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The oceans: A source or a sink of methyl bromide?

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Abstract. The global ocean/atmosphere flux of methyl bromide has been estimated from shipboard measurements of the saturation anomaly. When such data are extrapolated globally on the basis of constant saturation anomaly, the ocean is a net sink for methyl bromide [*Lobert et al.*, 1995]. The same data can also be extrapolated on the basis of steady-state production rate of methyl bromide in the water column, allowing regional and seasonal variations in temperature to affect the saturation anomaly. We have carried out this type of extrapolation, and we found that the oceans are a strong net source of methyl bromide to the atmosphere. The difference arises mainly due to slow degradation rates in water of higher latitudes. A reduction of the applied production rate by more than 35% is needed in order to switch the ocean from a source to a sink of methyl bromide. These results demonstrate the sensitivity of current estimates of oceanic flux to assumptions about methyl bromide production and destruction in the water column.

Introduction

Methyl bromide (CH_3Br) is considered to be a major source of bromine to the stratosphere and an important contributor to the destruction of stratospheric ozone [*WMO*, 1994]. This issue has led to attempts to regulate the anthropogenic use of methyl bromide through the Montreal Protocol and the Clean Air Act [*USEPA*, 1993]. The implicit assumption is that reducing anthropogenic emissions of methyl bromide will lead to a reduction in its concentration in the atmosphere, in a manner similar to that of chlorofluorocarbons.

Unlike chlorofluorocarbons, methyl bromide has both natural and anthropogenic sources. It is both produced and destroyed in the oceans, and the rates of these processes can exert a major control on atmospheric methyl bromide concentrations. Recently, *Lobert et al.* [1995] observed that eastern Pacific Ocean surface waters were undersaturated in most areas except for coastal and upwelling regions. They extrapolated these observations globally and concluded that the oceans act as a net sink for methyl bromide. *Lobert et al.* [1995] also used a simple model of methyl bromide cycling in the surface ocean to estimate the production rate needed to support the observed saturation state in the water column along their cruise track. Those calculations assumed that methyl bromide concentrations reflect a steady-state between production (presumably biological), chemical losses, vertical mixing and air-sea exchange [*Butler*, 1994]. Some of the parameters used in such calculations are strongly temperature dependent, notably the solubility and the chemical loss rate of methyl bromide in seawater [*Elliott and Rowland*, 1993]. For this reason, it can be argued that the *Lobert et al.* [1995] data set should be extrapolated globally on the basis of

the calculated production rates, rather than the observed saturation anomalies. In fact, there are unsupported assumptions associated with either method of extrapolation and these contribute to uncertainty in our ability to estimate the global ocean/atmosphere flux. In this paper we estimate the global flux from production rate-based extrapolations in order to estimate this uncertainty.

Model Description

In this effort we have used the approach of *Butler* [1994] to model the methyl bromide concentration in discrete 2° x 2° regions of the surface wind-mixed area of the ocean. The basic equation describing the evolution of the concentration of methyl bromide in each cell extending from the air-ocean interface to the bottom of the surface layer is:

$$\frac{dc_0}{dt} = p_0 - k_d\, c_0 - \frac{K_w}{z}\left(c_0 - \frac{p_g}{H}\right) - \frac{k_{ed}\, c_0}{z} \qquad (1)$$

where c_0 is the methyl bromide concentration (mol m^{-3}), p_o is the production of methyl bromide in the grid cell, k_d is the aquatic degradation rate constant (yr^{-1}), K_w is the air-sea exchange coefficient (m yr^{-1}), p_g is the partial pressure of methyl bromide over the grid (atm), H is the Henry's Law constant (m^3 atm mol^{-1}), k_{ed} is the eddy diffusion rate constant for the removal of methyl bromide downward from the surface layer (m yr^{-1}) and z is the depth of the surface layer (m).

The known chemical losses of methyl bromide consist of hydrolysis and nucleophilic substitution, primarily by chloride ion, with the latter reaction being the primary removal mechanism. *King et al.* [1996] have measured the overall chemical loss rate, k_d, in filtered seawater and fit the data with an Arrhenius expression, that we have incorporated in our model. The methyl bromide solubility, H, was calculated by applying a salting out coefficient [*De Bruyn and Saltzman*, unpublished data] to the pure water data reported by *Wilhelm et al.* [1977]. The air-sea exchange coefficient, K_w, is approximated with a quadratic relationship to wind speed [*Wanninkhof*, 1992], using recently measured Schmidt numbers, Sc, in seawater [*De Bruyn and Saltzman*, 1996]. The mixed layer depth is assumed to be constant and equal to 75 m [*Li et al.*, 1984], while the eddy diffusion rate of removal, k_{ed}, is given by the equation:

$$k_{ed} = \left(D_z\, k_d\right)^{0.5} \qquad (2)$$

where the average vertical mixing coefficient for the oceanic thermocline, D_z, is equal to 5361.1 m yr^{-1} [*Li et al.*, 1984]. In the base-case simulation the concentrations of methyl bromide in the atmosphere were assumed to be 12 and 9 ppt for the northern and southern hemispheres, respectively [*Reeves and Penkett*, 1993; *Lobert et al.*, 1995]. Sea surface temperatures, salinity, and wind speeds were extracted from the Comprehensive Ocean-Atmosphere Data Set, COADS, [*Wright*, 1988]. The selected data represent over forty years of shipboard measurements,

compiled as monthly averages over a 2° x 2° grid. The segment of the COADS data set used in this work is that described by *Yvon and Butler* [1996].

For the duration of each month, since the meteorological parameters remain unchanged and the gas phase concentrations of methyl bromide are constant, Equation (1) can be solved analytically to give the concentration of methyl bromide at each grid, as a function of time

$$c_0(t) = \frac{C_2}{C_1} + \left(c_0(t^*) - \frac{C_2}{C_1}\right)e^{-C_1(t-t^*)} \qquad (3)$$

where $C_1 = k_d + (K_w + k_{ed})/z$, $C_2 = p_0 + K_w p_g /Hz$ and t^*, t are the initial and final times, respectively. As a result, the net flux, F, of methyl bromide, between t^* and t, is given by the equation:

$$F = \int_{t^*}^{t} K_w A \left[c_0(\tau)\frac{P_g}{H}\right] d\tau = K_w A \left(\frac{C_2}{C_1} - \frac{P_g}{H}\right)(t - t^*)$$
$$-K_w A C_1^{-1}\left(c_0(t^*) - \frac{C_2}{C_1}\right)(e^{-C_1(t-t^*)} - 1) \qquad (4)$$

where A is the area of the air-sea interface.

Model Application

The major task associated with the oceanic component of the methyl bromide budget is parameterizing the regional and temporal variability in the production rate of methyl bromide in seawater. As a "best guess" scenario we used the saturation anomaly data of *Lobert et al.* [1995] and associated seawater
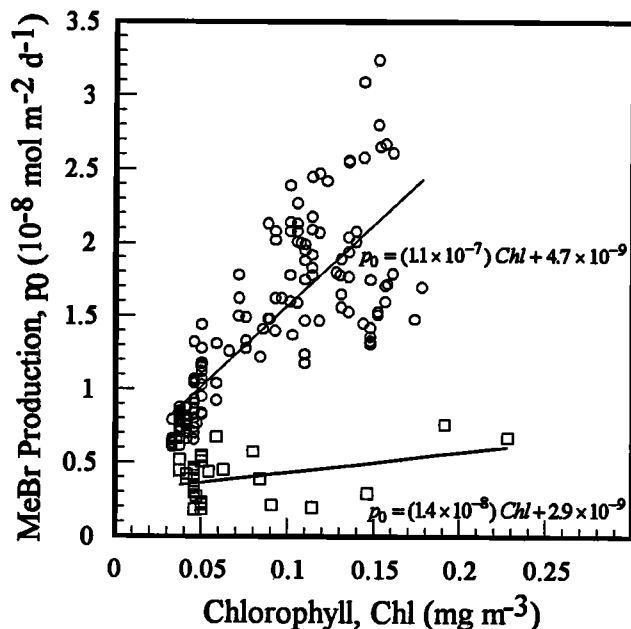

Figure 1. Methyl bromide production as a function of chlorophyll concentration. Circles correspond to 142 high latitude summer and low latitude production rates. The standard error in the slope is 7.3×10^{-9}, while the standard error in the intercept is 3.8×10^{-9}. Squares correspond to 33 high latitude winter production rates. The standard error in the slope is 5.9×10^{-9}, while the standard error in the intercept is 1.4×10^{-9}. Production rates have been extracted from the measurements of *Lobert et al.* [1995].

fluorescence data to derive a relationship between chlorophyll and methyl bromide production. We subdivided the data set into two regimes: tropical/subtropical latitudes and high latitude wintertime (Figure 1). Due to the lack of measurements, we assumed that high latitude summertime has the same behavior as the tropical/subtropical latitudes. We then used the Coastal Zone Color Scanner (CZCS) monthly color images of phytoplankton pigment concentrations to develop monthly gridded concentrations of chlorophyll in the oceans and from those obtained a gridded data set of methyl bromide production compatible with the model. The estimated global production rate of methyl bromide was 183.9 Gg yr^{-1} in reasonable agreement with the 151.2 Gg yr^{-1} estimated by *Lobert et al.* [1995]. The total uncertainty in the estimated production rate is about 20%. Major components of this uncertainty are the oceanic loss rate, the air-sea exchange coefficient, the solubility, as well as the linear relationship between production and chlorophyll. The loss rate is the largest component of this uncertainty, and the contribution would become greater if the uncertainty in the magnitude of biological removal had been included. However, since insufficient data are currently available to extrapolate the biological removal rate globally, the loss rate was only calculated in terms of the chemical removal.

Although methyl bromide production and chlorophyll are adequately correlated, as shown in Figure 1, it should be viewed skeptically in terms of causality, as there are many characteristics of seawater which vary in concert with chlorophyll in a given oceanic regime. *Moore et al.* [1995], for example, have reported that preliminary results of their experiments indicate that marine phytoplankton do produce methyl bromide, but with rates that account for only a fraction of the global production rates estimated by *Lobert et al.* [1995]. In order to examine the dependence of the oceanic behavior on this assumption, we performed a second set of simulations, with the same global methyl bromide production rate, but uniformly distributed across the oceans.

Figure 2 illustrates the saturation anomaly, A_g, of the surface ocean for the month of January for both simulations. The saturation anomaly, in percent, is defined as the departure of the partial pressure in seawater from equilibrium, $A_g = 100(p_w - p_g)/p_g$. The saturation anomaly is the quantity which is directly determined in field studies and used to derive the air/sea flux [*Lobert et al.*, 1995]. This quantity is highly dependent on the air and seawater concentrations and on the temperature of the waters. As shown in Figure 2a, the seasonality in biological emissions exerts a strong effect on the saturation state, particularly in the high latitudes, where the oceans tend to act as a summertime source (southern hemisphere) and a wintertime (northern hemisphere) sink. The results are in excellent agreement with *Lobert et al.* [1995], in the region where data were collected. This is not surprising, as the relationships used to estimate oceanic production are derived from those field measurements. The results are also in excellent agreement with recent measurements in the Atlantic Ocean by the same research group [*Butler et al.*, 1995]. One interesting result from the simulation is the very high predicted supersaturation for the Southern Ocean, a region where few data have been collected. Given that the biological nature of these waters is quite different from those in the mid-latitude and tropical ocean, we consider this result to be a hypothesis requiring experimental verification. The model predicts that the net flux of methyl bromide from the ocean is 22.5 Gg yr^{-1}, i.e. the ocean is a net source of methyl bromide.

(a)

(b)

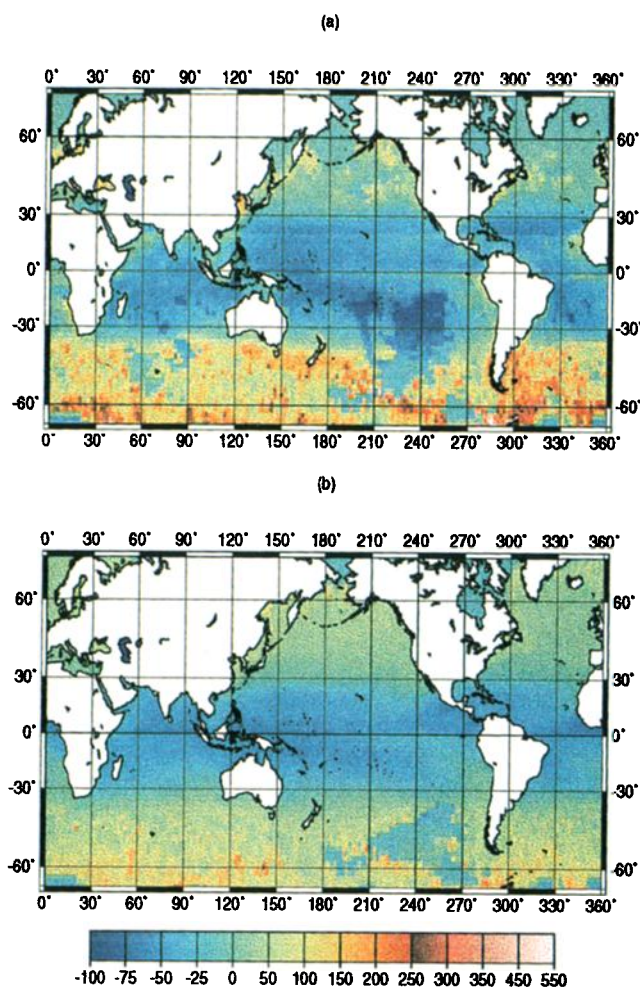-100 -75 -50 -25 0 50 100 150 200 250 300 350 450 550

Figure 2. January saturation anomalies predicted by the model. The saturation anomaly, in percent, is defined as the departure of the dissolved amount from equilibrium, $A_g = 100(p_w-p_g)/p_g$. (a) Production rates used are those estimated from chlorophyll concentrations, (b) Uniform production rates are used.

Figure 2b presents the results of the second set of simulations, in which a uniform production rate is assumed. The high latitudes are predicted to be supersaturated in methyl bromide, while the low latitudes remain undersaturated. Since in this case a uniform production rate is assumed, the predicted saturation anomalies no longer agree with the data of *Lobert et al.* [1995]. Figure 2b clearly shows the strong effect of the chemistry on the saturation state of the oceans. Colder waters become supersaturated, simply because of the slow rate of chemical destruction. Close to the equator the water temperature is higher and as a result the destruction of methyl bromide is faster, resulting in undersaturation. As in the previous case, the oceans are a net source of methyl bromide, and the amount emitted is 16.0 Gg yr^{-1}. Therefore the net flux of methyl bromide is sensitive to the assumption used to estimate the production rate in our base case scenario, but in both cases the ocean is predicted to be a net source of methyl bromide.

The above finding is of major importance, because it indicates that there may be a strong positive natural net flux of methyl bromide from the oceans, that cannot be eliminated with any control of anthropogenic emissions. If the above results are

correct, even within a factor of two, it is expected that the oceanic flux will increase substantially, as the anthropogenic emissions are reduced. If, for example, we assume that the average concentration of methyl bromide in the northern hemisphere is reduced to 10 ppt, our model predicts that the global flux from the oceans will increase by about 6 Gg yr^{-1}. The prediction that the ocean is a net source of methyl bromide may also help in the effort of reconciling the methyl bromide budget [*Butler*, 1995]. Balancing the sources and sinks of methyl bromide, while accounting for the observed interhemispheric gradient is one of the biggest issues facing scientists in the field. For example, if the ocean is a net sink of methyl bromide, what are the sources of methyl bromide in the southern hemisphere that result in an atmospheric methyl bromide concentration as high as 9 ppt? We have carried out simulations with a full three dimensional Chemical Transport Model (GRANTOUR) including current best estimates of anthropogenic emissions and biomass burning. Preliminary results indicate that, if the oceans are a net sink, the methyl bromide concentrations in the southern hemisphere should be much lower than 9 ppt [*Pilinis et al.*, 1995]. On the other hand, if the recent estimate of a global annual soil sink of 42 Gg [*Shorter et al.*, 1995] is correct, most of which exists in the northern hemisphere, it is hard to explain 9 ppt of methyl bromide in the southern hemisphere due to oceanic sources alone, while reconciling the N/S gradient of 1.3. Another possible source is biomass burning, but it has no significant emphasis in either hemisphere [*Butler*, 1995].

In order to examine the sensitivity of the saturation state of the ocean to the production rate used, we performed two additional sets of simulations. In the first set the total production was reduced by 18% to 151.2 Gg yr^{-1}, the global production rate estimated by *Lobert et al.* [1995]. The model predicted a net oceanic flux of 13 Gg yr^{-1}, a reduction of about 42% from the base-case simulation. Therefore, despite the sensitivity of the net flux to the production rate, the oceans are still predicted to be a net source of methyl bromide. In the second set of simulations, the total production was reduced by 35%, to 119.8 Gg yr^{-1}. The model predicted that, for this reduced production rate, the net oceanic flux is 0.0 Gg yr^{-1}, i.e. the ocean is neither a net source nor sink of methyl bromide. Reducing the total production rate of methyl bromide even further causes the ocean to behave as a net sink of methyl bromide. If methyl bromide is also removed from the oceans biologically, the result would be equivalent to a reduction in the net production rate in the oceans. Since neither the mechanisms nor the magnitude of this removal are known, the simulations with reduced production rates presented above provide an estimate of the effects of an increase in the loss rate due to biological activity.

An additional set of runs were performed to examine the sensitivity of the oceanic flux to the choice of the depth of the mixed layer. An increase of the mixed layer depth by 20% resulted in a decrease of the net oceanic flux by about 30%, while a decrease of the mixed layer depth by 20% resulted in an increase of the net flux by 40%. Therefore, in all cases, the ocean is still predicted to be a net source of methyl bromide.

Conclusions

Production-based extrapolations yield a positive global net flux of methyl bromide from the ocean to the atmosphere of 22.5 Gg yr^{-1}, while the saturation state-based extrapolation performed by *Lobert et al.* [1995] yields a global negative flux of approximately 13 Gg yr^{-1}. Both approaches suffer from the relatively limited geographic coverage of field measurements and from our

limited understanding of the biological processes involved in production and destruction of methyl bromide in the water column. The saturation state-based extrapolation involves the implicit assumption that regional and seasonal variability in production and destruction rates are tightly coupled. This is perhaps possible if the water column losses of methyl bromide are biologically controlled, rather than chemically, as assumed in the model. The production-based extrapolations assume that there is no coupling between production and destruction, and in this approach the temperature dependence of the chemical loss largely drives the variability in the saturation state. At this time we have no basis with which to assess the validity of the assumptions inherent in the two approaches. Given the importance of the global oceanic flux of methyl bromide and its sensitivity to assumptions about the production and destruction rates, further research into the processes controlling the methyl bromide distribution is warranted.

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