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Marguerite L. White
University of New Hampshire, Durham

Ruth K. Varner
University of New Hampshire, Durham, ruth.varner@unh.edu

Patrick M. Crill
Stockholm University

Cindy H. Mosedale
University of New Hampshire, Durham

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Controls on the seasonal exchange of CH_3Br in temperate peatlands

Marguerite L. White and Ruth K. Varner
Climate Change Research Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampshire, USA

Patrick M. Crill
Department of Geology and Geochemistry, Stockholm University, Stockholm, Sweden

Cindy H. Mosedale
Climate Change Research Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampshire, USA

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[1] Measurements of CH_3Br exchange at two New Hampshire peatlands (Sallie's Fen and Angie's Bog) indicate that net flux from these ecosystems is the sum of competing production and consumption processes. Net CH_3Br fluxes were highly variable and ranged from net emission to net uptake between locations within a single peatland. At Sallie's Fen, net CH_3Br flux exhibited positive correlations with peat temperature and air temperature during all seasons sampled, but these relationships were not observed at Angie's Bog where flux varied according to microtopography. The major CH_3Br production process at Sallie's Fen appeared dependent on aerobic conditions within the peat, while CH_3Br production at Angie's Bog was favored by anaerobic conditions. There was evidence of aerobic microbial consumption of CH_3Br within the peat at both sites. In a vegetation removal experiment conducted at Sallie's Fen with dynamic chambers, all collars exhibited net consumption of CH_3Br. Net CH_3Br flux had a negative correlation with surface temperature and a positive correlation with water level in collars with all vegetation clipped consistent with aerobic microbial consumption. Vegetated collars showed positive correlations between net CH_3Br flux and air temperature. A positive correlation between net CH_3Br flux and surface temperature was also observed in collars in which all vegetation except *Sphagnum* spp. were clipped. These correlations are consistent with seasonal relationships observed in 1998, 1999, and 2000 and suggest that plants and/or fungi are possible sources of CH_3Br in peatlands. Estimates of production and consumption made on two occasions at Sallie's Fen suggest that peatlands have lower rates of CH_3Br consumption compared to upland ecosystems, but a close balance between production and consumption rates may allow these wetlands to act as either a net source or sink for this gas.

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1. Introduction

[2] Methyl bromide (CH_3Br) is the most abundant bromine containing gas in the troposphere with ambient mixing ratios of 8–10 pptv [*Kurylo et al.*, 1999; *Yokouchi et al.*, 2002; *Montzka et al.*, 2003]. Inorganic halogen radicals produced by dissociation of this and other halogenated compounds catalyze the destruction of ozone in the stratosphere [*Brasseur et al.*, 1999]. Under current stratospheric conditions, bromine radicals are approximately 50 times more efficient at depleting ozone than chlorine radicals [*Daniel et al.*, 1999]. This combination of destructive capability and relative abundance has prompted significant concern over CH_3Br sources and sinks to the atmosphere.

[3] Decreases in atmospheric CH_3Br concentrations since 1998 partly reflect phase-out of its fumigation use according to the Montreal Protocol and suggest that the global budget for this gas needs to be reassessed [*Yokouchi et al.*, 2002; *Montzka et al.*, 2003; *Reeves*, 2003]. Terrestrial wetlands, including peatlands [*Varner et al.*, 1999; *Dimmer et al.*, 2001], salt marshes [*Rhew et al.*, 2000] and rice fields [*Redeker et al.*, 2000], account for approximately 13% of known sources. This estimate is questionable as the current global budget for CH_3Br is out of balance with sinks exceeding sources by 60 Gg/yr [*Yvon-Lewis*, 2000]. Furthermore, our limited understanding of how CH_3Br cycles through these ecosystems

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provides significant uncertainty when defining the impact of natural systems on the global budget.

[4] Field measurements of CH_3Br exchange vary between emission and uptake at the same site indicating that both production and consumption mechanisms contribute to net flux [*Rhew et al.*, 2001, 2002; *Varner et al.*, 2003]. Controls over CH_3Br flux from soils are not well defined. Several mechanisms of natural methyl halide production and consumption have been identified. The oxidation of organic matter in the presence of iron and halide ions can produce several methyl halides including CH_3Br [*Keppler et al.*, 2000]. A variety of plants and fungi can also produce methyl halides via an enzyme mediated methyl transferase reaction [*Wuosmaa and Hager*, 1990; *Attieh et al.*, 1995; *Rhew et al.*, 2003]. Whole plant and fungal culture studies have confirmed CH_3Br production for *Brassica* spp. [*Gan et al.*, 1998], a subset of saprophytic wood-rotting fungi [*Harper*, 1985], and several species of ectomycorrhizal fungi [*Redeker et al.*, 2004]. In addition, *Jeffers et al.* [1998] found that leaves of a variety of plants could consume elevated levels of CH_3Br. Microbial consumption of fumigant and ambient levels of CH_3Br has also been identified in a variety of bacteria [*Connell et al.*, 1997; *Miller et al.*, 1997; *Hines et al.*, 1998; *Goodwin et al.*, 2001].

[5] In Irish peatlands, *Dimmer et al.* [2001] noted a high degree of spatial and temporal variation in methyl halide emissions that appeared dependent on light levels and vegetation. The magnitude of net flux at a given site changed considerably within a few meters which the authors attributed potentially to vegetation and microtopography differences as well as localized fungal activity within the peat. *Rhew et al.* [2000, 2002] also observed significant spatial and temporal variations in CH_3Br and CH_3Cl emissions from coastal salt marshes that corresponded to changes in vegetation community and growing season. Studies of agricultural rice fields [*Redeker et al.*, 2000; *Redeker and Cicerone*, 2004] linked seasonal variations in methyl halide emissions to the specific growth stage of the rice plants, soil halide concentrations, air temperature, and soil water saturation. High variability in rates of emission have also been observed among plant species [*Saini et al.*, 1995], fungal species [*Redeker et al.*, 2004], and even different cultivars of rice [*Redeker and Cicerone*, 2004] under identical conditions.

[6] In two New Hampshire peatlands during 1998, *Varner et al.* [1999] found strong correlations between net CH_3Br flux and peat temperature indicating a dominant belowground biological production process. Subsequent measurements revealed high variability in these relationships from site to site and year to year. This paper examines these seasonal studies as well as a vegetation removal experiment for evidence of the major controlling factors over net CH_3Br exchange in peatlands.

2. Methods

2.1. Site Descriptions

[7] Sallie's Fen in Barrington, New Hampshire (43°12.5′N 71°03.5′W) is a small nutrient poor peatland. With a surface area of 1.9×10^4 m^2, it has an ombrotrophic center (low pH, approximately 4.7) and minerotrophic edges (higher pH, approximately 5.7). The vegetation includes *Sphagnum* spp. (mosses), *Carex* spp. (sedges) and ericaceous shrubs. CH_4 and CO_2 exchange have been measured at this site since 1989 [*Frolking and Crill*, 1994] while CH_3Br exchange has been studied since 1998 [*Varner et al.*, 1999]. A meteorological station located in the center of the fen recorded continuous, hourly averaged data throughout the sampling period including water level, wind speed, relative humidity, photosynthetically active radiation (PAR), barometric pressure, and a temperature profile from 25 cm above the surface to 90 cm below the peat surface.

[8] Angie's Bog is located next to Merrymeeting River and Merrymeeting Lake in New Durham, New Hampshire (43°26.2′N, 71°10.4′W). With dominant *Sphagnum* spp. cover and an average pH of 5.2, this peatland is most similar to a nutrient-rich fen. Controlled water releases from the lake maintain relatively uniform water-levels throughout the year. CH_4 and CO_2 exchange were measured at this site from 1989 to 1994 while CH_3Br, CH_4 and CO_2 exchange were measured from 1998 to 2000. An automated meteorological station recorded hourly averaged water level, air temperatures at 50 cm above the peat surface and peat temperatures at the surface and at 5 and 10 cm depths from April 1999 through June 2000. Malfunctions with the meteorological datalogger prevented water level monitoring during the second half of the 2000 season.

2.2. Seasonal Large Static Chamber Measurements, 1999–2000

[9] Gas flux measurements were made at both sites using a transparent, climate-controlled Lexan and Teflon chamber (63 cm × 63 cm × 100 cm or 50 cm depending on vegetation height). The chamber was placed on previously established aluminum collars (63 cm × 63 cm) embedded in the peat. The collars at Sallie's Fen were put in 3 to 10 years prior to this study (Figure 1). Collars 2 and 4 were sampled approximately weekly to capture the temporal variability in net CH_3Br flux at this site. A third collar was randomly selected weekly for sampling from the remaining nine collars spread across the fen to provide some indication of spatial variability at this site. Collar 2 vegetation was dominated by leatherleaf (*Chamaedaphne calyculata*) and red maple seedlings (*Acer rubrum*). Collar 4 vegetation was primarily sedge (*Carex rostratum*) and cranberry (*Vaccinium oxycoccus*). There was also an alder sapling (*Alnus rugosa*) present. The other collars sampled were generally a mixture of leatherleaf, cranberry, red maple, and sedge.

[10] Two collars were placed in Angie's Bog in August 1998 to examine the effects of microtopographic differences in the peat surface on net CH_3Br flux variability. One collar was placed on a hummock 4.5 cm higher than the other which was established in a hollow. The predominant vegetation in the hummock collar was leatherleaf while sedges and cranberry dominated the hollow collar. The two collars were both sampled approximately weekly during the 1999 and 2000 growing seasons. Measurements were made at both sites between 0900 local time (LT) and 1500 LT local

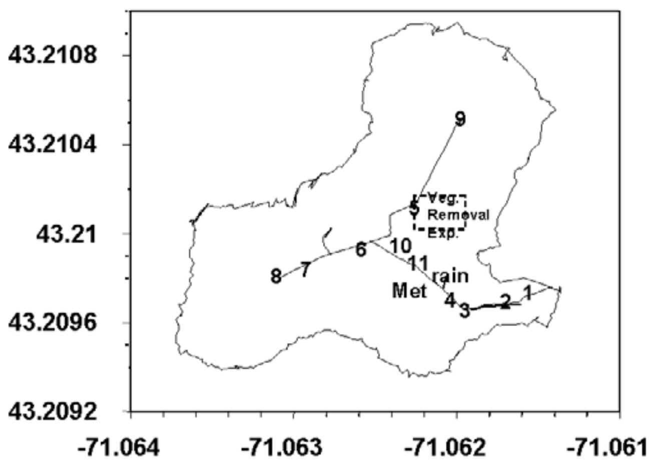

Figure 1. Map of sampling collar locations at Sallie's Fen. The large collars sampled with static chambers during the 1998, 1999, and 2000 field seasons are labeled 1, 2, 3, 4, etc. The labels "Met" and "rain" indicate the location of the met station and the rain gauge. The smaller collars for the 2002 vegetation removal experiment were all located in the area labeled "Veg. Removal. Exp." All collars were accessed via a previously established boardwalk.

time. The exact time of sampling varied but most frequently occurred between 1000 LT and 1300 LT.

[11] To measure gas exchange, the chamber was placed on the collar and sealed with water. Four 2.5 L headspace samples were removed over 16 min (t = 1, 6, 11, and 16 min after chamber placement). An ambient air sample was also collected for each flux measurement. All gas samples were compressed in evacuated 0.5 L stainless steel cylinders for laboratory analysis. Chamber, air, surface peat, and 10 cm depth peat temperatures were also measured manually at each collar during gas collection. All temperatures measured at the collar were generally higher than those recorded at the meteorological station. Since the manual thermometer had a tendency to overheat in the sun, hourly averaged meteorological station air and 10 cm peat depth temperatures were used whenever possible during data analysis. The average temperature rise within the static chambers during deployment was 2.5°C above ambient.

[12] Gas samples were analyzed in the laboratory for CH_3Br, CH_4, and CO_2 within 24 hours of collection. CH_3Br concentrations were determined using a gas chromatograph equipped with an oxygen-doped electron capture detector (GC-ECD). The instrument analysis error of this system for ten repeated measurements of ambient air was ±6%. Samples were calibrated against a purchased standard (Scott Specialty Gas, Inc., CH_3Br = 270.1 ± 7.8 ppbv) diluted to ambient concentrations as described by *Kerwin et al.* [1996]. CH_4 and CO_2 mixing ratios were determined using a gas chromatograph with flame ionization detector (GC-FID) and a gas chromatograph with thermal conductivity detector (GC-TCD), respectively. Samples were calibrated against purchased compressed air (NorthEast Airgas) standardized with a National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory Standard (CO_2 = 380.49 ± 0.05 ppmv, CH_4 = 1.832 ± 0.002 ppmv). All chamber concentrations were corrected for ambient air dilution during collection prior to flux calculations.

[13] Gas fluxes (F) were calculated from the change in chamber headspace concentration over time as follows:

$$F = (\mathrm{d}C_h/\mathrm{d}t) \times (V_c/A_c), \qquad (1)$$

where $\mathrm{d}C_h/\mathrm{d}t$ is the linear regression slope of the chamber headspace concentration over time (nmol $L^{-1}d^{-1}$ for CH_3Br, or mmol $L^{-1}d^{-1}$ for CH_4 and CO_2) and V_c is the chamber volume (L) and A_c is the collar area (m^2).

2.3. Vegetation Removal Experiment

[14] A vegetation removal experiment was conducted in 2002 at the Sallie's Fen site to determine the effect of changes in vegetation community on net CH_3Br exchange. The vegetation removal experiment was located in a central portion of the fen dominated by *Carex rostratum*, *Vaccinium oxycoccus* (cranberry), and *Sphagnum* spp. (Figure 1). The following treatments were applied randomly to 12 small Teflon-coated aluminum collars (30 cm × 30 cm) cut into the peat in 2001 and the early spring of 2002 (n = 3 for each treatment).

[15] 1. N Collars are those where all aboveground vegetation was clipped. No plants (N) remained.

[16] 2. S Collars are those where *Carex rostratum* and *Vaccinium oxycoccus* were clipped leaving only *Sphagnum* spp. (S).

[17] 3. V Collars are those where only *Carex rostratum* were clipped. *Vaccinium oxycoccus* (V) and *Sphagnum* spp. remained.

[18] 4. C collars are those where vegetation was left undisturbed as a control. *Carex rostratum* (C) dominated the collars.

[19] Vegetation was initially clipped 2 months prior to first sampling. Treatment levels were maintained throughout the sampling period with additional clipping as necessary.

[20] Gas fluxes were measured at the small collars on a weekly basis from June to August 2002 using a transparent dynamic flux chamber constructed of Teflon film with a Lexan frame (30 cm × 30 cm × 30 cm) [*Morrison and Hines*, 1990; *de Mello and Hines*, 1994]. Ambient air was pushed into the chamber through a 0.5 cm inlet at 2.5 L min^{-1}. A mass flow controller attached to the inlet pump maintained a constant inlet sweep flow rate. A 1.0 cm diameter outlet on the opposite wall of the chamber allowed sweep air to vent without obstruction. The pressure differential between the closed chamber and the atmosphere ranged from 0.000 to 0.004 torr and should not have significantly affected gas exchange processes during measurement. One wall of the chamber was replaced with 1/4 inch thick Lexan on which a cold-water condensor and small fan were mounted. This cooling system minimized chamber temperature increases with an average rise over ambient of 2°C. Ambient air was allowed to sweep through for 75 to 90 min before sampling. Prior tests indicated that chamber gas concentrations reached equilibrium or constant values between 60 and 90 min. Fluxes measured on the

same collar and day using this chamber in dynamic and static mode were comparable in magnitude and direction of flux.

[21] Headspace gas samples were collected at a rate of 1.5 L min^{-1} from Teflon tubing (0.165 cm diameter) inserted through the vent into the center of the chamber. Two 2.5 L samples of headspace air and one 2.5 L sample of ambient sweep air were compressed into evacuated 0.5 L electropolished stainless steel cylinders for laboratory analysis. Ambient air was pulled from the sweep line immediately after sampling using the same pump system. Measurements of temperature (air, chamber, surface peat and 10 cm peat depth), photosynthetically active radiation (PAR) and water level were made at each collar during sampling. Vegetation cover (leaf area for *Carex* and *Vaccinium* spp., surface area for *Sphagnum* spp.) was also measured as appropriate in each collar on a weekly basis. Leaf area in situ was estimated from blade length for *Carex* spp. and leaf density for *Vaccinium* spp. using allometric equations calculated with representative plant samples collected nearby.

[22] Gas samples were analyzed in the laboratory for CH_3Br, CH_4 and CO_2 mixing ratios as described for the previous large static chamber measurements. Gas fluxes were calculated using the following equation:

$$F = (C_h - C_a) \times (I_{in}/A_c), \quad (2)$$

where F is the flux in nmol $m^{-2}d^{-1}$ for CH_3Br and mmol $m^{-2}d^{-1}$ for CH_4 and CO_2. C_h and C_a are the headspace concentration and the ambient inlet air concentration, respectively (nmol L^{-1} CH_3Br and mmol L^{-1} CH_4 and CO_2). I_{in} represents the inlet air flow rate (2.5 L min^{-1} or 3600 L d^{-1}) and A_c is the area of the collar (0.093 m^2).

[23] Concentrations of CH_3Br 2 to 4 times ambient (20 to 40 pptv) were observed in the small chamber when empty. These concentrations accumulated over the course of the flux measurement. A series of temperature and light manipulations conducted with the empty chamber sealed with Teflon coated paper indicated that the magnitude of headspace CH_3Br concentrations varied directly with the level of light exposure when the chamber was stored outside. Manipulations of chamber air temperature were also made while the chamber was shrouded (no light) by running hot water through the chamber cooling system. There were no significant emissions even when chamber air temperature reached 45°C. CH_3Br emissions were not significant in the larger static chambers used in the seasonal studies which were made out of the same material but had a much higher volume to surface area ratio. It is very possible that these emissions were actually dependent on the surface film temperature which might vary more directly with light than chamber air temperature. Because the light response was consistent over two and a half months of testing and with the chamber used in static and dynamic mode, all small chamber headspace CH_3Br concentrations were corrected for blank emissions using the following regression equation (R^2 = 0.79):

$$y = 3.24 + 0.00814x, \quad (3)$$

where y is the chamber CH_3Br emission in nmol m^{-2} d^{-1} and x is photosynthetically active radiation in μmol m^{-2} s^{-1}.

2.4. Production and Consumption Estimates

[24] On two occasions (August 1 and August 2, 2002), a *Carex* dominated (C) collar was sampled twice. The first flux measurement was with all chamber vents sealed. Headspace gas samples were collected every 3 min over a 12 min period similar to the large chamber static flux measurements. The chamber was removed from the collar for 30 minutes, then replaced for a second measurement with the chamber in the dynamic flux mode. Flux was calculated as discussed previously for static and dynamic collection techniques.

[25] An intercomparison of the headspace concentrations during both types of flux measurements was then used to calculate a consumption rate constant, k_{uptake}, and estimate gross production and consumption under ambient conditions. It was assumed for both types of measurements that the net flux measured, d[CH_3Br]/dt or F, was equal to the production of CH_3Br from the fen, P, plus any blank emissions from the chamber, B, and the consumption of CH_3Br (considered a negative flux).

$$F = P + B + C. \quad (4)$$

The blank chamber emissions were calculated using the linear regression correction equation (3) based on both static and dynamic blank chamber tests and the average PAR levels during each flux. The production rate, P, was assumed to be a constant for the collar independent of headspace concentration. We assume that the microbial uptake of CH_3Br followed first order kinetics with a rate constant, k_{uptake}, such that

$$C = -k_{uptake}[CH_3Br]_{headspace}. \quad (5)$$

At equilibrium headspace concentrations, $[CH_3Br]_{eq}$, the consumption rate of CH_3Br should equal the rates of production, P, and blank chamber emissions, B, or

$$P + B = k_{uptake}[CH_3Br]_{eq}. \quad (6)$$

Substituting equations (5) and (6) into (4) and integrating net flux, F, as d[CH_3Br]/dt yields the following:

$$\ln\left([CH_3Br]_{eq} - [CH_3Br]_{headspace}\right) = -k_{uptake}t + \ln\left([CH_3Br]_{eq} - [CH_3Br]_o\right). \quad (7)$$

[26] The dynamic chamber equilibrium concentration was assumed to be $[CH_3Br]_{eq}$. Using the static chamber headspace concentrations as $[CH_3Br]_{headspace}$ measured over 3 min time intervals and solving the linear regression of this equation with y equal to $\ln([CH_3Br]_{eq} - [CH_3Br]_{headspace})$ and x equal to time, t, gives the slope as $-k_{uptake}$. This value was substituted into equation (6) and the rate of blank chamber emissions was subtracted to calculate an estimate of gross

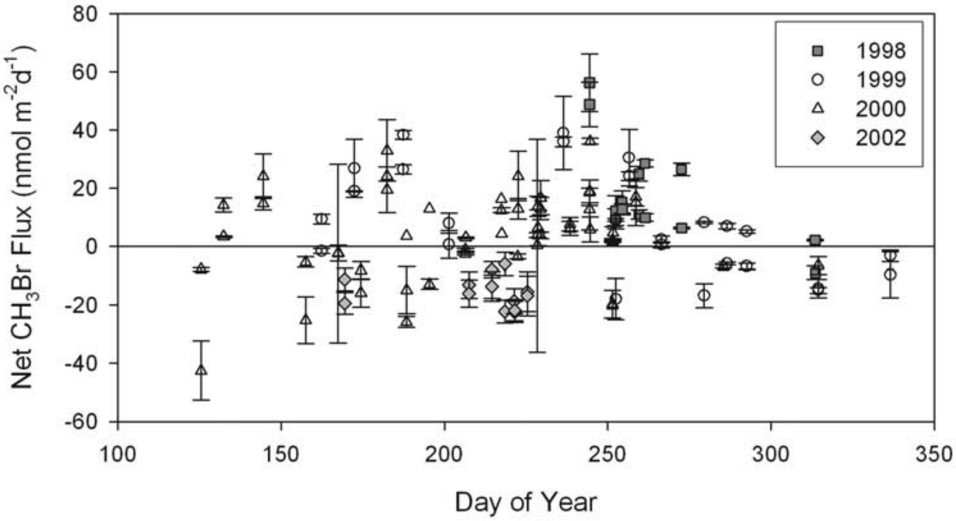

Figure 2. Sallie's Fen net CH_3Br flux measurements by day of year from 1998 to 2002. Fluxes measured from 1998 to 2000 were made with a large static chamber and include all collars sampled. Error bars represent the error of the slope of the linear regression fit of the chamber headspace measurements of [CH_3Br] versus time. The 2002 measurements were made with a small dynamic chamber and include only fluxes from the Carex dominated (C) collars. Vegetation was not disturbed in this treatment, and these measurements can be considered most representative of natural CH_3Br exchange rates at the Fen for that year. Error bars represent the standard error associated with analysis of the ambient and headspace gas samples.

production within the collar sampled. An estimate of the consumption rate at that collar under ambient conditions was calculated by substituting the ambient CH_3Br concentrations measured during each flux into equation (5).

3. Results and Discussion

3.1. Seasonal Net CH_3Br Flux Measurements at Sallie's Fen and Angie's Bog

[27] The range of net fluxes measured at Sallie's Fen and Angie's Bog from 1998 to 2002 indicate that net exchange of CH_3Br in peatlands represents a balance between production and consumption processes. During the 1999, 2000, and 2002 field seasons, rates of exchange ranged from +50 to −40 nmol $m^{-2}d^{-1}$ (Figures 2, 3, 4, 5, and 6; negative values indicate uptake from the atmosphere; see also auxiliary materials[1]). These are comparable to previous measurements made at the same sites in 1998 (+60 to −10 nmol $m^{-2}d^{-1}$; Figure 2 [*Varner et al.*, 1999]). The only other study conducted in natural peatland environments did not report uptake although the magnitude of average emissions (+3 to +61 nmol $m^{-2}d^{-1}$) was comparable to observations at Sallie's Fen and Angie's Bog. These flux measurements were collected in Irish peatlands over a single month and may not have captured the full variability of gas exchange at these sites [*Dimmer et al.*, 2001].

[28] Seasonal mean net fluxes measured at the large static chamber collars decreased at Sallie's Fen from 1998 through 2000 (Table 1) reflecting differences in sampling period and collars most frequently measured from year to year. Sampling was conducted in 1998 only from September to November as vegetation senesced and temperatures dropped. The most frequently measured collar during this time was collar 9 which was largely dominated by sedges (Figure 1). In contrast, the 1999 and 2000 sampling seasons extended from April to November or December. During these years, collars 2 and 4, located in more shrub-dominated areas of the fen (Figure 1), were sampled most often. This larger sampling period and area encompassed a much wider range of conditions throughout the fen and seasonal means from these two years are more representative of net CH_3Br emissions from this site. Seasonal mean net fluxes are less varied at Angie's Bog from 1998 to 2000 as the same two collars were measured each year.

3.2. Environmental Effects on Seasonal Net CH_3Br Fluxes

[29] A closer examination into the factors influencing the magnitude of net CH_3Br exchange at Sallie's Fen and Angie's Bog suggests that the dominant production process at the two sites is different. CH_3Br emissions at Sallie's Fen appear to be largely due to a temperature dependent aerobic production process. Net emissions were greatest with higher temperatures and lower water levels (Figures 3 and 4). During 1998, 1999, and 2000, net CH_3Br flux exhibited direct linear relationships with air and peat temperature (Figure 7, Table 2). The effect of temperature on net CH_3Br flux has been observed in other wetland ecosystems as well. Rates of CH_3Br emission from rice plants exhibited a

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gb/2004GB002343.

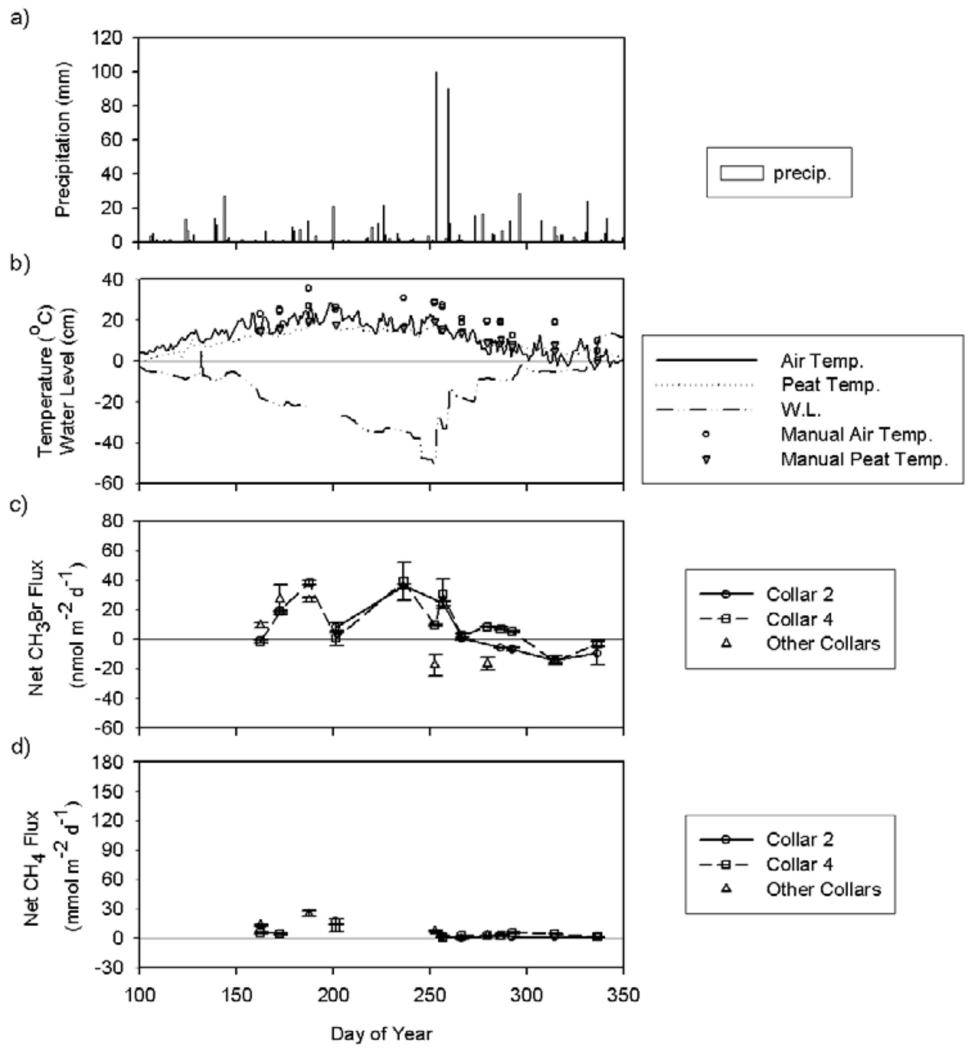

Figure 3. Sallie's Fen 1999. (a) Daily total precipitation (mm) and (b) average daily air temperature (°C) at 25 cm above the surface, peat temperature (°C) at 10 cm depth, and water level (cm below peat surface). Measurements were taken at a centrally located meteorological station every minute and averaged hourly. Daily averages are for 1200 local time (LT). Manual temperature measurements were taken with a handheld thermometer at the collar while collecting gases. (c) Net CH_3Br flux (nmol $m^{-2}d^{-1}$) and (d) net CH_4 flux (mmol $m^{-2}d^{-1}$) at collars 2 (circles) and 4 (squares). The final data (triangles) are measurements from collars randomly sampled throughout the Fen. Error bars represent the error of the slope of the linear regression fit of the chamber headspace measurements of [CH_3Br] versus time.

response to air temperature that varied between cultivars and specific growth stage of the plants [*Redeker and Cicerone*, 2004]. In a salt marsh study, net CH_3Br and CH_3Cl fluxes followed diurnal changes in temperature with maximum emissions corresponding to the highest daily air temperatures [*Rhew et al.*, 2000].

[30] Water level and net CH_3Br flux were also inversely proportional in 1999 suggesting that the production is aerobic. This relationship is less consistent than the temperature relationship from year to year, however, and may simply reflect covariance with temperature in 1999. That summer was hot, clear and dry. Water levels at Sallie's Fen dropped significantly as temperatures rose throughout the summer until two major rainfall events in September restored them to pre-drought conditions (Figure 3). More consistent rainfall in 2000 resulted in high water levels throughout the summer that only dropped slightly below the level of the peat in September (Figure 4). While there was not a correlation between net CH_3Br flux and water level during 2000 (Table 2), net uptake was more frequent during the 2000 season. The lowest measurements of net emission during the 1998 season also corresponded to the highest water levels. These low CH_3Br emissions were also measured in November, however, and could reflect drops in

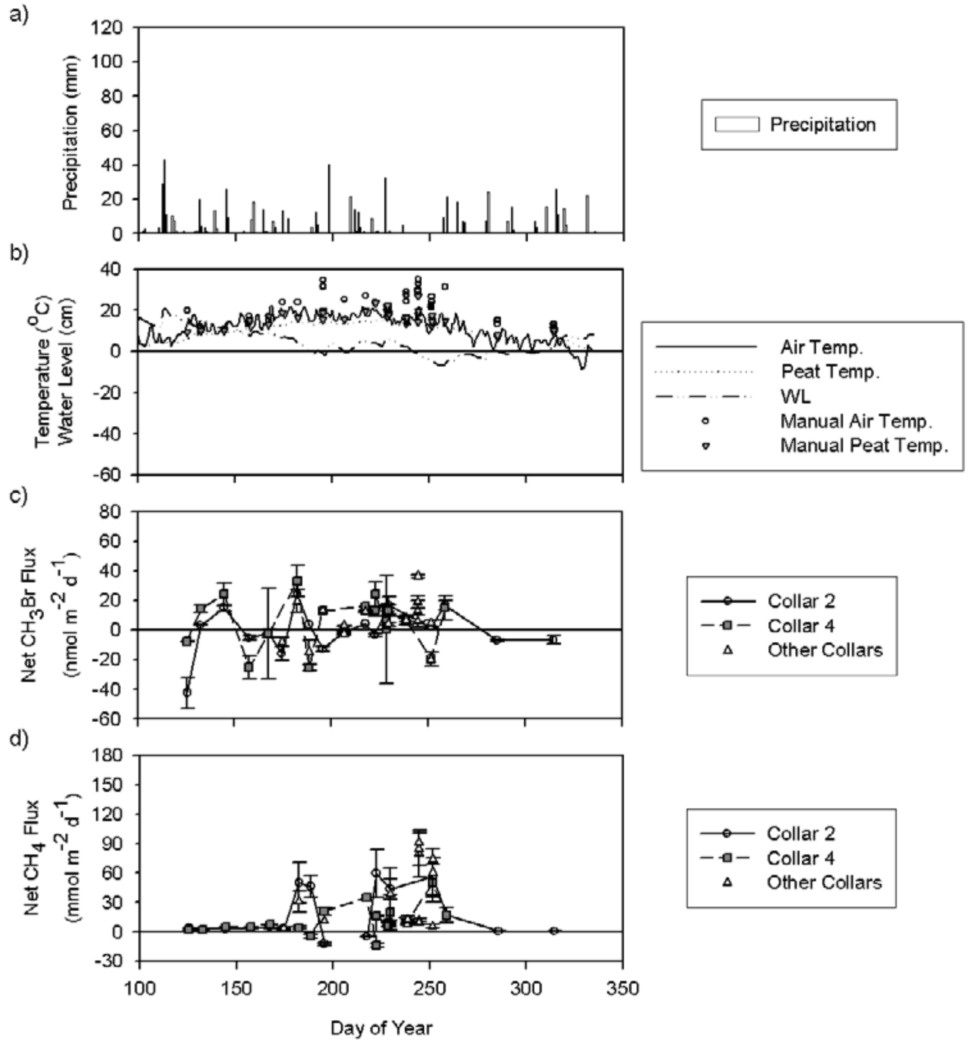

Figure 4. Sallie's Fen 2000. (a) Daily total precipitation (mm) and (b) average daily air temperature (°C) at 25 cm above the surface, peat temperature (°C) at 10 cm depth, and water level (cm below peat surface). Measurements were taken at a centrally located meteorological station every minute and averaged hourly. Daily averages are for 1200 LT. Manual temperature measurements were taken with a handheld thermometer at the collar while collecting gases. (c) Net CH_3Br flux (nmol $m^{-2}d^{-1}$) and (d) net CH_4 flux (mmol $m^{-2}d^{-1}$) at collars 2 (circles) and 4 (squares). The final data (triangles) are measurements from collars randomly sampled throughout the Fen. Error bars represent the error of the slope of the linear regression fit of the chamber headspace measurements of [CH_3Br] versus time.

temperature and the reduction of biological activity at the fen.

[31] Despite this unclear relationship between water level and net CH_3Br exchange, anomalous measurements made on one day during the summer of 1999 suggest that the dominant production process at the fen is limited by peat moisture increases. The outliers noted on Figure 7 occurred on 9 September (day 252) when water level was at its lowest for the season. Three days of small precipitation events preceded day 252 causing an influx of water to the dried out fen that probably rewet particle surfaces and made peat microenvironments more anaerobic without changing the water level. This alteration may also have lowered the concentration of bromide ions available for CH_3Br production and could have provided a barrier to diffusion for CH_3Br produced in the peat.

[32] Lower net emissions of CH_4 during the 1999 season reflect increased methanotrophy consistent with lower water table and more aerobic conditions within the peat (Figure 3). Soil studies indicate that microbial consumption of ambient CH_3Br is largely aerobic as well [*Hines et al.*, 1998] leading to the expectation that more aerobic conditions would favor enhanced consumption. While this may have occurred in 1999, net CH_3Br emissions suggest that CH_3Br production was also enhanced at the time. Net CH_3Br uptake was actually more frequent during 2000 when higher water table and correspondingly high CH_4 measurements reflect a more limited aerobic zone (Figure 4). Assuming that aerobic

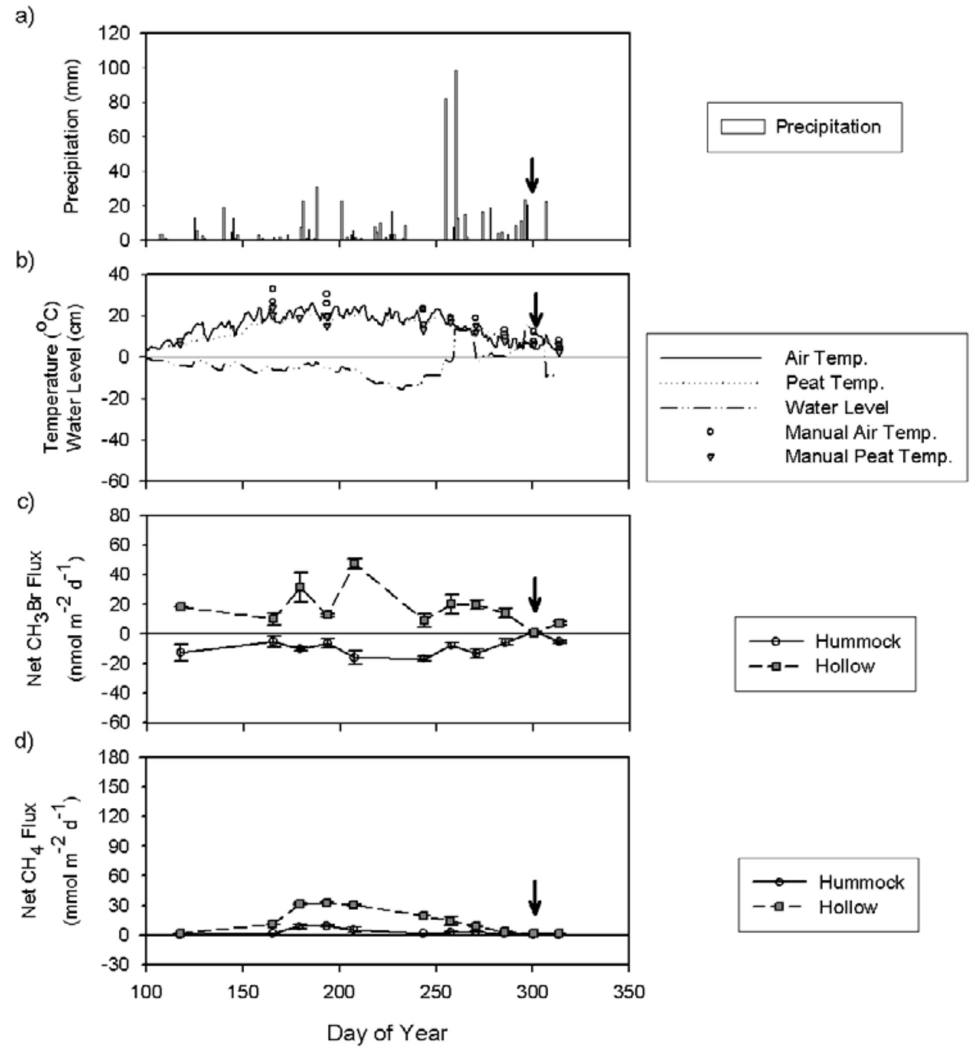

Figure 5. Angie's Bog 1999. (a) Daily total precipitation (mm) and (b) average daily air temperature (°C) at 25 cm above the surface, peat temperature (°C) at 10 cm depth, and water level (cm below peat surface). Measurements were taken at the adjacent meteorological station every minute and averaged hourly. Daily averages are for 1200 LT. Manual temperature measurements were taken with a handheld thermometer at the collar while collecting gases. (c) Net CH_3Br flux (nmol $m^{-2}d^{-1}$) and (d) net CH_4 flux (mmol $m^{-2}d^{-1}$) at hummock (circles) and hollow (squares). Error bars represent the error of the slope of the linear regression fit of the chamber headspace measurements of [CH_3Br] versus time. Arrows indicate days on which the collars were flooded during sampling.

microbial consumption is the main uptake mechanism for CH_3Br at the fen, this switch from net emission to net uptake further supports the presence of an aerobic production mechanism at Sallie's Fen and suggests that changes in water saturation in the peat have a larger effect on production than consumption.

[33] Unlike Sallie's Fen, higher water levels at Angie's Bog corresponded with larger net emissions of CH_3Br in both 1999 and 2000 (Figures 5 and 6). In 1999, the collar located in the hollow consistently emitted CH_3Br while the drier hummock collar took up the gas. These differences support measurements made by *Dimmer et al.* [2001] in Irish peatbogs where hollows at two different blanket bog sites exhibited higher CH_3Br emission than hummocks. During 2000, however, both hummock and hollow collars at Angie's Bog exhibited similar patterns of net uptake (Figure 6). Varying strength of aerobic microbial CH_3Br consumption could explain the different patterns of exchange between collars and years at Angie's Bog. The 4.5 cm difference in height above the water level between the two collars created a larger aerobic zone for the hummock. This is reflected in lower net CH_4 emissions from increased methane oxidation at the hummock collar and appears to have favored a significant role for microbial CH_3Br consumption as well. Lower overall water level in 2000 increased the aerobic zone for the lower hollow collar,

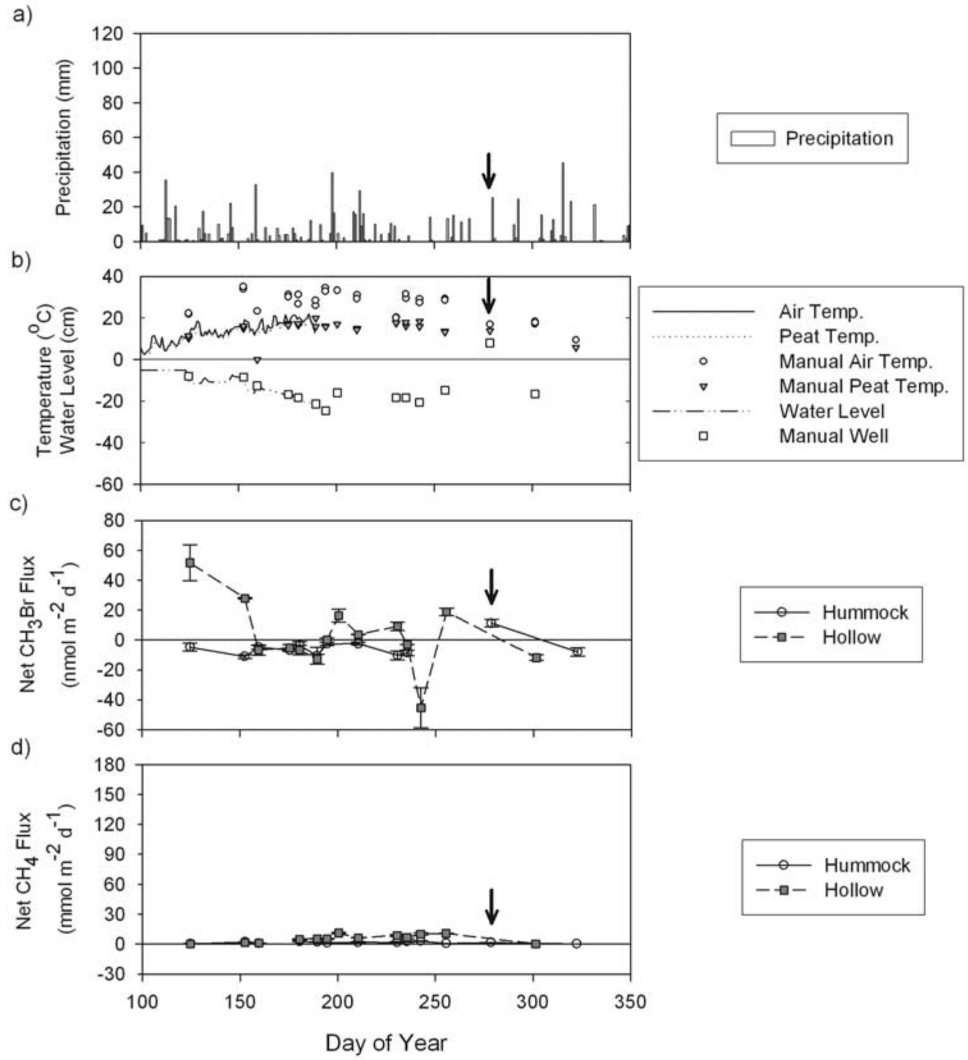

Figure 6. Angie's Bog 2000. (a) Daily total precipitation (mm) and (b) daily air temperature (°C) at 25 cm above the surface, peat temperature (°C) at 10 cm depth, and water level (cm below peat surface). Measurements were taken at the adjacent meteorological station every minute and averaged hourly. Daily averages are for 1200 LT. Datalogger malfunction prevented automated measurements of temperature and water level during the second half of the season. Manual temperature measurements were taken with a handheld thermometer at the collar while collecting gases. Manual well measurements were made at the datalogger well using a tape measure. (c) Net CH_3Br flux (nmol $m^{-2}d^{-1}$) and (d) net CH_4 flux (mmol $m^{-2}d^{-1}$) at hummock (circles) and hollow (squares). Error bars represent the error of the slope of the linear regression fit of the chamber headspace measurements of [CH_3Br] versus time. Arrows indicate days on which the collars were flooded during sampling.

making the microtopography height difference less significant, and resulted in similar net CH_4 and CH_3Br exchange at both collars (Figure 6).

[34] It should be noted that CH_3Br and CH_4 production and consumption processes may have similar environmental requirements but otherwise do not appear related. Aerobic consumption of ambient CH_3Br and CH_4 in upland soils do have different depth profiles with maximum rates of CH_3Br consumption in the top 5 cm [*Hines et al.*, 1998] while methane oxidation is greatest between 3 and 7 cm [*Crill*, 1991]. *Redeker et al.* [2002] also observed that emissions of CH_4, CH_3Br, and CH_3I in rice paddies were all dependent on pore water saturation but reached maximum rates during different stages of rice growth implying separate production mechanisms. These decoupled relationships would explain the lack of correlation between net CH_3Br and net CH_4 exchange at both peatland sites in this study.

[35] Increases in the aerobic zone did not result in increases in CH_3Br production at Angie's Bog. This suggests that the aerobic production mechanism evident at Sallie's Fen is less prevalent or not present at Angie's

Table 1. Seasonal Mean Net Fluxes (± Standard Error) for All Gases Measured at Both Sallie's Fen and Angie's Bog From 1998 to 2002[a]

	Mean CH_3Br Flux, nmol $m^{-2}d^{-1}$	Mean CH_4 Flux, mmol $m^{-2}d^{-1}$	Mean CO_2 Flux, mmol $m^{-2}d^{-1}$
		Sallie's Fen	
All collars 1998 (n = 14)[b]	18 ± 5	27 ± 6	−110 ± 30
All collars 1999 (n = 26)	7 ± 3	13 ± 8	−120 ± 20
All collars 2000 (n = 59)	4 ± 2	30 ± 10	−130 ± 20
		Veg. Removal Experiment 2002	
All treatments (n = 48)	−12 ± 2	10 ± 3	−20 ± 60
Carex (C) collars	−17 ± 1	14 ± 3	−200 ± 7
Vaccinium (V) collars	−12 ± 2	8 ± 1	−20 ± 20
Sphagnum (S) collars	−9 ± 2	14 ± 4	50 ± 30
No vegetation (N) collars	−11 ± 2	3 ± 1	80 ± 30
		Angie's Bog	
Both collars 1998 (n = 7)[b]	−2 ± 5	30 ± 10	−90 ± 20
Hummock 1998 (n = 3)[b]	−15 ± 3	30 ± 10	−70 ± 10
Hollow1998 (n = 4)[b]	8 ± 4	40 ± 20	−110 ± 30
Both collars 1999 (n = 22)	4 ± 4	9 ± 2	−120 ± 30
Hummock 1999 (n = 11)	−9 ± 2	3 ± 1	−40 ± 20
Hollow 1999 (n = 11)	17 ± 4	14 ± 4	−210 ± 50
Both collars 2000 (n = 24)	−1 ± 4	4 ± 1	−160 ± 30
Hummock 2000 (n = 11)	−6 ± 1	1.7 ± 0.3	−69 ± 8
Hollow 2000 (n = 13)	4 ± 6	6 ± 1	−240 ± 30

[a]The seasonal means are averages of all fluxes for that time period and site. Negative values indicate uptake of the gas from the atmosphere.
[b]The 1998 data were originally published by *Varner et al.* [1999].

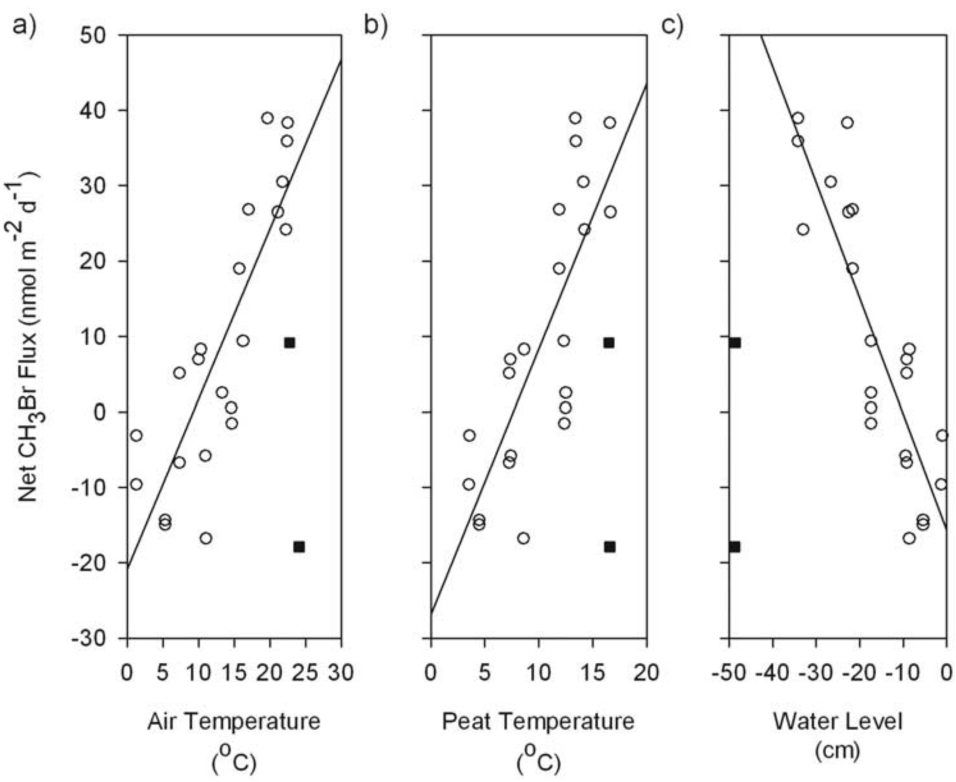

Figure 7. Sallie's Fen 1999 relationships between net CH_3Br flux at all collars and environmental variables. The outliers (squares) were observed at collars 3 and 4 on September 9 after several days of small rain events which did not substantially increase water levels. (a) Net CH_3Br flux versus hourly averaged met station air temperatures measured at +10 cm during collar sampling, $R^2 = 0.70$, $p < 0.0001$. (b) Net CH_3Br flux versus hourly averaged met station peat temperatures measured at −10 cm during collar sampling, $R^2 = 0.62$, $p < 0.0001$. (c) Net CH_3Br flux versus hourly averaged water level at the met station during collar sampling, $R^2 = 0.74$, $p < 0.0001$. The p values represent probability that regression slope is zero.

Table 2. A Comparison of the Linear Regression Relationships Between the Major Environmental Variables and Net CH_3Br Flux at Sallie's Fen for the Seasonal Large Collar Studies[a]

Year	Regression Statistics	Peat Temperature (−10°C)	Air Temperature (+10°C)	Water Level, Centimeters Below Peat
1998	Slope	3.7	1.6	0.04
	R^2	0.40	0.40	0.0001
	p	0.02	0.02	0.96
1999	Slope	3.5	2.5	−1.5
	R^2	0.64	0.74	0.70
	p	0.0001	0.0001	0.0001
2000	Slope	2.2	1.9	−0.21
	R^2	0.15	0.24	0.005
	p	0.004	0.0002	0.59

[a]Linear regressions were calculated with y as net CH_3Br flux and x as temperature or water level. The p values represent the probability that the slope is equal to 0.

Bog. Instead, the major CH_3Br production mechanism at Angie's Bog appears dependent on water saturated peat environments. Net CH_3Br emissions were measured only once at the hummock collar during each season (day 300, 1999, Figure 5; day 278, 2000, Figure 6). Both these sampling days were immediately after water was released from Merrymeeting Lake and both collars were under water. Greater freshwater input at Angie's Bog could have affected peat halide ion concentrations and contributed to methyl halide flux variability between the sites. Increased precipitation may have also altered the concentrations of halide ions to which fungi and the roots of the vegetation were exposed. Several studies have shown that both plant and fungal emission rates of methyl halides are positively correlated to soil halide concentrations [*Harper and Kennedy*, 1986; *Saini et al.*, 1995; *Gan et al.*, 1998; *Redeker and Cicerone*, 2004]. Soil halide concentrations were not measured at either Sallie's Fen or Angie's Bog so their effect on peatland CH_3Br exchange is currently uncertain and represents a potential area for future study.

[36] Differences in the vegetative and microbial community very likely contributed to the divergent effects of aerobic and anaerobic peat conditions on CH_3Br exchange at these two peatlands. *Redeker and Cicerone* [2004] observed that environmental conditions could affect rice plants differently with low soil water enhancing CH_3Br emissions from one cultivar of rice and not others. Vegetation communities were different between the two peatland sites. Sallie's Fen vegetation was more diverse and included a wide variety of woody shrubs. In contrast, Angie's Bog was dominated by *Sphagnum* moss with some sedges, leatherleaf and cranberry. While peatland plants such as sedges, mosses, and ericaceous shrubs have not been tested specifically for methyl transferase activity, the diverse number of plants that are capable of different rates of methyl halide emissions does support the possibility [*Saini et al.*, 1995]. Furthermore, the variation in CH_3Br emission rates between hummock plant groups observed by *Dimmer et al.* [2001] suggests changes in vegetation can play a role in peatland CH_3Br exchange.

[37] Peatlands also support a diverse collection of fungi [*Williams and Crawford*, 1983]. Fungi isolated specifically from Sallie's Fen and cultured in the laboratory have also produced CH_3Br (R. K. Varner, unpublished data, 2003). *Redeker et al.* [2004] observed large differences in the rate of CH_3Br production from different species of ectomycorrhizal fungi that implies fungal community changes can also affect net CH_3Br exchange. Although the microbial community composition is not known at either site, differences in the vegetation and hydrological regimes probably supported variations in the fungal species present which might have influenced the conditions and rates of CH_3Br production at each site.

3.3. The Vegetation Removal Experiment

[38] The vegetation removal experiment in 2002 was designed to examine vegetation community effects on CH_3Br exchange in peatlands more specifically. In contrast to the large static chamber measurements made at Sallie's Fen from 1998 to 2000, all of the vegetation removal collars, regardless of treatment level, consumed CH_3Br (Table 1). These results most likely reflect differences in the location and time of sampling. Considering the wide variability in the magnitude of net CH_3Br exchange measured within each site, it is probable that the vegetation removal experiment was simply in a low production, high consumption area. Collars for this experiment were located in a portion of the fen with a high sedge and a very low woody shrub concentration which was more similar to the plant community at Angie's Bog than the large collars most frequently sampled in other years.

[39] It is also possible that the dynamic chamber affected CH_3Br exchange conditions in the vegetation removal collars. The increased turbulence associated with the dynamic flow could have influenced the magnitude and direction of gas flux during sampling. However, the measurements of net CH_4 and CO_2 exchange are reasonably consistent with the treatment level and peat moisture conditions at the time of sampling (Table 1) suggesting that physical parameters affecting flux were not significantly altered by the dynamic chamber. Headspace CH_3Br concentrations in the dynamic chamber were also approximately 2 to 4 times the ambient and therefore could have influenced the magnitude of net flux. In large static chamber measurements at this site, significant reduction in net CH_3Br flux rates have been observed with headspace

Table 3. A Comparison of the Linear Regression Relationships Between the Major Environmental Variables and Net CH_3Br Flux in the Vegetation Removal Experiment at Sallie's Fen[a]

	Regression Statistics	Collar Treatment			
		C	V	S	N
Peat temperature, °C	Slope	0.53	−0.21	−0.063	−1.57
	R^2	0.10	0.02	0.0005	0.64
	p	0.33	0.64	0.93	0.005
Surface temperature, °C	Slope	0.56	0.17	1.54	−2.18
	R^2	0.21	0.06	0.22	0.86
	p	0.14	0.43	0.05	0.0001
Air temperature, °C	Slope	0.74	0.53	0.24	−0.22
	R^2	0.33	0.34	0.02	0.01
	p	0.05	0.03	0.59	0.76
Water Level	Slope	0.15	0.13	−0.079	0.56
	R^2	0.10	0.11	0.007	0.55
	p	0.31	0.28	0.74	0.01

[a]Linear regressions were calculated with y as net CH_3Br flux and x as temperature or water level. The *p* values represent the probability that the slope is equal to 0.

concentration increases as small as 5 pptv (unpublished data). The corrected net fluxes were consistent with measurements made during the previous seasonal studies at the same time of year, however (Figure 2). Bearing in mind that the vegetation removal experiment may not represent the balance of production and consumption processes at other collars in the Fen, the measurements made with this experiment still offer insight into factors influencing CH_3Br consumption in peatlands.

[40] Vegetation removal did have an effect on CH_3Br uptake (ANOVA, $p = 0.03$). Tukey's multiple comparison tests showed a significant difference between mean net CH_3Br fluxes for the *Carex* dominated (C) and *Sphagnum* only (S) collars ($p < 0.05$) (Table 1). Increased consumption observed with the presence of *Carex* spp. in the C collars could reflect actual consumption by the plants. *Jeffers et al.* [1998] found that a variety of plant species are capable of enzymatic CH_3Br consumption when exposed to elevated levels of the gas (100 ppmv to 500 pptv). In a greenhouse study of *Brassica* spp., *Gan et al.* [1998] estimated that plants and soil consumed 23–35% of the CH_3Br produced by the plants. Specific consumption rates varied between species suggesting that the vegetation did influence uptake. In the Sallie's Fen vegetation removal experiment, there was no correlation between vegetation cover, specifically *Carex rostratum* leaf area, and net CH_3Br uptake as might be expected with direct plant consumption. Considering little is known about the actual mechanism or location of potential plant CH_3Br consumption, this is not conclusive proof for or against *Carex* spp. uptake of the gas.

[41] It is also very possible that the presence of *Carex* spp. in the C collars simply enhanced conditions for aerobic microbial consumption in the peat. The correlations between surface temperature, water level and net CH_3Br flux in the N collars (Table 3) are consistent with studies of aerobic microbial CH_3Br consumption in upland soils [*Hines et al.*, 1998]. If this microbe is also present in the vegetated collars, it is likely that the enhanced aeration provided by the root systems of vascular plants in the aerobic zone would foster increased CH_3Br uptake.

[42] The presence of the vascular plants *Carex rostratum* and *Vaccinium oxycoccus* in the C and V collars coincides with significant positive correlations between air temperature and net CH_3Br flux (Table 3). These relationships are similar to those observed during the seasonal studies at Sallie's Fen (Table 2) and suggest that CH_3Br production is still a significant contributor to surface atmosphere exchange of this gas even under conditions of net uptake. Unlike the seasonal studies, net CH_3Br flux in the C and V collars does not exhibit a significant correlation with peat temperature implying that production was primarily associated with the aboveground portions of sedge and cranberry plants.

[43] A positive correlation between surface temperature and net CH_3Br flux in S collars implies that an additional surface production mechanism may exist (Table 3). Methyl halide production in *Sphagnum* spp. and other bryophytes has not been identified to date. Considering a similar enzymatic pathway for methyl halide production has been isolated in vascular plants, wood-rotting fungi, and marine algae; [*Wuosmaa and Hager*, 1990; *Saini et al.*, 1995; *Saxena et al.*, 1998], this potential source does merit further study.

[44] Fungi in the peat represent another possible source of CH_3Br in the S collars. In support of this possibility, the only measurement of net CH_3Br emission in the vegetation removal experiment occurred in collar S2 in which mushrooms did appear at the end of the summer. Whether the fungus was responsible for the observed emissions or even if it would have been present in the undisturbed collar is uncertain. It is possible that the decomposing plant material left after clipping the vascular plants provided a substrate for fungal growth that would not have been present in the C collars. It should be noted that mushrooms have been observed growing in undisturbed portions of the fen and fungi cultured from the Fen did emit CH_3Br in the laboratory (R. K. Varner, unpublished data, 2003).

3.4. Consumption and Production Estimates

[45] Calculations of gross production and consumption rates for the *Carex* dominated collars C1 and C3 in the vegetation removal experiment indicate that consumption was greater than production at these locations and corroborate the net negative flux measurements made with the small chamber (Table 4). The estimated production and consumption rates are also within the lower end of the ranges calculated for an upland forest ecosystem in New Hampshire [*Varner et al.*, 2003]. The larger $k_{uptakes}$ used for the College Woods calculations are modeled from laboratory incubations of upland soils and are probably not comparable to peatland conditions. Significant assumptions, such as the consistency of k_{uptake} and equilibrium headspace concentrations between static and dynamic flux measurements, were made while calculating k_{uptake} at Sallie's Fen for these two days. However, the Sallie's Fen rate constants are comparable in magnitude to those calculated by *Serca et al.* [1998] with peat bog microcosms exposed to elevated levels of CH_3Br (10 ppbv). This does suggest that CH_3Br consumption rates in peatlands are lower compared to upland ecosystems but the close balance between produc-

Table 4. Estimates of Gross Production and Consumption Based on the Consumption Rate Constant, k_{uptake}, Calculated From Dynamic and Static Flux Measurements Made on the Same Collar and Day[a]

	PAR, μmol/m²/s	Measured Net Flux, nmol/m²/d	Calculated k_{uptake}, min^{-1}	Calculated Production, nmol/m²/d	Calculated Consumption, nmol/m²/d
Sallie's Fen, NH					
Carex collar C1					
(1 August 2002)					
Dynamic flux	1618	−6 ± 5	0.074	5	−12
Static flux	1390	−16 ± 3	0.074	7	−12
Carex collar C3					
(2 August 2002)					
Dynamic flux	1712	−14 ± 5	0.094	8	−14
Static flux	450	−8 ± 3	0.094	14	−18
NCAR Peat Microcosms [*Serca et al.*, 1998]			0.025 to 0.16		
College Woods, NH [*Varner et al.*, 2003]		−40 to 34	0.2 to 1.1	1 to 202	−0.4 to −168

[a]Measured net fluxes and calculated production estimates have been corrected for blank chamber CH_3Br emissions. Calculated consumption estimates are based on ambient CH_3Br concentrations and should reflect initial conditions within the chamber without the influence of blank chamber CH_3Br emissions.

tion and consumption may allow these wetlands to act as either a net CH_3Br source or sink.

4. Conclusions

[46] The results of these seasonal studies and the vegetation removal experiment indicate that CH_3Br exchange in peatland environments is highly variable. Net flux can vary from emission to uptake both between different peatlands and from one site to another within a single peatland. CH_3Br exchange in these environments is most likely dependent on vegetation and microbial community composition and environmental variables like peat moisture appear to affect rates of production within these communities differentially. Wetland environments do exhibit high variability in trace gas fluxes spatially. *Redeker et al.* [2002] found that at least three replicate measurements were necessary in homogenous rice fields to determine mean fluxes within 20% for CH_3Br and CH_3I. In a uniform tundra peatland, *Whalen and Reeburgh* [1988] determined that coefficients of variation between CH_4 field measurements could also vary 50 to 100%. Considering the diversity of biological communities and peat conditions globally, estimates of global CH_3Br flux from this source are highly uncertain. Sampling for only one season and in one location can potentially over or underestimate a source.

[47] Peatlands are dynamic ecosystems with vast reservoirs of stored carbon. Considering that the balance between CH_3Br production and consumption in these environments is highly variable, they may respond to future climate change by becoming more significant global net sinks or sources of this gas. In order to better estimate net CH_3Br exchange from peatlands globally and predict the effect of climate change on flux from these ecosystems, a greater diversity of peatlands must be studied. More detailed studies on the actual CH_3Br production and consumption processes specific to peatlands and their controlling factors in natural settings are also necessary to better characterize variability in these ecosystems as a whole.

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P. M. Crill, Department of Geology and Geochemistry, Stockholm University, SE-106 91 Stockholm, Sweden.

C. H. Mosedale, R. K. Varner, and M. L. White, Climate Change Research Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Morse Hall, Durham, NH 03824, USA. (marguerite.white@unh.edu)