

Recent changes in the air-sea gas exchange of methyl chloroform

Paul O. Wennberg,^{1,2} Synte Peacock,³ James T. Randerson,^{1,2,4} and Rainer Bleck⁵

Received 7 May 2004; revised 14 June 2004; accepted 16 July 2004; published 24 August 2004.

[1] Atmospheric measurements of methyl chloroform provide important constraints on the rate of oxidation of hydrocarbons in Earth's atmosphere. Estimates of the loss of methyl chloroform to the oceans play a small but important role in these calculations. Here, we examine the ocean-atmosphere interaction of methyl chloroform in a global ocean model. Contrary to previous assumptions, these simulations suggest that the high-latitude oceans are currently a source of this chemical to the atmosphere. If confirmed, this finding alters estimates of the change in the atmospheric oxidation rate of hydrocarbons. We highlight the potential usefulness of methyl chloroform as a tracer of ocean circulation. **INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry. **Citation:** Wennberg, P. O., S. Peacock, J. T. Randerson, and R. Bleck (2004), Recent changes in the air-sea gas exchange of methyl chloroform, *Geophys. Res. Lett.*, *31*, L16112, doi:10.1029/2004GL020476.

1. Introduction

[2] Manufacture of the solvent 1, 1, 1-trichloroethane (CCl₃CH₃, methyl chloroform, here after MC) was first controlled and later essentially banned by amendments to the Montreal Protocol on Substances that Deplete the Ozone Layer. Because its atmospheric lifetime is about five years, the concentration of MC in the atmosphere has fallen from its peak value of ~130 pptv in 1991/1992 to less than 35 pptv today [e.g., Prinn *et al.*, 2001]. The decline in the concentration of MC is responsible for most of the decrease in stratospheric chlorine levels observed to date [Montzka *et al.*, 1999].

[3] Atmospheric measurements of the global distribution of MC have provided important constraints on the rate of oxidation of hydrocarbons in Earth's troposphere. Because the location, quantity, and timing of MC release to the atmosphere are well known [McCulloch and Midgley, 2001], measurements of the atmospheric concentration allow its lifetime to be reasonably estimated [e.g., Prinn

et al., 2001]. As with many hydrocarbons, this lifetime is determined primarily by gas phase oxidation initiated by hydroxyl radicals (OH). With knowledge of the oxidative lifetime of MC, the lifetimes of numerous other compounds with similar chemistry, such as methane [Hein *et al.*, 1997] and hydrochlorofluorocarbons (HCFCs), can be estimated.

[4] Recently, inversion of the atmospheric MC record by Prinn *et al.* [2001] suggested that the atmospheric lifetime of MC had increased markedly in the 1990s. Prinn *et al.* concluded that the increase in the lifetime resulted from a ~10–15% decrease in the concentration of OH during this time period. Such a finding is alarming because it implies a significant increase in the atmospheric lifetime of numerous greenhouse gases, including the CFC replacements (HCFCs).

[5] We report here simulations of the uptake and redistribution of MC by the ocean. As hypothesized by Krol and Lelieveld [2003], our simulations suggest MC began to outgas from the high-latitude oceans following its rapid decrease in the atmosphere in the mid and late 1990s. The change in ocean exchange described here reduces the inferred trend in the atmospheric lifetime of MC. Prinn *et al.* [2001] suggested that a 'missing source' of about 117 Gg (~1 × 10⁹ moles) during the five year period from 1995 to 2000 would be required to yield no trend in the atmospheric lifetime. The change in the ocean-atmosphere interaction described here accounts for ~30% of this deficit.

2. Interaction of Methyl Chloroform With Ocean Water

[6] Wine and Chameides [1989] first described the interaction of MC and ocean water. Ship-based measurements of its concentration in surface water and in the overlying air confirmed that the oceans were an important sink for MC [Butler *et al.*, 1991]. Although only sparingly soluble in water [Gossett, 1987], a significant amount of MC has entered the ocean during the last thirty years. Significant transfer from the atmosphere to the ocean occurs in the warm tropical oceans, driven mainly by chemical loss (hydrolysis) in the surface waters. Uptake has also occurred at mid- and high- latitudes, due to the higher solubility of MC in colder waters and two distinct high-latitude water-mass transformation processes: high-latitude deep convection, and wind-forced lateral subduction into the main thermocline of the ocean.

[7] It is well established that MC is chemically removed in warm ocean water. Observations by Butler *et al.* [1991] in the tropics showed significantly lower dissolved MC than expected from equilibrium with the atmosphere. They demonstrated that the flux of MC from the atmosphere to the ocean was broadly consistent with physical uptake [Gossett, 1987] and subsequent hydrolysis [Jeffers *et al.*, 1989; Gerken and Franklin, 1989]. The hydrolysis lifetime in ocean water, however, is strongly dependent on temper-

¹Division of Geological and Planetary Science, California Institute of Technology, Pasadena, California, USA.

²Also at Division of Engineering and Applied Sciences, California Institute of Technology, Pasadena, California, USA.

³Department of Geophysical Sciences, University of Chicago, Chicago, Illinois, USA.

⁴Now at the Department of Earth System Science, University of California, Irvine, California, USA.

⁵Los Alamos National Laboratory, Los Alamos, New Mexico, USA.

ature. At 25°C, the lifetime against hydrolysis is about one year. This increases to ~50 years at 3°C, though this value is quite uncertain because it is determined by extrapolation of the laboratory data from warmer temperatures [Jeffers *et al.*, 1989; Gerken and Franklin, 1989].

[8] In previous studies of the atmospheric lifetime of MC, loss from the atmosphere to the ocean has been treated as a simple first order process. Consistent with the recommendation of Butler *et al.* [1991], a lifetime ($1/k_{a-o}$) of ~60 years with respect to the atmospheric reservoir is generally prescribed. Such a simple parameterization is adequate for the component of MC lost by hydrolysis in warm ocean water, where the lifetime in ocean water (~1 year) is shorter than in the atmosphere (~5 years). It is, however, inadequate for loss via physical uptake in the cold (~3°C), high latitude ocean. In this process, the flux is sensitive to both the time derivative of the atmospheric concentration and the rate at which mixing of the surface waters into the deep ocean occurs – as both determine the saturation properties of the surface waters. Thus, when the atmospheric concentration of MC was growing exponentially, the flux into the ocean was proportional to $[\text{CH}_3\text{CCl}_3]$. After 1990, when the atmospheric concentration abruptly began to decrease, loss to the high latitude ocean was a complicated function of both atmospheric MC concentration and ocean dynamics.

3. Global Ocean Model

[9] In this study, we have used a 60-year simulation of ocean transport from the Miami Isopycnal Coordinate Ocean Model (MICOM) to investigate the uptake of MC. MICOM is a primitive equation numerical general circulation model that describes the evolution of momentum, mass, heat and salt in the ocean [Bleck *et al.*, 1992, 1989]. Further details of the model are provided in auxiliary material¹.

[10] We have forced MICOM with observed (and into the future with modeled) concentrations of atmospheric MC. We used the emissions inventory of McCulloch and Midgley [2001] along with the tropospheric and stratospheric loss rates suggested by Prinn *et al.* [2001] to calculate the concentration in a three box model (northern extra tropics, the tropics and southern extratropics). The exchange rate between the hemispheres was picked such that the latitudinal gradient observed between 1970 and 1990 was captured. In this model, atmospheric measurements of MC are reproduced to better than 10%.

[11] Tracers (MC and CFC-11) were advected offline using 30-day averages of isopycnal and diapycnal mass fluxes. These were obtained by transforming instantaneous horizontal fluxes in the two non-isopycnal model layers representing the surface mixed layer and a “fossil” mixed layer to density coordinates, integrating over time, and inferring diapycnal fluxes from mass conservation. Air-sea gas exchange was parameterized using the protocol described by Dutay *et al.* [2002].

4. Results

[12] Figure 1 shows the calculated, annually averaged flux of MC into and out of the ocean in 1990, 2000, and

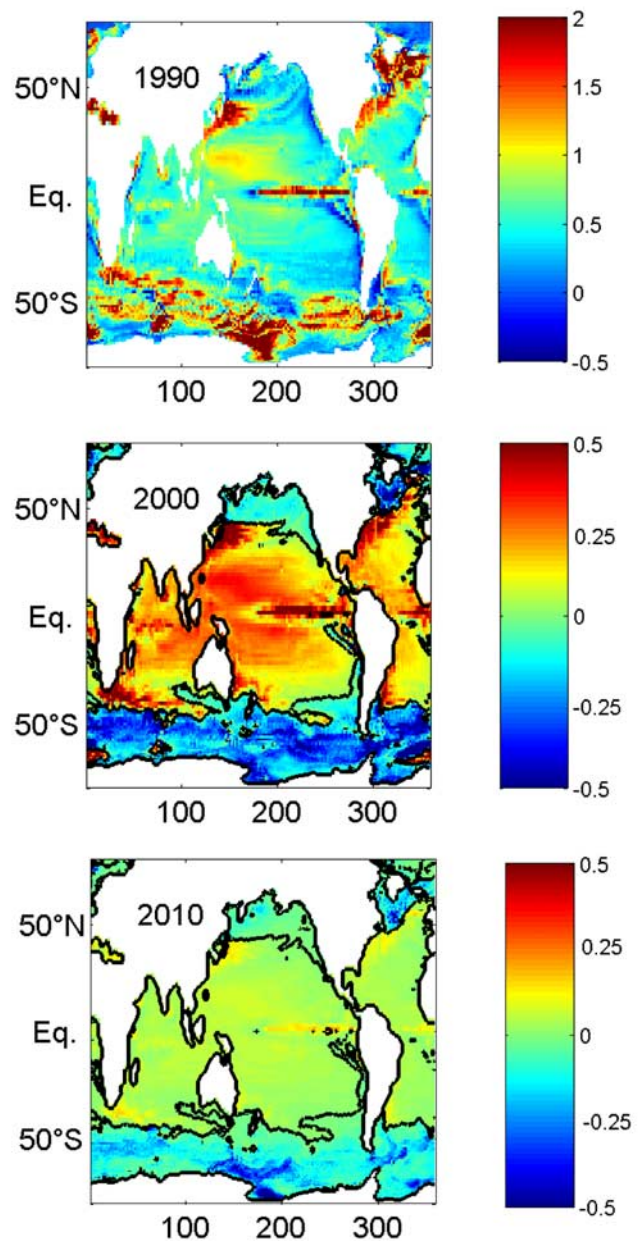


Figure 1. Yearly time-averaged net air-sea flux of methyl chloroform for 1990, 2000 and 2010 in $\text{moles km}^{-2} \text{yr}^{-1}$. Positive fluxes are into the ocean. The zero contours are highlighted in black.

2010. In 1990, the flux is everywhere into the ocean. The largest fluxes are at low-latitudes. Outside the tropics, the uptake pattern reflects the thermal asymmetry of the anticyclonic subtropical gyres. In 2000, while significant losses to the ocean are calculated in the tropics, these are nearly balanced by a net source to the atmosphere from the high latitude oceans - particularly in the southern hemisphere. By 2010 the net air-sea flux over most of the low- and mid-latitude ocean is close to zero, reflecting the expectation that the atmospheric burden has dropped to nearly zero. The high-latitude northern and southern oceans remain net sources to the atmosphere, although smaller than in 2000.

[13] The calculated time series of the net MC flux into the ocean, and an inert tracer (no hydrolysis) with the same

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/gl/2004GL020476>.

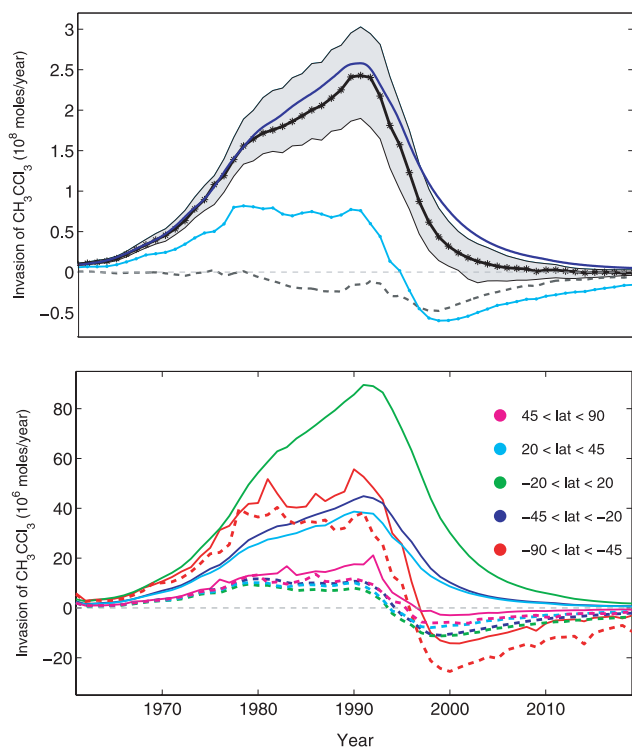


Figure 2. Air-sea flux of methyl chloroform for the globe (top) and by latitude band (bottom). Positive is into the ocean. In the top panel, the black curve (with uncertainty bounds) shows the calculated air-sea flux; the blue curve shows the first-order loss parameterization used in previous inversions and the dashed line shows the difference. Also shown for reference is the calculated air-sea flux for a hypothetical tracer which is methyl chloroform without the hydrolysis loss (top - light blue; bottom dashed).

solubility, is shown in Figure 2. Also shown is the ocean loss parameterization used in previous inversions [e.g., Prinn *et al.*, 2001]. Prior to 1980, when atmospheric MC concentrations were increasing rapidly, the first-order loss calculated with an assumed $1/k_{a-o}$ of 60 years agrees well with the total loss calculated here. Between 1980 and 1992, the first-order loss parameterization is slightly larger than the best estimate calculated here. Between 1992 and 2000, the difference between the MICOM-calculated loss and the first-order loss estimate gradually increases. Between 1980 and 2000, the integrated difference is 5×10^8 moles with much of the difference (3×10^8 moles) occurring between 1992 and 2000. We have attempted to estimate the uncertainty in this calculation due to poor knowledge of the hydrolysis rate at cold temperatures. As described in the auxiliary material, the error-bars in the upper panel of Figure 2 correspond to our estimate of the lower and upper bounds of the hydrolysis rate. In the lower panel of Figure 2, the fluxes are shown for various latitude bands. Most of the chemical loss occurs equatorward of 45° while physical uptake, and later release, occurs at high latitudes.

5. Model Evaluation

[14] There are only a few published measurements of MC in the ocean to evaluate the model representation of the

coupled chemistry and physics. For evaluation of the calculated chemical loss at warm temperature, we rely on the tropical and subtropical MC surface saturation measurements described by Butler *et al.* [1991] and Lobert *et al.* [1995]. In the tropics, the sub-saturation calculated in this work is similar to that reported by Lobert *et al.* [1995] and somewhat smaller than those of Butler *et al.* [1991]. In cold water, depth profile measurements of MC illustrate that MC is quite conservative (very slow biological or abiological hydrolysis loss). Profiles from the north Pacific are described by Lobert *et al.* [1995]; additional profiles were obtained during the 1993, 1994, 1995, 1996, and 1998 World Ocean Circulation Experiment (WOCE) repeat cruise tracks in the Labrador Sea (AR07W). In both cases, the profiles are similar to the inert CFC-11 and CFC-12, showing (unlike CCl_4) no evidence of rapid loss. See auxiliary material for further discussion and comparisons of our calculations with these and other data.

[15] To evaluate the calculation of the physical uptake of MC and its subduction through the thermocline we have compared calculations of the air-sea exchange of CFC-11 with measurements of CFC-11 made during the WOCE. Because the atmospheric temporal trajectory of MC (until 1992) and CFC-11 are very similar this is a reasonable comparison. The calculated inventory of CFC-11 in 1995 was 5.6×10^8 moles, remarkably close to the $5.5 \pm 1 \times 10^8$ mole inventory estimated from WOCE [Willey *et al.*, 2004]. This suggests that, in the absence of chemical loss, the model MC inventory would also be quite accurate.

[16] In summary, the losses of MC to the tropical ocean appear to be reasonably well represented by this calculation. The fluxes out of the high latitude Southern Ocean in the period 1990–2000 are more uncertain. The Southern Ocean is, in general, poorly simulated by most ocean models [Dutay *et al.*, 2002]. On an encouraging note, a sensitivity run in which gas exchange was set to zero at all latitudes south of 60°S (thereby preventing any tracer from entering the ocean at high southern latitudes) yielded very similar results to the control run. This was mainly due to anomalously large air-sea gradients forming in the region just north of 60°S as water moved across this boundary, which in large part compensated the zero-air-sea-flux requirement. However, the most important test of these conclusions would be measurements of MC depth profiles and surface saturation measurements in the Southern Ocean.

6. Conclusions

[17] Consistent with the conclusion of Krol and Lelieveld [2003], this study suggests that accurately assessing trends in the atmospheric lifetime of MC during the period of rapidly changing emissions (1990–2000) is challenging and perhaps impossible. Any reservoir for MC with a lifetime longer than ~ 5 years, later released to the atmosphere, will produce a significant error in attempts to infer the atmospheric lifetime of this compound. Here we address one such reservoir – the high latitude ocean. There are, undoubtedly others. Krol and Lelieveld note, for example, that a delay in the emission of just 65 Gg MC from the early to the late 1990s (for example by stockpiling in advance of the Montreal Protocol controls [McCulloch and Midgley, 2001]) would be sufficient to remove the entire OH trend

inferred by Prinn *et al.* [2001]. Such delayed emissions have been observed in both Europe [Krol *et al.*, 2003] and in North America [Barnes *et al.*, 2003; Millet and Goldstein, 2004]. Following the rapid decline in its emission in 1990, MC alone is not likely to be a useful tracer of changes in the gas-phase oxidation rates in Earth's troposphere. Its future utility may lie, however, in its pulse-like appearance in the ocean.

[18] Measurements of the pulse of ^{14}C following atmospheric bomb tests in the 1960s provided significant constraints on ocean circulation [Broecker *et al.*, 1985]. This study suggests that the rapid rise and fall of atmospheric MC may provide a new tracer against which to test models of ocean circulation. Unlike bomb tritium, which also had a pulse-like atmospheric source, MC is a gas whose atmospheric dispersion does not rely on incorporation into raindrops, and hence is more easily modeled. Thus, ocean observations of MC combined with measurements of CFC-11 and CFC-12 may provide a significant constraint on diffusive/advective transport in the oceans on the 50–100 year timescale critical for understanding how the ocean uptake of CO_2 may change over the next century [Hall *et al.*, 2002]. The interactions of MC with ocean water are in some ways simpler than $^{14}\text{CO}_2$ (apparently no interaction with the biosphere) and in other ways more complicated (hydrolysis). Both MC and ^{14}C are similar, however, in that the ocean is currently changing from an atmospheric sink to an atmospheric source [Caldeira *et al.*, 1998].

References

- Barnes, D. H., S. C. Wofsy, B. P. Fehla, E. W. Gottlieb, J. W. Elkins, G. S. Dutton, and S. A. Montzka (2003), Urban/industrial pollution for the New York City–Washington, D. C., corridor, 1996–1998: 1. Providing independent verification of CO and PCE emissions inventories, *J. Geophys. Res.*, *108*(D6), 4185, doi:10.1029/2001JD001116.
- Bleck, R., H. P. Hanson, D. M. Hu, and E. B. Kraus (1989), Mixed layer thermocline interaction in a 3-dimensional isopycnic coordinate model, *J. Phys. Oceanogr.*, *19*, 1417–1439.
- Bleck, R., C. Rooth, D. M. Hu, and L. T. Smith (1992), Salinity-driven thermocline transients in a wind-forced and thermohaline-forced isopycnic coordinate model of the North-Atlantic, *J. Phys. Oceanogr.*, *22*, 1486–1505.
- Broecker, W. S., T. H. Peng, G. Ostlund, and M. Stuiver (1985), The distribution of bomb radiocarbon in the ocean, *J. Geophys. Res.*, *90*, 6953–6970.
- Butler, J. H., J. W. Elkins, T. M. Thompson, B. D. Hall, T. H. Swanson, and V. Koropalov (1991), Oceanic consumption of CH_3CCl_3 -implications for tropospheric OH, *J. Geophys. Res.*, *96*, 22,347–22,355.
- Caldeira, K., G. H. Rau, and P. B. Duffy (1998), Predicted net efflux of radiocarbon from the ocean and increase in atmospheric radiocarbon content, *Geophys. Res. Lett.*, *25*, 3811–3814.
- Dutay, J.-C., et al. (2002), Evaluation of ocean model ventilation with CFC-11: Comparison of 13 global ocean models, *Ocean Model.*, *4*, 89–120.
- Gerkens, R. R., and J. A. Franklin (1989), The rate of degradation of 1, 1, 1-trichloroethane in water by hydrolysis and dehydrochlorination, *Chemosphere*, *19*, 1929–1937.
- Gossett, J. M. (1987), Measurement of Henry's law constants for C1 and C2 chlorinated hydrocarbons, *Environ. Sci. Technol.*, *21*, 202–208.
- Hall, T. M., T. W. N. Haine, and D. W. Waugh (2002), Inferring the concentration of anthropogenic carbon in the ocean from tracers, *Global Biogeochem. Cycles*, *16*, 1131, doi:10.1029/2001GB001835.
- Hein, R., P. J. Crutzen, and M. Heimann (1997), An inverse modeling approach to investigate the global atmospheric methane cycle, *Global Biogeochem. Cycles*, *11*, 43–76.
- Jeffers, P. M., L. M. Ward, L. M. Woytowitch, and N. L. Wolfe (1989), Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes, and propanes, *Environ. Sci. Technol.*, *23*, 965–969.
- Krol, M., and J. Lelieveld (2003), Can the variability in tropospheric OH be deduced from measurements of 1, 1, 1-trichloroethane (methyl chloroform)?, *J. Geophys. Res.*, *108*(D3), 4125, doi:10.1029/2002JD002423.
- Krol, M. C., et al. (2003), Continuing emissions of methyl chloroform from Europe, *Nature*, *421*, 131–135.
- Lobert, J. M., T. J. Baring, J. H. Butler, S. A. Montzka, R. C. Myers, and J. W. Elkins (1995), OAXTC 92: Ocean/atmosphere exchange of trace compounds 1992, *NOAA Tech. Memo., ERL CMDL-9*, 43 pp.
- McCulloch, A., and P. M. Midgley (2001), The history of methyl chloroform emissions: 1951–2000, *Atmos. Environ.*, *35*, 5311–5319.
- Millet, D. B., and A. H. Goldstein (2004), Evidence of continuing methylchloroform emissions from the United States, *Geophys. Res. Lett.*, doi:10.1029/2004GL020166, in press.
- Montzka, S. A., J. H. Butler, J. W. Elkins, T. M. Thompson, A. D. Clarke, and L. T. Lock (1999), Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature*, *398*, 690–694.
- Prinn, R. G., et al. (2001), Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, *Science*, *292*, 1882–1888.
- Willey, D. A., R. A. Fine, R. E. Sonnerup, J. L. Bullister, W. M. Smethie Jr., and M. J. Warner (2004), Global oceanic chlorofluorocarbon inventory, *Geophys. Res. Lett.*, *31*, L01303, doi:10.1029/2003GL018816.
- Wine, P. H., and W. L. Chameides (1989), AFEAS report in scientific assessment of stratospheric ozone, vol. 2, *Rep. 20*, pp. 273–295, Global Ozone Res. and Monit. Proj., World Meteorol. Org., Geneva.

R. Bleck, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. (bleck@lanl.gov)

S. Peacock, Department of Geophysical Sciences, University of Chicago, Chicago, IL 60637, USA. (synte@geosci.uchicago.edu)

J. T. Randerson, Department of Earth System Science, University of California, Irvine, Irvine, CA 92697, USA. (jranders@uci.edu)

P. O. Wennberg, Division of Geological and Planetary Science, California Institute of Technology, Pasadena, CA 91125, USA. (wennberg@caltech.edu)