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 CCl₃F (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 CH₄ 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 CH₄ 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 265 pptv (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 entirely 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 CH₄ should affect the temporal evolution of the deep water CH₄ 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 CH₄ undersaturation relative to the present atmospheric CH₄ 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 CH₄/²²²Rn measurements indicate very rapid rates in hydrothermal plumes [De Angelis et al., 1990; 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 1⁻¹

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Figure 1. Atmospheric concentrations of CH₄ and CFC11 over the last 150 years. (+): CH₄ 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 CH₄ concentrations from 1841 to 1878 (---), and methane concentrations at Station M (66° N, 2° E) from 1841 to 1978 (•) [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].
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 = 5 pptV) 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 over-saturation of surface waters often found in lower latitudes, which is caused by the production of methane in anoxic micro-environments 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
versus CFC11 correlation by integrating each atmospheric rate of CH4 oxidation

Figure 3. CH4 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 $\sigma_o = 27.74$ and 27.80. Labrador Sea Water (LSW) is located between $\sigma_o = 27.74$ and $\sigma_o = 27.80$.

The entire survey area. A plot of CH4 versus CFC11 for all paired measurements shows that the percent saturations are correlated almost linearly with a CH4 intercept of about 20% (Fig. 4).

Rate of CH4 Oxidation

We estimate the oxidation rate of methane from the CH4 versus CFC11 correlation by integrating each atmospheric history with a one-dimensional advection-diffusion model, given by

$$\frac{\partial C}{\partial t} = k_b \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - k_1 C$$

where $C$ indicates the dissolved concentration of either gas, and $K_b$ 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 CH4 signal. The flux of the dissolved gases to the deep water is presumed to be $u \times C_{ad}(t)$, where $C_{ad}(t)$ 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 $K_b/u$, and the absolute value of $k_1$, in the case of CH4.

The lines in Figure 4 show a sequence of CH4 versus CFC11 trends as simulated according to various $k_1$. Here, the physical parameters ($K_b$ 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 CH4 to CFC11 would be considerably 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 CH4 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...
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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