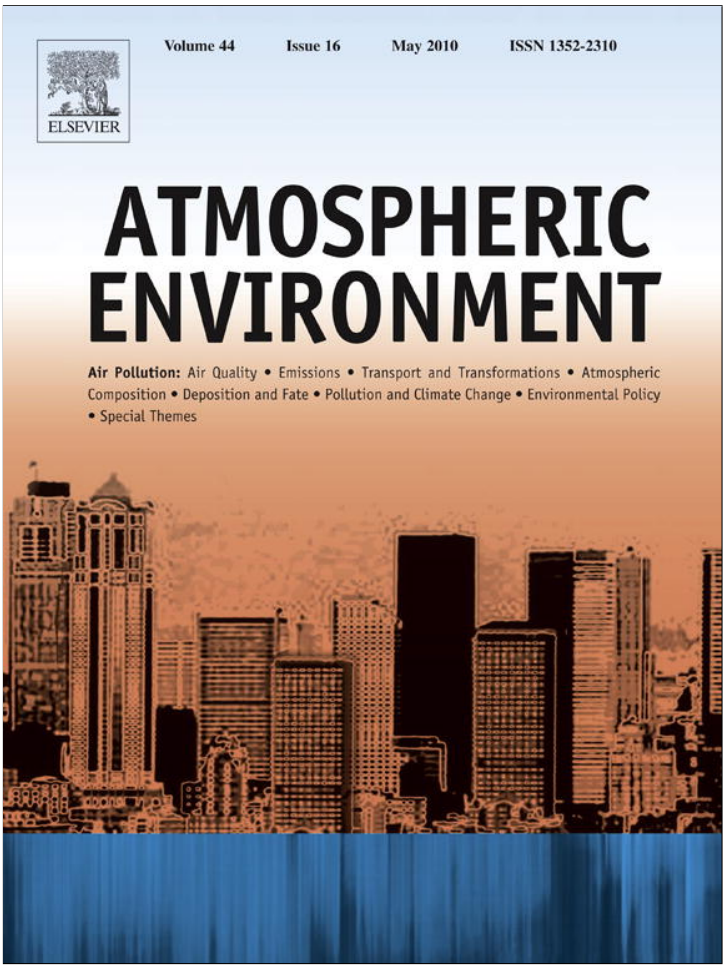

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Gross fluxes of methyl chloride and methyl bromide in a California oak-savanna woodland

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ABSTRACT

Temperate woodland ecosystems are believed to be both a source and sink for atmospheric methyl bromide and methyl chloride. To separate the gross production and consumption fluxes in this ecosystem, we applied a stable isotope tracer technique in field and laboratory-based experiments. Flux measurements were conducted in a California oak-savanna woodland ecosystem at several intervals throughout the day during the wet and dry seasons to observe the diurnal and seasonal variability of fluxes. While gross production was small and variable, gross consumption showed a clear difference between seasons, with much larger rates during the wet season and negligible rates during the dry season. Laboratory incubations confirmed that fluxes were strongly affected by soil moisture. Consumption rates of methyl bromide, however, are less than half of the previous estimates of temperate woodland soil uptake rates during the growing season. Nevertheless, woodlands cover a significant portion of the world's land surface area and may still be an important component of the soil sink for these methyl halides.

1. Introduction

A persistent problem in our understanding of the atmospheric budget of methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) is that their estimated sources do not fully account for their estimated sinks (Clerbaux and Cunnold, 2007; Montzka and Fraser, 2003). Resolving this uncertainty is important in order to predict the future status of stratospheric ozone because these compounds will become the major sources of stratospheric halogens as the restricted anthropogenic halocarbons targeted by the Montreal Protocol (and its amendments) decline.

Recent progress has been made in significantly reducing the CH_3Cl budget gap, with large emissions discovered from tropical plants and rainforests (Gebhardt et al., 2008; Saito et al., 2008; Yokouchi et al., 2007). In addition, the abiotic degradation of plant matter can also release CH_3Cl (Hamilton et al., 2003) and may be a dominant mechanism for emission from terrestrial ecosystems (Keppler et al., 2005). Additional natural terrestrial sources have also been found for CH_3Br, including mangroves (Manley et al., 2007), ectomycorrhizal fungi (Redeker et al., 2004), and abiotic decomposition of organic matter or plant components (Hamilton et al., 2003; Keppler et al., 2000; Wishkerman et al., 2008). However, a large budget imbalance remains for CH_3Br, with about 30% of the estimated sources still unidentified. In addition, field measurements have not confirmed the magnitude of most of these terrestrial sources, exacerbating the uncertainties.

Oxidation by soil bacteria is believed to be a major sink mechanism for CH_3Br (Shorter et al., 1995) and CH_3Cl (Clerbaux and Cunnold, 2007). Four terrestrial biomes – temperate forests, woodlands, shrublands and grasslands – are estimated to account for over 70% of the CH_3Br soil sink, with average growing season uptake rates of 47 nmol m^{-2} d^{-1} (Shorter et al., 1995). Each of these biomes are a grouping of diverse ecosystems that share some overarching structural similarity but have very different climates, soil types, biodiversity and hydrology. Subsequent field studies in shrublands, forests and woodlands have found much smaller net CH_3Br uptake rates and/or net emissions, suggesting that at some sites, the presence of CH_3Br sources may obscure or overwhelm the sink activity (Drewer et al., 2008; Rhew et al., 2001; Varner et al., 2003). Such studies highlight the necessity to separately measure gross production and gross consumption rates in terrestrial ecosystems.

Gross production and consumption rates have been measured in temperate annual grasslands and shortgrass steppe using a stable isotope tracer technique (Rhew and Abel, 2007; Teh et al., 2008),

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and these studies show that these soils have much smaller gross CH_3Br uptake rates during the growing season than expected. Hence, part of the imbalance in the CH_3Br budget may be attributed to a smaller soil sink than previously believed rather than entirely being a result of "missing" sources. Here we apply an isotope tracer technique to determine gross production and consumption of CH_3Br and CH_3Cl in an oak-savanna woodland in the western United States. Very few methyl halide studies have been conducted in woodlands (Drewer et al., 2008), although they occupy a large proportion of the global terrestrial surface area and figure significantly in soil sink estimates.

2. Methods

2.1. Site description

Three field studies were conducted between February 2006 and January 2009 at Tonzi Ranch (38.43°N, 120.97°W), an oak-savanna woodland in the foothills of the Sierra Nevada mountain range in California. The climate in the region of the site is Mediterranean, with an annual mean air temperature of 16.5° and mean annual precipitation of ~560 mm. Rainfall occurs primarily between October and May, with wintertime air temperatures averaging 8–15 °C. Summers are dry, with air temperatures averaging 20–26 °C (Ma et al., 2007).

The tree overstory is predominantly deciduous blue oak (*Quercus douglasii*) and covers roughly 40% of the landscape within a kilometer of sampling sites (Kim et al., 2006). The site is classified as woodland under the UNESCO biome classification scheme, with open stands of trees taller than 5 m covering at least 40% of the land surface (UNESCO, 1973). The grass understory is a mixture of cool-season C3 annual species, including *Brachypodium distachyon* L., *Hypochaeris glabra* L., *Trifolium dubium* Sibth., *Trifolium hirtum* All., *Dichelostemma volubile* A., and *Erodium botrys* Cav. (Ma et al., 2007). The soils are Auburn very rocky silt loam (Lithic haploxerepts) with a depth of 0.75 m over fractured rock. For this study, field sites were chosen adjacent to a 23 m tower measuring CO_2 and water vapor fluxes by eddy covariance and meteorological variables (Ma et al., 2007). In conjunction with these field outings, soil cores were collected for a series of laboratory soil incubation studies.

2.2. Field sampling

Flux measurements were made using two-component, mirror-polished aluminum, static flux chambers (Livingston and Hutchinson, 1995), with a maximum enclosed volume of 188 L and a surface area footprint of 0.264 m^2. Chamber bases were seated 2–5 cm into the soil from 1 h to three days before sampling. A lid was placed into a water-filled channel on the rim of the base to initiate the enclosure. Chamber control experiments over an aluminum sheet with Viton gaskets showed no significant reactivity or emission. Additional details regarding the chamber design are described in Rhew et al. (2007). Soil temperatures at 5 cm depth were measured with thermocouples, and volumetric water content (%VWC, 0–5 cm) was measured at the second and third outings with a ThetaProbe ML2x (Dynamax Inc., Houston, TX) applying the mineral soil calibration, although the dry soils in mid-summer were too compact to allow for penetration of probes beyond 4 cm. For the first outing, VWC was calculated from the water content of 3 soil cores collected 3 days prior to the experiment. Soil VWC was also measured with segmented, time-domain reflectometer (TDR) probes (MoisturePoint, Model 917, Environmental Sensors Equipment Corporation) at 12 sites around Tonzi Ranch on a roughly biweekly basis between 2006 and 2008 (Miller et al., 2007).

Flux measurements were conducted in 3 campaigns over a 3 year period, with samples collected during both wet and dry seasons (Table 1). The first field campaign was conducted on February 26, 2006 during the wet season. Flux measurements were collected at three sites located ~5 m apart, with two of the three sites underneath an oak tree canopy, underlain by grass and forb cover. Two consecutive flux measurements were performed at each site, both taken within the same chamber footprint: a net flux measurement ("unspiked") to quantify background exchange rates and an isotope tracer measurement ("spiked"), where ^{13}C-tracers were applied to the chamber headspace to quantify gross production and consumption fluxes (Rhew and Abel, 2007; Rhew et al., 2003; Teh et al., 2008). The net flux measurements were conducted over a 30 min enclosure period, with samples drawn at 1, 15, and 30 min. Isotope tracer measurements were conducted over 32 min enclosure period, with air samples collected at 2, 12, 22 and 32 min, to ensure sufficient mixing of the spiking gas within the chamber. Between measurements, the chamber was ventilated for 10 min to restore chamber air to background atmospheric concentrations.

The second field campaign was conducted during the height of the dry season on July 1, 2008. Nine flux measurements were performed at 3 sites, located ~5 m apart, ranging from shaded to exposed. All grasses were dry and senescent. All chamber experiments were spiked with a laboratory gas mixture (N_2 with 464 ppb $^{13}CH_3Br$, 4.62 ppm $^{13}CH_3Cl$, and 4.61 ppm CFC-113 (CCl_2FCClF_2)), resulting in initial chamber headspace concentrations of roughly 100 ppt $^{13}CH_3Br$, 1000 ppt $^{13}CH_3Cl$, and 1000 ppt CFC-113. Enclosures were 22 min long with samples taken at 2, 12, and 22 min. Each of the three sites was measured three times, separated by 2 h intervals to assess diurnal variability in the fluxes. The third and final campaign was conducted during the wet season on January 30, 2009, when short grasses and forbs were growing. Nine flux measurements were again made at 3 adjacent sites, ~10 m apart, ranging from shaded to fully exposed. Chamber sampling methods were identical to the second outing, with sampling of each chamber three times at 2 h intervals.

2.3. Air analyses

Air canister samples were measured twice by gas chromatography/mass spectrometry (Agilent 6890N/5973 GC/MS) in selective ion monitoring mode and compared against a natural air working standard (561 ppt CH_3Cl and 9.4 ppt CH_3Br on the SIO-2005 scale). Details of the cryotrapping and sample inlet system, chromatographic separation, mass spectrometer settings, gas standards, and calibration methods are described elsewhere (Rhew et al., 2007;

Table 1
Soil and weather conditions during the 3 outings at Tonzi Ranch, CA.

Date	Times (PST)	No. of expts.	Air temp (°C)	Soil temp 5 cm (°C)	Soil H_2O (% VWC)	Weather conditions during experiments
February 26, 2006	11:30–15:50	6	11–19°	12°	42 ± 5[a]	Overcast, rain after 1st expt.
July 1, 2008	10:40–16:20	9	29–35°	31°	1 ± 1	Sunny, clear, hot
January 30, 2009	11:00–16:40	9	13–17°	12°	30 ± 7	Sunny, clear, cool

PST = Pacific Standard Time = GMT − 8 h.
[a] VWC calculated from soil cores.

Rhew and Abel, 2007). For this study, instrumental precision (1σ) based on daily standards after applying drift corrections were 6% for CH_3Cl and 8% for CH_3Br. Using these precisions and typical chamber conditions, we estimate the minimum detectable flux to be 70 nmol m^{-2} d^{-1} for CH_3Cl and 2 nmol m^{-2} d^{-1} for CH_3Br.

2.4. Laboratory incubations

For each outing, three cylindrical soil cores (17.81 cm^2 surface area) were extracted using a soil corer (AMS Inc., American Falls, ID) and stored in stainless steel or aluminum sleeves with a fitted metal base. Cores were either short (5.08 cm deep, 90.5 ml volume) or long (15.24 cm deep, 271.5 ml volume). For the first outing, cores (5 cm) were collected 3 days prior from adjacent sites. Cores for the second (15 cm) and third (5 cm) outings were collected from the center of each chamber site after field measurements were completed.

In the laboratory, each soil core was placed inside a glass Mason jar (1.9 L) which was then partially submerged in a temperature controlled water/ethylene glycol bath (Model 1180S, VWR International, West Chester, PA). Incubations were initiated by sealing the jar with a stainless steel lid with compression fittings and a Viton gasket. An aliquot of 70 ppb $^{13}CH_3Cl$, 7 ppb $^{13}CH_3Br$, and 65 ppb F-113 in N_2 gas was injected to the headspace immediately after closure to bring initial headspace concentrations up to roughly 100 ppt $^{13}CH_3Br$, 1000 ppt $^{13}CH_3Cl$, and 1000 ppt CFC-113. Soil core incubation experiments were 43–90 min long, with ~25 ml air samples drawn at 3, 23, and 43 min (2, 30, 60, and occasionally 90 min for the cores from the first outing). These air samples were drawn directly into the sample trapping/inlet system of the GC/MS.

Two sets of laboratory-based incubations were conducted on the soil cores. The first set of incubations ("simulated field conditions") included all soil cores collected on each of the three outings. These intact cores were incubated while inside their metal sheaths and bases under field moisture and temperature conditions. Thus, incubations were conducted at 16 °C for the winter outing cores (i.e., first and third field campaigns) and at 30 °C for the summer outing cores (i.e., second field campaign). Each soil core was incubated twice, except for the first outing cores which were each incubated once. The objective of this study was to compare measured fluxes from field and laboratory studies and to see if they showed the same seasonal differences.

The second set of incubations ("soil moisture manipulations") involved the three soil cores collected from the first outing incubated at a constant 16 °C; soils were removed from their sheaths and subjected to a range of gravimetric water content manipulations, ranging from air dry to field moisture conditions. Soils were incubated first at field moisture levels (25 ± 1% GWC). Then they were air-dried for over 6 weeks, with a small soil subsample oven-dried to determine the gravimetric water content (5.5% average). Over the course of 10 days, the soil water content was systematically increased in the soils by adding deionized water, bringing water contents up to 12%, 16% and 25% GWC on average. Incubations were performed at each soil moisture level to observe its effect on the gross production and consumption rates. After the incubations, the soil cores were oven-dried at 105 °C overnight to determine the final water content. All GWC values are reported as percent water mass relative to the original wet soil weight (% wet weight).

2.5. Flux calculations

Net fluxes were calculated by applying a linear least squares fit to the measured dry air mole fractions versus time of sampling, and multiplying by the number of moles of air in the chamber or jar. Positive slopes represented net emission. Negative slopes represented net uptake; these were converted to first order uptake rates k (min^{-1}) by plotting the natural log of the concentration versus time and multiplying by initial concentrations of 535.7 ppt CH_3Cl and 10.4 ppt CH_3Br, representative of their respective mean northern Hemisphere baseline mole fractions from 1998 to 2001 (Simmonds et al., 2004). Because these are first order rates and CH_3Br concentrations are declining in the atmosphere (Montzka et al., 2003; Yokouchi et al., 2002), new uptake rates can be calculated for different time periods by multiplying fluxes by the ratio of new to old concentrations.

Gross fluxes were calculated using a stable isotope tracer technique, which has been described in detail elsewhere (Rhew and Abel, 2007; Rhew et al., 2003). Briefly, the $^{12}CH_3X$ (X = Cl or Br) and $^{13}CH_3X$ concentrations were plotted against time and subjected to a recursive procedure to determine the best fit of concentration changes to a gross production and gross consumption box model. The natural abundance of carbon-13 is only ~1% that of carbon-12; thus the production rate of $^{13}CH_3X$ is negligible except in chambers with large net emissions. Thus, the decreasing $^{13}CH_3X$ concentrations over the enclosure time represents the biological/chemical loss of these compounds as well as the physical loss (advective and diffusive) of the compounds from the chamber; the latter term is quantified using the inert tracer (F-113) concentrations. Methyl halide concentrations and gross fluxes were calculated using the mass spectrometer signals of all four major isotopologues of CH_3Cl ($^{12}CH_3{}^{35}Cl$, $^{13}CH_3{}^{35}Cl$, $^{12}CH_3{}^{37}Cl$, and $^{13}CH_3{}^{37}Cl$) and CH_3Br ($^{12}CH_3{}^{79}Br$, $^{13}CH_3{}^{79}Br$, $^{12}CH_3{}^{81}Br$, and $^{13}CH_3{}^{81}Br$). This yields two separate model results for gross production and gross consumption for each methyl halide. These values were averaged and the standard deviation is reported as the individual flux error. Unless otherwise specified, fluxes are reported in nanomoles per square meter per day (nmol m^{-2} d^{-1}), although enclosure times were typically less than an hour. For clarity, this study reports consumption (gross or net) rates as negative values, while production (gross or net) rates are reported as positive values.

3. Results

3.1. Field results

In the first field outing (February 2006), the 3 pairs of consecutively run unspiked and spiked chambers showed similar net flux values, differing by only 47 ± 96 nmol m^{-2} d^{-1} for CH_3Cl and −2.0 ± 2.1 nmol m^{-2} d^{-1} for CH_3Br (unspiked minus spiked). These differences are similar to the flux detection limits (i.e., 70 nmol m^{-2} d^{-1} for CH_3Cl and 2 nmol m^{-2} d^{-1} for CH_3Br) and indicate that adding the spiking gas does not significantly change the net flux behavior for the methyl halides (Rhew and Abel, 2007; Teh et al., 2008).

Overall the net fluxes were strongly negative, averaging −440 ± 116 nmol m^{-2} d^{-1} for CH_3Cl and −10.8 ± 1.8 nmol m^{-2} d^{-1} for CH_3Br ($n = 6$). As the spiked chamber experiments demonstrate, these net fluxes are the combination of large gross uptake rates (−617 ± 67 for CH_3Cl, −16.7 ± 3.3 for CH_3Br) dominating the small and variable gross production rates (102 ± 75 for CH_3Cl, 3.5 ± 1.2 for CH_3Br).

In the second outing (summer, July 2008), net fluxes were small and variable, and not dominated by either gross production or consumption (Fig. 1a and c). Net CH_3Cl fluxes averaged 21 ± 133 nmol m^{-2} d^{-1}, while gross production averaged 91 ± 86 and gross consumption averaged −45 ± 65 nmol m^{-2} d^{-1}. Net CH_3Br fluxes averaged −0.8 ± 5.0 nmol m^{-2} d^{-1}, while gross production averaged 1.3 ± 1.7 and gross consumption averaged −0.9 ± 0.9 nmol m^{-2} d^{-1}.

In the third outing (winter, January 2009), net fluxes were strongly negative, dominated by large gross uptake rates

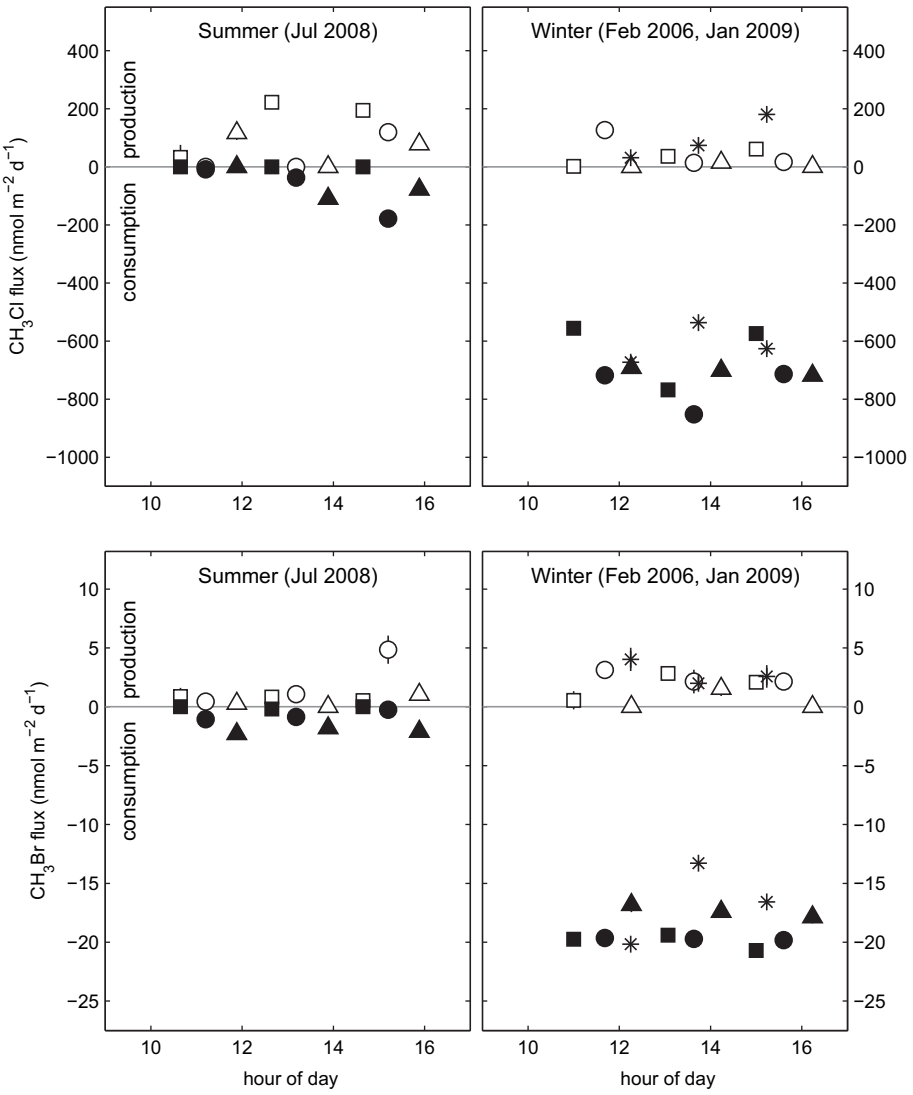

Fig. 1. Field measurements of gross fluxes for CH_3Cl (top panels) and CH_3Br (bottom panels) versus time of day. Open (white) symbols represent gross production rates and filled (black) symbols represent gross consumption rates. Different symbols represent different chamber sites; asterisks (*) represent the February 2006 measurements. Note that each flux chamber yields both a production and a consumption flux. Mid-summer (left panels) and mid-winter (right panels) measurements show little difference in gross production but a dramatic difference in gross consumption rates.

(Fig. 1b and d). Net CH_3Cl fluxes averaged -675 ± 101 nmol m^{-2} d^{-1}, while gross production averaged 33 ± 45 and gross consumption averaged -702 ± 91 nmol m^{-2} d^{-1}. Net CH_3Br fluxes averaged -18.0 ± 3.0, while gross production averaged 1.5 ± 1.2 and gross consumption averaged -19.2 ± 1.2 nmol m^{-2} d^{-1}.

Collectively, these measurements show no seasonality in gross production but a very strong seasonality in gross uptake rates. During the wet winter months (February 2006 and January 2009), gross uptake rates averaged -681 ± 91 nmol m^{-2} d^{-1} for CH_3Cl and -18.5 ± 2.0 nmol m^{-2} d^{-1} for CH_3Br. Averaged summer uptake rates (July 2008, reported above) were much smaller, only 5–7% of the winter uptake values. Measurements do not show a clear diurnal trend, either for production or consumption, although the temporal resolution and precision of measurements may not be fine enough to discern a trend (Fig. 1).

Because the climate is Mediterranean, the summer measurements corresponded with high air temperatures (>30 °C) and very low soil moistures (<2% VWC) while the wintertime measurements corresponded with cooler temperatures (<20 °C) and high soil moistures (>20% VWC). While gross production showed no clear relationship to temperature or soil moisture, gross consumption rates showed a clear difference between seasons corresponding with soil moisture (Fig. 2). Consumption rates appear to dramatically increase between 0% and 22% volumetric water content in the 0–5 cm layer, although measurements at intermediate moisture levels were lacking. At soil moistures above 30%, gross consumption rates appear to level off or even decrease. The shape of the curve fit is inferred from soil core incubations (see results below).

3.2. Laboratory soil core results

The first set of soil core incubations ("simulated field conditions") yielded gross fluxes that were reasonably well matched with the magnitudes and patterns in their associated field flux chamber measurements, demonstrating their utility in process-based studies. For the first outing, the combined average of the three chamber sites was compared to the average of the three soil core incubations. For the second and third outings, the average of the diurnal field flux measurements ($n = 3$) was compared to the

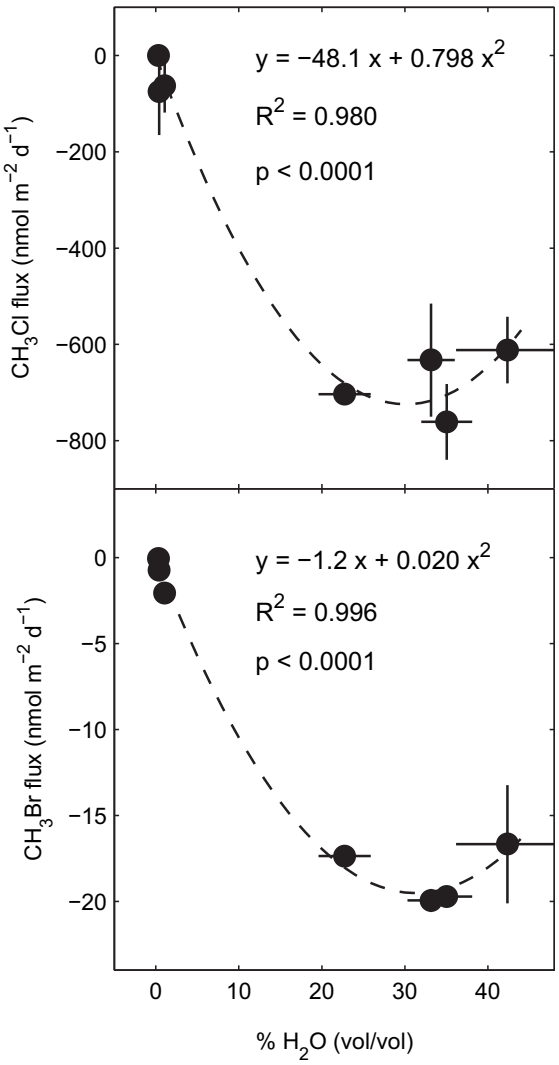

Fig. 2. Field measurements of gross consumption rates for CH_3Cl (top) and CH_3Br (bottom) versus volumetric soil moisture. Each point represents the average ± 1 s.d. of three chamber experiments. The averaged measurements were from the same chamber site measured three times, except for the wettest point, which averages the three separate chamber sites from the first outing.

core incubations ($n = 2$) for each of the chamber sites. The gross consumption rates were well-correlated between field and laboratory counterparts for CH_3Cl ($R^2 = 0.79$) and CH_3Br ($R^2 = 0.91$), with an overall linear fit close to 1 (Fig. 3). However, differences at individual sites were as large as 310 nmol m^{-2} d^{-1} for CH_3Cl and up to 6 nmol m^{-2} d^{-1} for CH_3Br.

Gross production rates show similar magnitudes between field and laboratory incubations and are moderately correlated for CH_3Br ($R^2 = 0.66$) but are not correlated for CH_3Cl (Fig. 3). This may be due to the fact that gross production rates are generally near the detection limit and/or have large relative variability within individual sites such that cores may selectively include or exclude localized sources.

The second set of soil core incubations ("soil moisture manipulations") were conducted without the core sheaths and therefore fluxes are reported in terms of nanomoles per gram of soil (dry weight) per day and compared to gravimetric soil moisture instead of VWC (Fig. 4). These soil moisture manipulations show that gross consumption rates and production rates of both CH_3Cl and CH_3Br are strongly influenced by soil moisture. At air-dried conditions (5.5% GWC), both production and consumption rates were negligible. At the middle moisture levels (12% and 16%), both production and consumption rates were the highest. At the field moisture and re-constituted moisture levels (25%), production and consumption rates were roughly half of the maximum values. It is notable that the fluxes were similar at the beginning of the experiment (field moisture) and at the end of the experiment (after soils were air-dried and stepwise brought back up to field moisture conditions). This provides evidence that the microbial activity was not adversely affected by the series of water manipulations over the 10-day period. This is not unexpected, given that soil microbes have necessarily adapted to large shifts in moisture associated with the summer drought and winter rains.

4. Discussion

The strong seasonality in gross consumption rates of CH_3Br and CH_3Cl of this oak-savanna woodland is similar to results reported from other California ecosystems, including semi-arid shrublands (Rhew et al., 2001) and annual grasslands (Rhew and Abel, 2007). All of these ecosystems experience a Mediterranean climate; thus, the consumption rates are high during the wet, winter growing season and very small during the dry, summer non-growing/senescent season. Here we consider whether temperature or water content changes are causing the marked difference between winter and summer consumption rates.

Because the consumption of CH_3Br and CH_3Cl in soils occurs through oxidation by soil bacteria (McAnulla et al., 2001; Shorter et al., 1995), the consumption rate is strongly affected by temperature, with a temperature optima for CH_3Br between 25 and 40 °C and much lower uptake rates between 5 and 15 °C (Hines et al.,

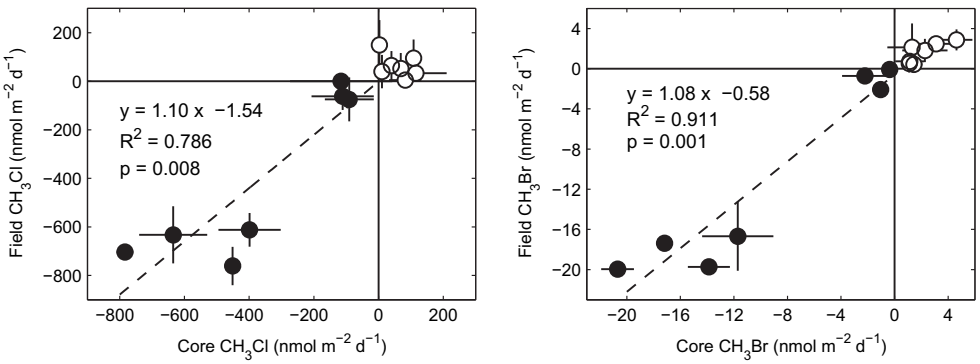

Fig. 3. Gross CH_3Cl (left) and CH_3Br (right) flux comparison between field chamber measurements versus "simulated field condition" soil core incubations for the corresponding sites and seasons. Open (white) symbols represent gross production rates and filled (black) symbols represent gross consumption rates. The dotted line and equations are for the gross consumption linear regressions only. Error bars represent ± 1 s.d. for the field ($n = 3$) and core ($n = 2$ or 3) measurements.

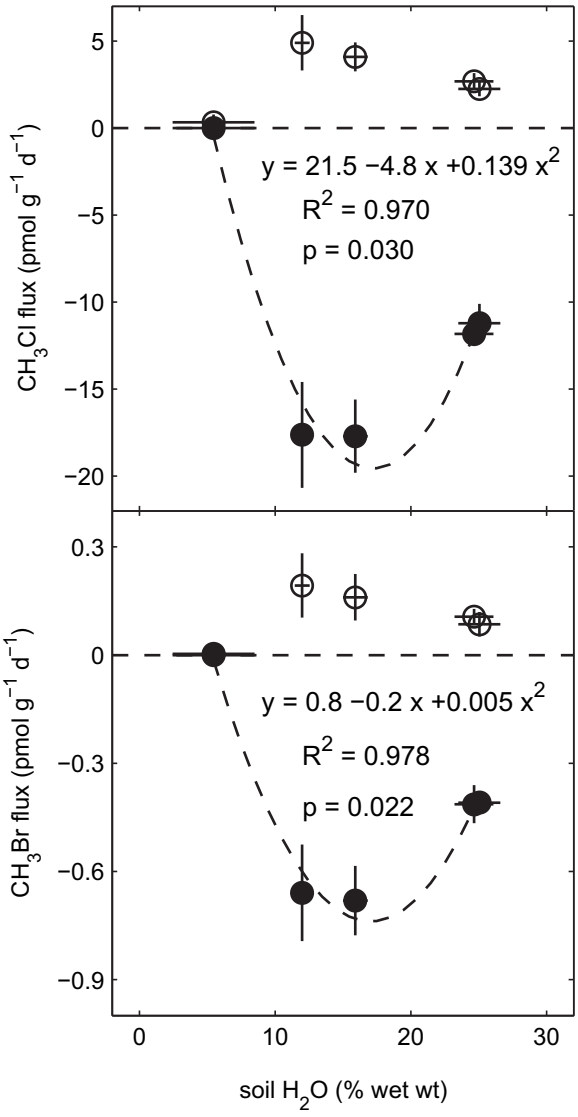

Fig. 4. Laboratory "soil moisture manipulation" results: incubations of unsheathed soil cores ($n = 3$ for each point) versus gravimetric water content. Gross production (open circles) and gross consumption (dark circles) are shown for CH_3Cl (top) and CH_3Br (bottom).

1998; Varner et al., 1999). In contrast, the consumption rates at Tonzi Ranch were actually much higher in winter (10–12 °C surface soils) than summer (~30 °C), when the uptake rates would be at a temperature optimum. This suggests that soil temperature is not the dominant factor in driving consumption rates. Instead, soil moisture is most likely the principal environmental factor controlling biological uptake rates at this site. This is illustrated in Fig. 2 which shows field uptake rates versus VWC, and Fig. 4, which shows laboratory core uptake rates versus GWC. Both show that uptake rates increase rapidly when soil moisture increases from summer drought conditions, but actually start declining at soil moistures that are typical of the wet season. Soil respiration studies at this site demonstrate that microbial activity rapidly responds to changes in soil moisture (Baldocchi et al., 2006; Xu et al., 2004).

A similar trend of methyl halide uptake with soil moisture was observed for Colorado shortgrass steppe soils, where field measurements and soil core incubations showed that gross methyl halide consumption rates rose steeply between 0.4 and 5% VWC and appeared to stabilize or decrease at 20% VWC or above (Teh et al., 2008). As soils become highly saturated, a sharp decrease in uptake rates has been found in Alaskan tundra and California grassland/riparian soils (Rhew and Abel, 2007; Teh et al., 2009). A parabolic trend of CH_3Br uptake versus soil moisture was also noted in agricultural and forest soils (Hines et al., 1998).

In contrast to consumption, gross production rates show no significant seasonal difference and are minor relative to gross uptake rates during the wet season. Hence, the net fluxes during the winter are strongly negative while net fluxes during the summer are small and variable. This is in contrast to measurements from a woodland in Scotland, where an 18 month time series of CH_3Br net flux measurements at four chamber sites showed no seasonal trends but rather an overall net emission, with sporadic high emissions during the winter months (Drewer et al., 2008). Although both studies involve woodlands, there are major differences between these particular woodland ecosystems, including their climate, plant species and soil conditions. The Tonzi Ranch sites had very low quantities of leaf litter from oak and annual grasses, whereas the Scottish sites contained a range of leaf litter types including coniferous needles, which showed significant CH_3Br emissions in separate incubations. Fungal activity during the decomposition of litter was suggested to be the source of CH_3Br from the woodland understory in Scotland.

Our wintertime average CH_3Br gross uptake rate (-18.5 ± 2.0 nmol m^{-2} d^{-1}) is less than half of the previous estimates for temperate woodland soil uptake for the growing season: -47 ± 26 nmol m^{-2} d^{-1} (Shorter et al., 1995) and 58 ± 46 nmol m^{-2} d^{-1} (Serça et al., 1998). The prior estimates, however, were actually temperate forest soil fluxes applied to woodlands. Woodland soils might be predicted to have lower uptake rates because they have lower soil organic carbon contents and less surface litter carbon than temperate forests (Schlesinger, 1997), factors which influence soil moisture and microbial activity.

To obtain accurate annual fluxes at our site, measurements are required at additional sites experiencing different microclimates and would need to be conducted year-round, especially after isolated summer rain storms (Baldocchi et al., 2006; Xu et al., 2004). However, the gross uptake rates at our site showed low variability at individual sites over the course of a day and between sites measured on the same day (Fig. 1). In addition, the soil moisture manipulations in the laboratory also showed consistent trends between different cores following increases in soil moisture (Fig. 4). We suggest that methyl halide oxidation rates at this site have less short-term (diurnal and weekly) variability than soil carbon dioxide efflux, which is a combination of heterotrophic microbial respiration and autotrophic root respiration.

If we assume that surface soil moisture regulates the gross uptake rates of CH_3Cl and CH_3Br at this site according to our derived function (Fig. 2), then we can use higher frequency and spatially distributed soil moisture measurements to estimate gross uptake rates throughout the year. We use soil moisture readings from three Tonzi Ranch sites that were taken approximately every other week for 3 years since 2006 (Miller et al., 2007). Applying the uptake rate function to the average soil moisture, we calculate a daily uptake rate and sum them up over the years 2006, 2007 and 2008. Using this method yields an overall average uptake rate of -152 ± 13 μmol m^{-2} yr^{-1} for CH_3Cl and -3.8 ± 0.3 μmol m^{-2} yr^{-1} for CH_3Br. These values are similar to those calculated using a simple two-season model where our mid-winter and mid-summer measurements are applied to a 240 day growing season and a 125 day non-growing season, respectively. This yields an overall uptake rate of -169 ± 23 μmol m^{-2} yr^{-1} for CH_3Cl and -4.6 ± 0.5 μmol m^{-2} yr^{-1} for CH_3Br.

Although often categorized as a single biome, woodlands globally (13.1×10^{12} m^2) actually encompass a wide range of ecosystems and climatic conditions, including xeromorphic forest/woodland,

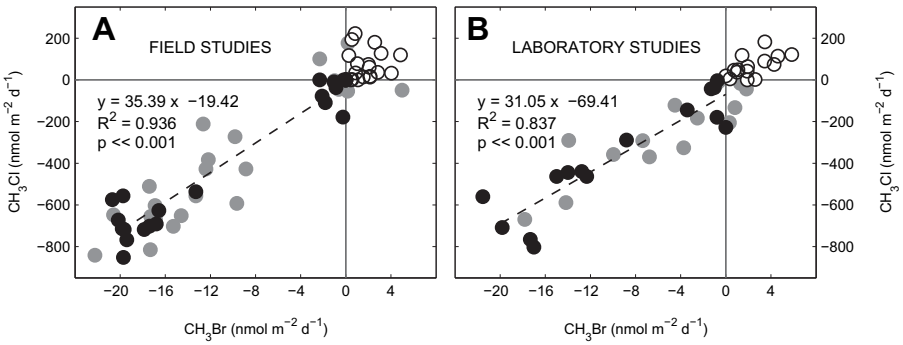

Fig. 5. Net (gray), gross production (white), and gross consumption (black) fluxes for CH_3Cl versus CH_3Br for (A) all field flux measurements and (B) all field simulated soil core incubations. Dotted line shows the linear fit to gross consumption fluxes only.

evergreen broadleaved sclerophyllous woodland, evergreen needle-leaved woodland, tropical/subtropical drought-deciduous woodland, and cold-deciduous woodland (Matthews, 1983). To understand the global fluxes from temperate woodlands would require more measurements from other woodland ecosystems. The observed differences between this California oak-savanna woodland (net CH_3Br sink) and a deciduous woodland in Scotland (net CH_3Br source) provide a case in point (Drewer et al., 2008).

However, these are the first measurements of gross uptake rates (versus net fluxes) from woodlands (versus forests or shrublands), and therefore it is a useful exercise to explore how revising the soil uptake rates for woodlands could alter the global CH_3Br soil sink estimate. In prior studies, the annual CH_3Br uptake rates for temperate woodland soils were estimated using a 240 day active season, yielding -11 ± 6 μmol m^{-2} yr^{-1} (Shorter et al., 1995) and -14 ± 11 μmol m^{-2} yr^{-1} (Serça et al., 1998), much larger than the uptake rates estimated for our site (up to -4.6 ± 0.5 μmol m^{-2} yr^{-1}). If woodlands accounted for 50% of the woodland/shrubland surface area (20% of the temperate forest/woodland/shrubland combined biome) in these studies, then their surface area would be 4.0×10^{12} m^2 (Shorter et al., 1995) or 5.7×10^{12} m^2 (Serça et al., 1998), yielding global uptake rates of 4.3–7.6 Gg yr^{-1}, respectively. Replacing the uptake rates with those from Tonzi Ranch would yield 1.7–2.5 Gg yr^{-1} instead. However, none of these studies provides a tenable means for extrapolation to the diversity of global woodlands, which cover a much larger surface area but likely consist of a patchwork of internal sources and sinks.

Soils are also believed to be a globally significant sink for CH_3Cl, consuming 256 Gg yr^{-1} (Clerbaux and Cunnold, 2007) to >1000 Gg yr^{-1} (Keppler et al., 2005), or 6% to >20% of the total tropospheric sink, respectively. Direct measurements of soil uptake rates of CH_3Cl show similar patterns to CH_3Br uptake rates, both in relationship to soil moisture and season (Rhew and Abel, 2007; Rhew et al., 2001, 2007; Teh et al., 2009; Teh et al., 2008). In Alaskan boreal forest soils, California annual grasslands, Colorado shortgrass steppe and Alaskan tundra, CH_3Cl and CH_3Br gross uptake rates are strongly correlated, with a molar ratio of ~40:1. We find a similar correlation at Tonzi Ranch, where gross CH_3Cl and CH_3Br uptake rates are strongly correlated in both field ($R^2 = 0.94$) and laboratory measurements ($R^2 = 0.84$) at a ratio of 31:1–35:1 (Fig. 5). Assuming that a similar correlation continues to be found in other terrestrial ecosystems, then it may be possible to estimate the CH_3Cl soil sink based on the more widely measured CH_3Br soil sink.

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