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Wetlands: a potentially significant source of atmospheric methyl bromide and methyl chloride

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Abstract. Tropospheric methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) are significant sources of ozone (O_3) destroying halogens to the stratosphere. Their O_3 depletion potential (ODP) can be determined from atmospheric lifetimes and therefore their atmospheric budgets, both of which are out of balance with known sink terms larger than identified sources. We have discovered a new source of CH_3Br and CH_3Cl emissions to the atmosphere at two wetland sites in the Northeastern United States. We have reason to believe that these compounds are biologically produced in situ. Our measurements indicate that the global annual flux of CH_3Br and CH_3Cl from wetlands could be as high as 4.6 Gg yr^{-1} of CH_3Br and 48 Gg yr^{-1} of CH_3Cl. These are preliminary estimates based on measurements made during the end of the 1998 growing season, a time period of decreased emissions of other trace gases such as methane (CH_4).

1. Introduction

Chlorine radicals destroy ozone (O_3) in the stratosphere causing areas of O_3 layer thinning and subsequently "holes" [*WMO*, 1989,1994]. Methyl chloride (CH_3Cl) is one of the largest reservoirs of reactive chlorine in the troposphere and therefore is important in the natural processes responsible for stratospheric O_3 destruction [*Graedel and Keene*, 1995; *Khalil and Rasmussen*, 1999]. Bromine radicals are estimated to be up to 50 times more efficient than chlorine in stratospheric O_3 destruction [*Yung et al.*, 1980; *Solomon et al.*, 1992; *WMO*, 1992; *Mano and Andreae*, 1994]. CH_3Br, used worldwide as a fumigant, is the largest source of bromine radicals in the atmosphere [*Wofsy et al.* 1975; *McElroy et al.* 1986]. This potential problem has led to the reduction and eventual cessation of the industrial production and use of CH_3Br in 2005 as reflected in the 1995 Montreal Protocol [*UNEP*, 1995].

The atmospheric CH_3Br mixing ratio is 10 to 15 parts per trillion by volume (pptv) in the Northern Hemisphere and approximately 7 to 9 pptv in the Southern Hemisphere [*Khalil et al.*, 1993; *Penkett et al.*, 1994]. Sources of CH_3Br include biological production and release from the ocean [*Khalil et al.*, 1994; *Pilinis et al.*, 1996], biomass burning [*Blake et al.*, 1993; *Cicerone*, 1994; *Mano and Andreae*, 1994], combustion of leaded gasoline [*Penkett et al.*, 1994; *Baker et al.*, 1998], emission from fumigation of cultivated land, structures, and perishables [*Yates et al.*, 1996; *Yates et al.*, 1997], and emission from terrestrial higher plants [*Gan et al.*, 1998]. Sinks of atmospheric CH_3Br include reaction with OH [*Penkett et al.*, 1994; *Prinn et al.*, 1995], loss to the ocean [*Butler*, 1994; *Lobert et al.*, 1995; *Yvon-Lewis and Butler*, 1997], uptake by soils [*Shorter et al.*, 1995; *Serça et al.*, 1998] and possibly uptake

by green plants [*Jeffers and Wolfe*, 1997; *Jeffers et al.*, 1998]. A large discrepancy remains in the global budget of CH_3Br with sinks exceeding sources by close to 70 Gg yr^{-1} [*Yvon-Lewis and Butler*, 1997].

CH_3Cl contributes from 13-25% of the annual chlorine input to the stratosphere depending on the measured tropospheric mixing ratio [*Graedel and Keene*, 1995; *Montzka et al.*, 1996; *Khalil and Rasmussen*, 1999]. The tropospheric budget of CH_3Cl contains significant components from marine sinks and sources, anthropogenic sources, biomass burning emissions, depletion by OH, and loss to the stratosphere [*Graedel and Keene*, 1995; *Khalil and Rasmussen*, 1999]. Our understanding of the magnitude of these budget components is incomplete because the identified sources are 1) less than the identified sinks and 2) less than that required to maintain the current atmospheric burden of 3.7 Tg yr^{-1} of CH_3Cl [*Graedel and Keene*, 1995; *Khalil and Rasmussen*, 1999]. The average global atmospheric concentration of CH_3Cl is 606 pptv with slightly higher concentrations measured in the tropics and slightly lower concentrations found in the polar regions of both hemispheres [*Khalil and Rasmussen*, 1999].

In an attempt to help identify missing sources in both the CH_3Br and CH_3Cl atmospheric budgets we undertook a measurement survey of potential sources. This survey included two Northeastern United States freshwater peatlands, Sallie's Fen and Angie's Bog, where we have made seasonal measurements of CH_4 and carbon dioxide (CO_2) efflux for close to ten years [*Frolking and Crill*, 1994]. Wetlands appeared to be a potential source of methyl halides because others have observed efflux of CH_3Cl and CH_3I from saturated organic rich soils [*Wuosmaa and Hager*, 1990; *Muramatsu and Yoshida*, 1995]. Measurements of CH_3Br and CH_3Cl were made weekly at the two sites from 1 September - 1 November 1998. The measurements revealed efflux of these trace gases in amounts that may have a significant impact on their atmospheric budgets.

2. Experimental Procedure

Sallie's Fen, a poor fen located in Barrington, NH (43°12.5'N, 71°03.5'W), has a surface area of 1.7 ha and is dominated primarily by *Sphagnum* spp., *Carex* spp., and ericaceous shrubs [*Frolking and Crill*, 1994]. The wetland ranges from minerotrophic wet edges to an ombotrophic central area [*Frolking and Crill*, 1994]. The site has been studied for CH_4 and CO_2 emissions to the atmosphere since 1989 [*Frolking and Crill*, 1994]. Continuous data for this site includes water level, wind speed, temperature (air and peat), precipitation, relative humidity, net radiation, photosynthetically active radiation, and barometric pressure.

The second sampling site, Angie's Bog, is a rich fen located adjacent to the Merrymeeting River in New Durham, New Hampshire (43°26.2'N, 71°10.4'W). It is also dominated by *Sphagnum* spp. Controlled water releases from Merrymeeting Lake maintain a uniform wetness in the wetland throughout the year. CH_4 and CO_2 fluxes were measured semi-continuously at this site from 1989

through 1994.

The gas flux measurements for CH_3Br, CH_3Cl, CH_4, and CO_2 were made using a transparent, climate controlled Lexan and Teflon chamber (100cm (or 50cm depending upon vegetation height) x 63cm x 63cm) placed on an aluminum collar imbedded in the wetland. Four gas samples of approximately 2 liters each were taken at specified intervals with a pump and stainless steel cylinders. The chamber, air, surface and 10 cm depth temperatures and pH were recorded during the measurements.

The sample canisters were returned to the laboratory and analyzed for CH_3Br, CH_3Cl, CH_4 and CO_2 within 24 hours. The CH_3Br and CH_3Cl mixing ratios were determined using a gas chromatograph equipped with an O_2 doped electron capture detector [*Kerwin et al.*, 1996]. A gas chromatograph equipped with a flame ionization detector (GC-FID) was used to determine concentrations of CH_4 and a thermal conductivity detector gas chromatograph was used for analysis of CO_2.

Fluxes were calculated using the linear regression slope of the measured gas concentration in the samples over time using the following equation:

$$\text{Flux} = \text{Slope } P/(RT) \text{ } Vc/Ac \text{ } (10^9 \text{ nmole/mole} \times 1440 \text{ min/d) } c \quad (1)$$

where Flux is in nmoles $m^{-2}d^{-1}$, Slope is equal to ppmv or pptv/min, P is air pressure of approximately 1 atm, R is the gas constant equal to 8.206×10^{-5} m^3 atm/K mol, T is the chamber temperature in Kelvin, Vc is the chamber volume, Ac is the collar area, and c is a constant to convert from mixing ratios (10^{-6} for ppmv measurements and 10^{-12} for pptv measurements).

3. Results and Discussion

Table 1 is a summary of the fluxes measured at both sites. Reported values are the average flux of n samples plus or minus the standard deviation. CO_2 fluxes are reported as negative values and represent uptake by the wetlands. The fluxes ranged from 2.2 - 56 nmoles m^{-2} d^{-1} of CH_3Br and 57.4 - 1109.1 nmoles m^{-2} d^{-1} of CH_3Cl. Sallie's Fen shows higher flux rates for all trace gases measured. This may be due to temperature variation during flux measurements at these sites.

The temperature/flux relationship (Figure 1) is similar to that measured between CH_4 and DMS and temperature at this site [*Frolking and Crill*, 1994; *DeMello*, 1992]. Since CH_4 and DMS are believed to be microbially mediated, we suggest that the mechanisms of production of CH_3Br and CH_3Cl might possibly be biological as well. Emission to the atmosphere may then be controlled by temperature, depth of the saturated zone and vegetative cover.

Table 1. Summary of Measured Variables at Two Wetland Sites in Northeastern United States

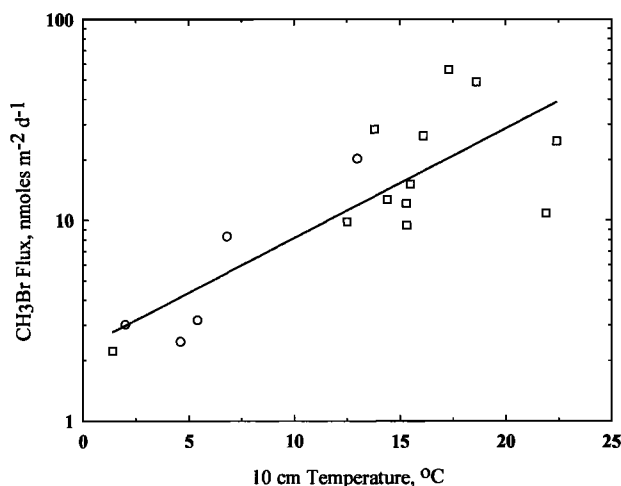| Measured Variable	Sallie's Fen	Angie's Bog
CH_3Br (nmoles/m^2/d)	21.4 ± 16.5	7.46 ± 7.56
CH_3Cl (nmoles/m^2/d)	525 ± 281	184 ± 113
CH_4 (mmoles/m^2/d)	30.4 ± 22.0	2.06 ± 1.63
CO_2 (mmoles/m^2/d)	-105 ± 119	-98.3 ± 50.4
10cm Temperature (°C)	16.6 ± 3.2	6.17 ± 4.1
Chamber Temperature (°C)	24.6 ± 6.3	10.2 ± 2.6
pH (pH units)	4.9 ± 0.7	5.5 ± 0.7
n	12	7

Figure 1. Relationship between CH_3Br and 10 cm temperature at two wetland sites in Northeastern United States. Linear regression of the 10 cm temperature (°C) versus the measured CH_3Br flux (nmoles $m^{-2}d^{-1}$) at Sallie's Fen (o) and Angie's Bog (□). Flux - 2.34 ($10^{0.055t}$) with an r^2 - 0.6686.

The ratio of the emissions of CH_3Br versus CH_3Cl (Figure 2) reveals a linear least squares regression slope of 4.6 x 10^{-2} with an r^2 of 0.67. In previous studies of biomass burning emissions from a boreal forest the molar ratio between these two compounds was determined to be 1.90 x 10^{-2} [*Mano and Andreae*, 1994]. Since our measured value reveals a somewhat higher ratio, this may indicate either less availability of Cl^- in the peat or a larger source of stored Br^-.

To obtain an estimate of the global emissions we used the following equation:

$$\text{Global Flux} = \text{Local Flux} \times \text{Growing Season} \times \text{Land Area} \quad (2)$$

where the Global Flux is calculated in Gg yr^{-1}, Local Flux is the highest measured flux equal to 56.1 nmoles m^{-2} d^{-1} for CH_3Br and 1109.1 nmoles m^{-2} d^{-1} for CH_3Cl, Growing Season is in days (240 days for temperate ecosystems), and Land Area of wetlands in the world is taken to be 3.56 x 10^{12} m^2 [*Gorham*, 1991]. The maximum measured flux rate was chosen because the methyl halide gas fluxes were measured at the end of the biologically active season. If these gases behave like CH_4 emission or CO_2 respiration at this site, our experience has been that early September fluxes are close to the annual mean fluxes of these gases from these wetlands. Measured CH_4 fluxes for early September show that they are anywhere from 8 to 65% of the maximum measured flux value for the growing season of 1998. The global estimate for emissions of CH_3Br by wetlands could be 4.6 Gg yr^{-1}, or approximately 5% of the "missing" source. 48 Gg yr^{-1} of CH_3Cl is estimated to be emitted from wetlands which could account for anywhere from 2 to 12% of the global atmospheric budget imbalance [*Graedel and Keene*, 1995].

These are compelling, if limited, flux data. They are preliminary estimates for the following reasons: the length of our sampling period was limited to 2 months, the sampling was conducted near the end of the growing season during senescence which in the past has shown less than the maximum emissions of other trace gases [e.g. *Frolking and Crill*, 1994; *DeMello*, 1992], and only a limited number of sites were sampled. Thus, our data is a starting point for an emission estimate. In order to refine the calculations of global
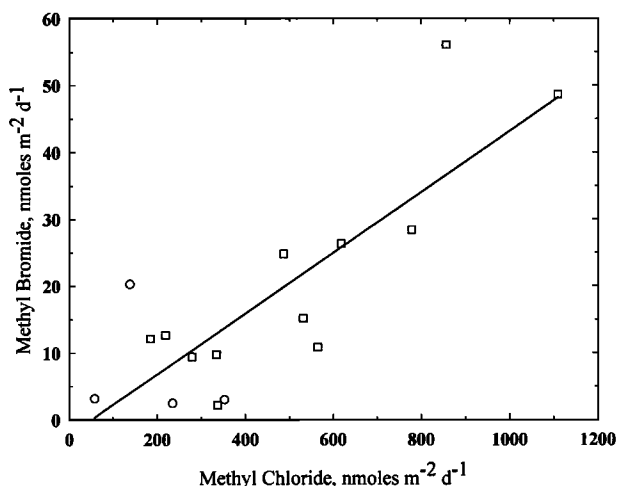
Figure 2. Relationship between measured fluxes of CH_3Br and CH_3Cl from two wetland sites in Northeastern United States. Linear regression of the flux of CH_3Cl (nmoles $m^{-2}d^{-1}$) and CH_3Br (nmoles $m^{-2}d^{-1}$) at Sallie's Fen (o) and Angie's Bog ($\square$). The equation for the regression line is $6 - 0.046x - 2.27$ with an $r^2 = 0.6747$.

emissions, we need: 1. To show that these emissions are a common feature of wetlands from the tropics to the tundra and 2. field studies must be completed over the entire growing seasons.

4. Conclusions

Our direct measurements indicate that wetlands are a potentially significant source of the methyl halides, CH_3Br and CH_3Cl, to the troposphere. We have observed this source in two different temperate wetland ecosystems. Others have observed rice agriculture and higher plants to be a source of CH_3I and CH_3Cl [*Wuosmaa and Hager*, 1990; *Muramatsu and Yoshida*, 1995], so this may be a common feature of saturated, anoxic organic soils. The temperature response of the field emissions may indicate that the fluxes are biologically mediated. These measurements are the first available numbers to start to make a realistic estimate of direct emissions to the atmosphere from wetland ecosystems. It is too early, therefore, to determine the effect they may have on the atmospheric budgets and lifetimes, and calculation of the ODP for these methyl halide gases.

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