSW) between 500-2000m. The 'youngest' LSW is found in the northern part of the section, in agreement with the circulation pattern recently suggested by *Sy et al.* (1997). Most of the water below 2000m is Gibbs Fracture Zone Water (GFZW). This is an older component of the NADW, which enters the western basin of the North Atlantic through the Gibbs Fracture Zone (GFZ) and is characterized by low concentrations of CFC11 [*Smethie and Swift*, 1989] and CH_4. Younger overflow water from the Denmark Strait (DSOW) circulates cyclonically in the Labrador Sea and is identified by the higher CFC11 and CH_4 concentrations near the bottom north of 57.5°N and in the Labrador Basin at the southern end of the section. Except for two stations near the east end of the Gibbs Fracture Zone, the strong correlation between CH_4 and CFC11 percent saturation extends throughout
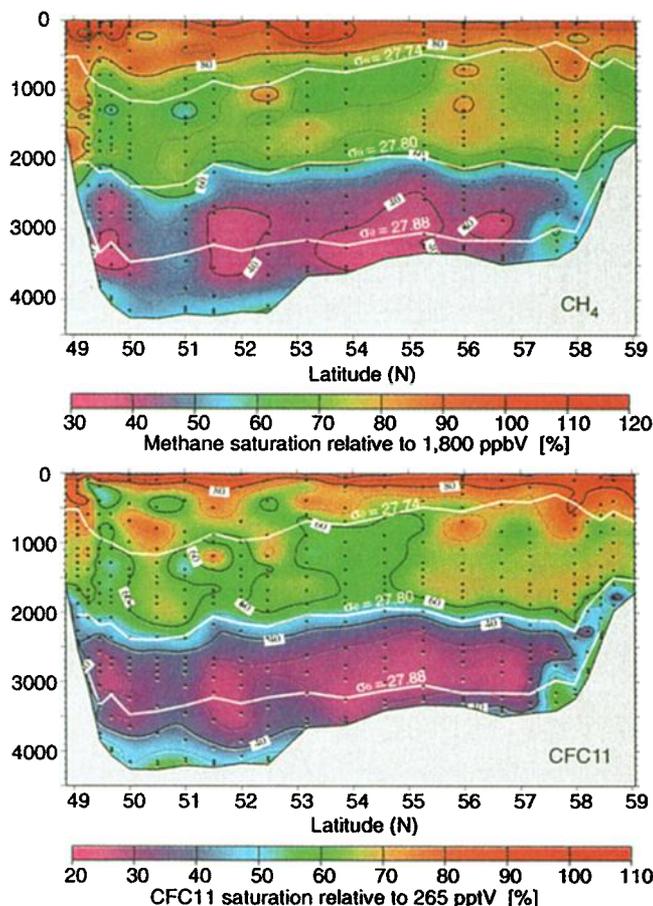
Figure 3. CH$_4$ and CFC11 distribution between Cape Farvel and Flemish Cap given as percent saturation relative to equilibrium with the present atmospheric mole fractions of 1,800 ppbV and 265 pptV, respectively. Also shown are the isopycnal surfaces σ_Θ = 27.74, 27.80 and 27.88. Labrador Sea Water (LSW) is located between σ_Θ = 27.74 and σ_Θ = 27.80.

the entire survey area. A plot of CH$_4$ versus CFC11 for all paired measurements shows that the percent saturations are correlated almost linearly with a CH$_4$ intercept of about 20% (Fig. 4).

Rate of CH$_4$ Oxidation

We estimate the oxidation rate of methane from the CH$_4$ versus CFC11 correlation by integrating each atmospheric history with a one-dimensional advection-diffusion model, given by

$$\frac{\partial C}{\partial t} = K_h \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - k_1 C \qquad (1)$$

where C indicates the dissolved concentration of either gas, and K_h and u are the eddy diffusivity and advection rate applied to both simulations. The oxidation of methane is assumed to be first order with rate constant, k_1; for CFC11, k_1 = 0. The model serves as a simple analog of the mixing and circulation affecting deep waters after they are formed. The principal effect of mixing in the model is to spread the relatively rapid temporal increase in chlorofluorocarbon input downstream to a greater extent than the more slowly increasing CH$_4$ signal. The flux of the dissolved gases to the deep water is presumed to be u × $C_{atm}(t)$, where $C_{atm}(t)$ is the concentration at equilibrium with

the atmospheric mixing ratio at time, t. With this boundary condition, the "newest" deep waters at x = 0 never achieve full saturation with the temporally varying atmospheric concentration because of mixing with lower concentrations downstream. The length scale of the model, L, is prescribed to be long enough to approximate the semi-infinite system. When u is scaled to L, $C(x/L, t)$ depends only on the ratio K_h^2/u, and the absolute value of k_1, in the case of CH$_4$.

The lines in Figure 4 show a sequence of CH$_4$ versus CFC11 trends as simulated according to various k_1. Here, the physical parameters (K_h and u) are set to yield 70% saturation of CFC11 at the present time in "newly-formed deep waters" (at x = 0). This corresponds to the CFC11 concentration observed in new LSW (near Greenland in Figure 3, for example). In the absence of methane consumption, the ratio of CH$_4$ to CFC11 would be considerable greater than the near 1 to 1 correspondence that is observed (k_1 = 0, Fig. 4). Increasing consumption reduces the inventory of methane in the spatial domain. The trend of CH$_4$ versus CFC11 simulated with k_1 = 0.02 yr^{-1} appears to be quite similar to the observations below 600 m in the survey area, indicating a residence time of methane of about 50 years. By comparing the methane concentrations simulated by k_1 = 0 and 0.02 yr^{-1}, one can estimate the relative contributions of atmospheric history and in-situ oxidation to the apparent methane undersaturation. In newly formed deep water (the 70% saturation level for CFC11 in Figure 4), it is predicted that methane saturation would be 90% in the absence of oxidation and 75% at k_1 = 0.02 yr^{-1}. On this basis, it appears that the
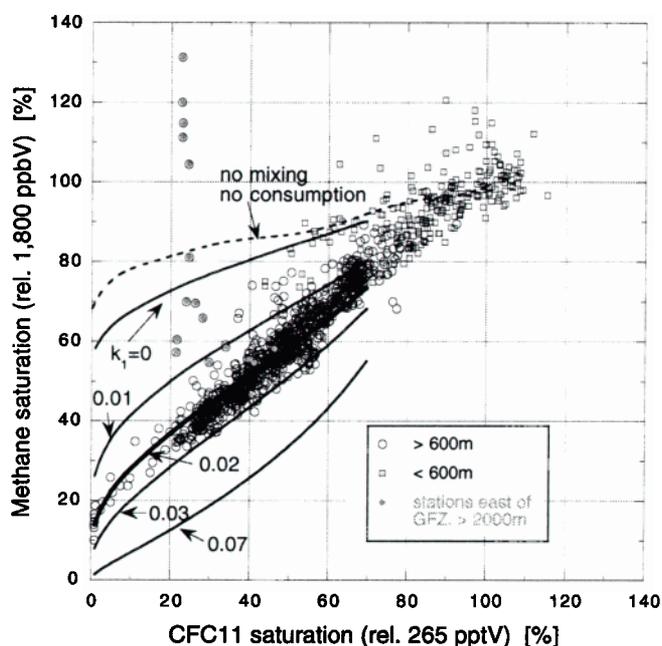
Figure 4. Percent saturation of CH$_4$ vs. CFC 11: Observations and model results. Measurements above and below 600m depth are shown by (□) and (○), respectively. The 600m cut-off was chosen because the model used is not appropriate to simulate the processes in the surface layer. (●): Data from below 2000m at two stations at the eastern end of the Gibbs Fracture Zone (51° 45.1'N, 30° 0.2'W and 52°N, 28° 57.6'W), are affected by an additional methane source. (——): Trends derived from model-simulated spatial distributions of CH$_4$ and CFC11. Numbers indicate the rate constant, k_1 [yr^{-1}], for methane consumption. (----): "Unprocessed" CH$_4$ vs. CFC11 saturation assuming no mixing and no CH$_4$ oxidation. The initial concentrations at t = 0 were set at zero for CFC11 and steady state with the 1850 atmospheric mixing ratio for CH$_4$ (800 ppbV). For the lines shown, K_h^2/u = 1.8 × 10^6 km^3/yr.

atmospheric history of methane contributes about 40% of the undersaturation in new LSW. This ratio increases to about 50% in older waters where methane approaches low concentrations.

Our estimate of k_1 is lower than *Scranton and Brewer's* [1978], and it can be seen in Figure 4 that if the residence time of methane were only 14 years, the CH_4 to CFC ratios simulated by our model would be significantly less than we observed. Their estimate is based on apparent methane utilization below 1 km depth at 52°N in the western Atlantic and $^3H/^3He$ ages of about 10 years for these waters. Lateral mixing with "older" water reduces the dissolved gas concentration, and at the same time, such mixing favors the age of the younger end-member in the tritium/helium ratio [Jenkins and Clarke, 1976]. The effects of increasing atmospheric CH_4 and lateral mixing may yield an overestimation of the CH_4 consumption rate.

Enhanced CH_4 concentrations near the Gibbs Fracture Zone

Methane concentrations significantly higher than expected from the general trend in the North Atlantic were observed near the eastern end of the Gibbs Fracture Zone (GFZ) (Fig.4, filled circles, for location see Figure 2). Active deep water hydrothermal sites are common between 11° and 40°N along the Mid-Atlantic Ridge, and one active site has been observed north of 57°N at the Reykjanes Ridge [*Baker et al.*, 1995], but none between 40° and 57°N. Our data clearly suggest a CH_4 anomaly in the rift valley intersecting GFZ at 52°N.

Concluding Remarks

Since biological production of CH_4 appears to have a negligible impact on cold, high latitude surface waters, the CH_4 pattern in the deep North Atlantic reveals a time transgressive atmospheric source term. The CH_4 distribution appears to trace deep water masses on a century time scale after their formation, and it documents a hitherto unknown hydrothermal source near the GFZ. The basin-wide residence time of methane on the order of 50 years, which is derived from comparing CH_4 and CFC11 distributions, might be the most significant of the implications. The oxidation rate of methane in the water column is one of the unknown parameters in the climate scenario of CH_4 emissions from gas hydrates to the atmosphere as the cause for past global warming [Dickens et al., 1997].

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