Consumption and Production of Methyl Halides from a Woodland Soil

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Abstract While synthetically created compounds such as chlorofluorocarbons are most well known for depleting the ozone layer, natural compounds also catalytically destroy ozone. Methyl halides, trace gases which include methyl bromide (CH_3Br) and methyl chloride (CH_3Cl), are important natural compounds that deplete stratospheric ozone. Methyl halides have natural sources such as oceans, certain plants and salt marshes, while anthropogenic sources exist such as biomass burning and pesticide applications. Soils are the major known sink of halomethanes, although sparse data exists on the relative importance of soil on an ecosystem scale. The current CH_3Br soil consumption model currently groups temperate forests, woodlands and shrublands together, comprising of half the global soil sink for the compound. I used flux chambers to measure halomethane fluxes at the woodland site. Consumption of CH_3Br and CH_3Cl was significantly higher during winter compared to summer. This discrepancy may be credited to moist and biologically active soils during winter. Overall, the woodland soils showed net consumption due to the high consumption level seen during the wet, winter season. Production was weak for both seasons, and consumption during summer was also negligible. Methyl bromide consumption did not fit the CH_3Br soil consumption model presented by Shorter (1995). The model's estimates were over 40 times higher than the CH_3Br summer consumption rate observed at the woodland, and over twice as strong as winter consumption fluxes. The CH_3Br consumption displayed followed the trend of past observed terrestrial ecosystems, which all have had lower consumption fluxes than expected.

Introduction

Stratospheric ozone absorbs practically all biologically harmful UV light while also regulating the temperature of the atmosphere (Rodriguez 1993). Man-made compounds such as chlorofluorocarbons (CFC) carry halogen molecules, which deplete these beneficial ozone compounds. While CFCs contribute about 60% of all halogenated compounds into the atmosphere, it is also important to explore compounds with naturally-derived sources in the atmosphere (Smythe-Wright *et al.* 2005). Methyl halides, namely methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), have both anthropogenic and natural sources, and understanding the natural sources and sinks are vital in calculating global budgets of these ozone-hazardous compounds. Methyl halides, or halomethanes, contribute about 25% of all halogenated compounds into the atmosphere, which is major enough to impact ozone depletion. The halogen molecules from a halomethane may separate from their methyl group, and the resulting free radicals catalytically destroy ozone molecules (Rhew *et al.* 2003).

Methyl halides break down ozone molecules by the freed halogens coupling with an oxygen atom from ozone (Stolarski1982). These halide molecules must reach the stratosphere to destroy ozone, which may not happen because some of the molecules break down before reaching the proper height in the atmosphere. If they arrive in the stratosphere, photolysis (when light decomposes a material) frees the halogen from the methyl halide, enabling the halogen to bind with ozone and break it down. The atmospheric lifetime helps dictate its destructive power. It is believed that the lifetime of methyl chloride and methyl bromide are approximately 0.6-0.9 years (McCauley *et al.* 1999). They have a short lifetime compared to synthetic compounds such as CFCs, but their relatively high concentrations mean these compounds play a fairly significant role in ozone depletion. Atmospheric concentrations of methyl chloride and methyl bromide are 11 and 550 ppt, respectively (Rhew *et al.* 2003). While methyl bromide concentrations are far lower than methyl chloride, a methyl bromide compound depletes more ozone than a methyl chloride molecule.

Methyl bromide catalytically destroys 50-60 times more ozone than its counterpart, methyl chloride (Butler 2002). Understanding methyl bromide is especially important because two-thirds of all bromine in the atmosphere is derived from this compound, while methyl chloride represents only a small net portion of chlorine in the atmosphere (Huang *et al.* 2000). The

primary human source of methyl bromide is pesticide use. The EPA states that it has been used as a fumigant for products such as tomatoes, strawberries, grass and pork products in the past. Due to the hazard it poses to stratospheric ozone, methyl bromide usage has been diminished significantly in the past few years. The compound is technically only allowed for critical use on certain products such as strawberries or under special circumstances because no feasible economic alternative is available (EPA 2009). The reduction in methyl bromide pesticide usage has led to lower concentrations of methyl bromide in the atmosphere, corresponding with the gradual phase out of the compound (Yokouchi *et al.* 2002). Methyl bromide is a very important fumigant with no cheap and effective alternative discovered; this has led to the compound's reduced yet continued use throughout the world despite bans (Baird and Cann 2008). In contrast, humans produce methyl chloride for different reasons.

Methyl chloride may not be as destructive as methyl bromide, but the methyl chloride budget is much larger in the atmosphere relative to methyl bromide. According to the EPA, methyl chloride became a threat to the atmosphere after humans emitted the compound far above ambient concentration. Its use as a refrigerant and a gasoline additive contributed to the rise in methyl chloride levels, although these two sources are on the decline. It is currently still used in the process of making silicone rubbers and as a solvent in some petroleum and rubber manufacturing (EPA 2007). Although humans contribute halomethanes into the atmosphere through various means, halomethanes share many common natural sources and sinks.

The major anthropogenic sources of methyl halides are biomass burning, fuel burning, industrial production and soil fumigants (McCauley *et al.* 1999). Natural sources play a huge role too, with oceans (Shorter *et al.* 1995), salt marshes (Rhew *et al.* 2002), tropical areas and coastal regions (Yokouchi *et al.* 2000) serving as some of the more prominent and known natural producers. Water rich ecosystems such as salt marshes tend to emit large amounts of methyl halides with 85% of all emissions between 30˚S and 30˚N latitude, which is predominantly a tropical and subtropical region (Khalil and Rasmussen 1999). High halomethane producing ecosystems such as salt marshes have a limited influence globally due to their low global surface area (Rhew *et al.* 2002). Methyl chloride emissions have been shown to be related to methyl bromide emissions and vice versa, signaling that they are likely derived from similar sources

(Rhew *et al.* 2000). Methyl halide production is difficult to measure and estimate due to the high variability of vegetation and other environmental factors at every location.

Plants, fungi, and abiotic processes have all been shown to produce methyl halides. Plants produce the compounds through enzymes transferring a methyl group to a halide (Rhew *et al.* 2003). Much uncertainty exists on the causes of methyl halide plant production, although factors such as halide ion abundance and methyltransferase activity within the plant cells relate to production levels (Saito and Yokouchi 2006). Specific plants are much more significant emitters, while most other plants do not appear to have much activity. The idea of halomethane producing plants is a relatively new concept, and understanding how and why they function may lead to important conclusions for the field. High emitting plants are vital to study and while difficult to identify due to lack of research on the subject, it is important to discover which plants fall into this category (Rhew and Abel 2007). A couple of known high emitting plants are *Salicornia* species, *Batis maritima* (Rhew 2000), and *Vitex rotundifolia* (Yokouchi *et al.* 2007). Conversely, abiotic oxidation-reduction reactions within an organic medium have been shown in laboratories to produce halomethanes (Keppler *et al.* 2000). Certain fungi have high methylation efficiency, which has led many scientists to believe fungi are emitters (Harper 1985). Production is highly dependent on whether the plants are strong emitters, on fungal presence, and other environmental variables that differ in even similar types of ecosystems. While ecosystems emit halomethanes, they are also consuming the compounds concurrently (Rhew *et al.* 2003).

Soils and the ocean have been shown to be the primary mediums of methyl halide consumption (Shorter *et al.* 1995). Oceans have been observed to be a strong producer and consumer at times, and it varies greatly upon temporal and spatial scales (Smythe-Wright *et al.* 2005). While the status of ocean as a net source or sink is up for debate, soil is believed to be a reliable sink of methyl halides (Rhew *et al.* 2003; Shorter *et al.* 1995).

When methyl bromide is consumed in the soil, methyl bromide may be removed from the soil through hydrolysis and methylation of organic matter (Tao and Maciel 2002) or through bacterial oxidation. Methyl bromide may be removed from soil through chemical degradation, but this process has not shown to remove methyl chloride. Various types of bacteria consume methyl halides as a carbon source, including methanotrophs and nitrifiers which can co-oxidize halomethanes (Laurence *et al.* 2004).

Soil uptake rate has been observed to correlate with increasing soil moisture up to a certain threshold point. Eventually the soil is oversaturated, decreasing microbial activity in the soil (Rhew and Abel 2007). It is believed that soil consumption is mostly due to microbial activity; especially since uptake is most prominent in highly aerobic soils (Shorter *et al.* 1995). An experiment that killed bacteria within soil samples showed an immediate decrease in uptake by 98%, further supporting the theory that bacteria is the primary medium of consumption (Hines *et al.* 1998).

Many gaps in knowledge exist in terms of sources and sinks of halomethanes (Butler 2002). At the terrestrial ecosystem level, grasslands appear to be a sink (Teh *et al.* 2007), which reflects the small amount of vegetation and relatively low water content of the soil. Scientists are still not sure where much of the global methyl bromide budget comes from and what the sinks are. Modeling studies performed by Reeves (2003) indicate that uncertainty in the budget is not due to overestimates as much as unidentified sources of methyl bromide. A recent study also states that the missing sources are either from unknown sources or underestimated natural sources (Yvon-Lewis and Saltzman 2009). More data needs to be collected from all types of ecosystems to fill the gaps in knowledge about sources and sinks, especially for terrestrial-based ecosystems.

Past studies have claimed that approximately half of the world's methyl bromide soil sink comes from temperate forests, woodlands and shrubland ecosystems (Shorter *et al.* 1995). These three ecosystems appear to play a very significant role in consumption, yet they are grouped together and treated as one. A dearth of information exists about methyl halide behavior from these temperate ecosystems overall. Each type of ecosystem has many different characteristics, bringing into question whether they should all be grouped in the first place. Shrublands that have been studied are weak emitters during the dry growing season, while no net emissions were observed during the wet season. The consumption data collected for shrublands were approximately twenty times lower than previous budgets. Consumption was highest during the wet growing season, and had lower fluxes during the dry season (Rhew *et al.* 2001). According to Rhew (2001), Shorter (1995) may have overestimated the soil consumption budget for shrublands. The paper concluded that shrublands are likely weak emitters, but not expected to be a major contributor of methyl halides at the global scale, although locally it may have a noticeable presence. I plan on comparing shrublands and woodlands, which may provide insight

to the validity of the Shorter (1995) model and illuminate the similarities between the two ecosystems.

One paper exists about temperate woodlands and it concluded that woodland soils are net emitters of methyl bromide (Drewer *et al.* 2008). A small net emission from woodlands may influence the global budget because of the high land area, although more data from woodlands is needed. This paper introduces the concept of woodland soils as producers, which goes against the model presented by Shorter (1995) of woodland soil primarily serving as a consumption source. As seen here, the current methyl bromide budget model may not be accurate and may need re-evaluation.

Sparse data exists for methyl halide behavior in woodland soils. Understanding methyl bromide emissions presented by Drewer (2008) is a strong first step towards understanding methyl chloride and methyl bromide consumption and emission. I aim to help characterize woodland methyl halide consumption and production, even though it is only one of many woodland ecosystems. I am going to examine methyl halide fluxes during the summer and winter season to ascertain the differences in seasonality. Most consumption is believed to occur during the wet, active season, so it is important to compare the two seasons. My secondary goal is to compare woodland emissions with current data on woodlands and shrublands in terms of soil consumption. Comparison with temperate forests is not possible at the moment, since no data on the ecosystem has been published as of yet. By obtaining consumption and production fluxes from the woodland study site, we will hopefully be closer to understanding methyl halide behavior and budgets in terrestrial ecosystems. Shrubland data thus far is not consistent with the consumption budget presented by Shorter, and learning more about woodlands will illuminate the validity of Shorter's (1995) consumption budget.

I hypothesize that the woodland studied will have a net consumption of methyl halides. I believe that soil consumption during the summer season will be weak, with little microbial activity due to the dry nature of the soil. Production will not be significant because of the dry soil. During the winter, I believe the consumption rate of methyl halides will be relatively strong, with much more moisture in the soil and an increased microbial presence. The wet seasons is 240 days compared to the dry season, making the values found in the winter field outing even more significant. I predict a stronger woodland consumption rate than shrubland

data due to more microbial activity (Rhew *et al.* 2001). Overall, I believe that the woodland sink will differ from shrubland and temperate forest sinks sufficiently enough to suggest a re-evaluation on how these ecosystems are presented. At the same time, I believe that woodland soils will exhibit a consumption rate much weaker than the high consumption level presented by Shorter (1995).

Methods

Field Site The entirety of the field work was conducted at Tonzi Ranch, an oak savanna ecosystem at the foothills of the Sierra Nevada that has been classified as a woodland (Baldocchi *et al.* 2004). Tonzi Ranch contains open grown oak trees and grey pines interspersed across the landscape. It is partially managed, with all the brush removed and some cattle grazing on the grasses. The woodland experiences a Mediterranean climate, with dry summers and wet winters (October to May). The woodland's dominant soil type is Auburn very rocky silt loam, the annual mean temperature is 16.6°C, and the annual precipitation is 559 mm. It is approximately 177 m in elevation with relatively flat topography.

Flux Chamber Sampling While at Tonzi Ranch, I used a two component aluminum static flux chamber that covers approximately .233 square meters of soil to measure soil air samples. This chamber adequately traps the air within the chamber from the atmosphere, and allows the soil and chamber air to come into equilibrium. This enabled me to collect air samples from the chamber that reflects the net soil emission or consumption flux. I spiked (which is when artificially enriched isotopes with known concentrations is added to the original sample) the chamber with isotopic forms of methyl chloride ($^{13}CH_3Cl$) and methyl bromide ($^{13}CH_3Br$), and CFC-113. CFC-113 is a compound used to trace the loss of the added isotopes and does not influence microbial activity or methyl halide behavior (Rhew *et al.* 2003). This compound allowed me to track the behavior of the methyl halide over time within the chamber and functioned as an objective compound to monitor if there are any large variations with time. Spiking the chamber allowed me to quantify the actual soil consumption and production components independently, compared to only acquiring a net flux. A fan ensured that the

temperature and air of the flux chamber stays as close to ambient conditions as possible (Rhew and Abel 2007).

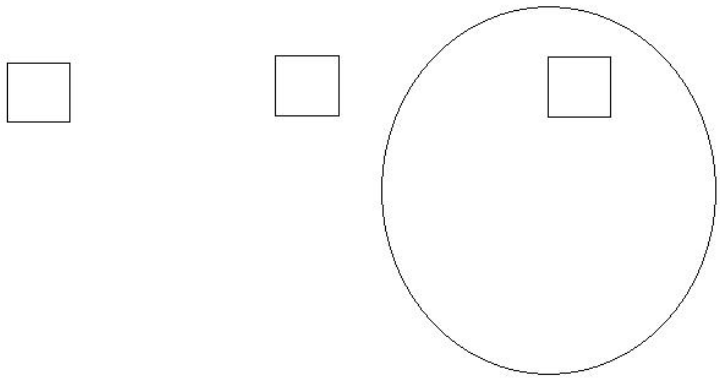

Figure 1: A layout of all three plots. Each plot is represented by a box while the circle represents an oak tree. The left plot is plot 1, the middle plot is plot 2, and the plot enclosed in the circle is plot 3. Plot 3 was placed under an oak tree. Plots 1 and 2 were exposed to the sun, while plot 3 was shaded by the tree. An aluminum base was installed around each plot area.

I personally selected three plots semi-randomly to collect samples (Fig. 1). I chose a plot under the same oak tree for both field outings and then the other two plots were selected based off of a random distance. We did not do random sampling because we felt it was more important to analyze areas that were indicative of the woodland with the limited number of samples we could obtain. All summer samples were collected July 1, 2008; all winter samples were collected January 31, 2009. For the summer measurements, the chambers were 5 meters (16.4 feet) apart. All the plots contained sparse amounts of dead plant life within them. For the winter measurements, the chambers were 9.14 meters (30 feet) apart. All winter plots enclosed a moderate amount of live grasses, which contrasted with the dead grasses observed during the summer. We sampled each plot three times throughout the day which lead to a total of 9 flux chambers (FC) per field outing: FC 1, 4, 7 are from plot 1; FC 2, 5, 8 from plot 2; FC 3, 6, 9 are from plot 3. Summer sampling took place between 11:30 AM until 5:15 PM, while winter sampling began 11:04 AM and ended 4:36 PM. At each location, I first installed a base to hold the flux chamber and formed as airtight a seal as possible between the soil and base.

Sampling entailed collecting an air sample 2, 12 and 22 minutes after we put the flux chamber on a plot base. The chamber is spiked immediately after setting the chamber on the base. Whenever we put the chamber down on the base we made sure the base's ditch along the

top was filled with water, which would allow the chamber and base to make an airtight seal. The chamber connected to a canister to hold the air sample, and each sample time required a new container. All air samples are held either in one liter electropolished stainless steel canisters or three liter silica-lined stainless steel containers, both which do not react with methyl halide compounds. I also collected multiple ambient air samples to see what the concentrations are in the woodland atmosphere, which I compared with the fluxes the soil produced.

After I finished collecting all the air samples for the day, I used a soil corer to dig up a soil sample from within each plot. I attempted to minimize disturbing the soil sample as much as possible in order to maintain soil profile and integrity. The soil samples were held in a metal casing wrapped in Parafilm (a plastic wrap) and kept cool. I measured soil temperature and soil moisture so we know the conditions from where our samples came from.

Laboratory Analyses All soil samples were run under controlled, laboratory conditions. Each soil sample was placed in a Mason jar and then placed in a water bath, which regulates the soil temperature. The water bath temperatures were set to the ambient temperature for summer (30°C) and winter (16°C) in order to recreate field temperature conditions. I connected the jar to a gas chromatography mass spectrometer (GCMS) and spiked the sample with methyl halide isotopes before running the machine. I spiked soil samples with isotopes for the same reason I spiked the chamber in the field.

In the laboratory, I ran each air sample twice on the GCMS to ensure the measurements are consistent. If the chromatograms did not have normal peaks, double peaks, disproportionate curves, or were much higher or lower than expected, I would run the sample again. I also had to run calibration curves to correct for the daily drift in measurements the machine would incur over time. I ran the samples and standards between 190.0 to 210.0 torr. Around this pressure, I am able to detect any significant differences in methyl halide concentrations for the samples, especially if concentrations are small.

Results

Comparing soil air samples and ambient air samples, methyl chloride presence in the ambient atmosphere (576 ppt) had only minor fluctuations from most of the methyl chloride concentrations exhibited by the soil gas samples (low of 441 ppt, high of 728 ppt). The calibration error reached as high as 20%, although error typically fell below 5%. Methyl

bromide concentrations for ambient samples and summer soil air samples were similar, both displaying a minute amount of methyl bromide (10±2 ppt), while ambient winter concentrations were higher (15.8 ppt).

Summer Behavior Each plot was examined separately because they characterized a different location in the woodland. During the summer, plot 1 did not consume any methyl chloride but produced an average of 163.5 nmol/m^2/d. Plot 1 was not consistent with plot 2, which instead consumed methyl chloride (71.7 nmol/m^2/d) while only producing methyl chloride in FC 8 (119 nmol/m^2/d). Plot 2 methyl chloride consumption rate had a noticeably sharp increase in consumption as the day progressed. Plot 3 did not have a definable trend compared to the other two plots. FC 3 produced methyl chloride (134.3 nmol/m^2/d) but had no consumption and FC 6 consumed (109.2 nmol/m^2/d) but had no production. FC 9 had both moderate production (79.7 nmol/m^2/d) and consumption (82.0 nmol/m^2/d), essentially canceling each other out.

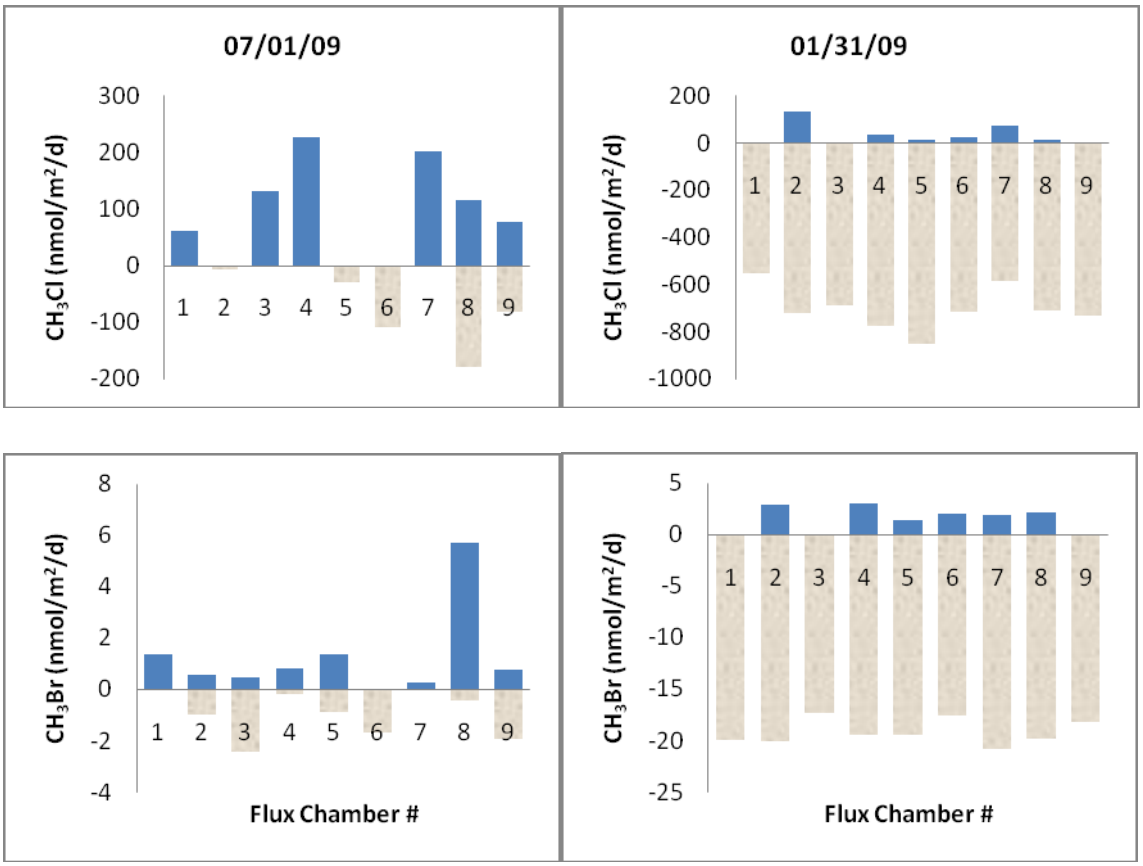

Figure 2. Methyl chloride and methyl bromide production and consumption for each chamber during summer and winter, respectively. The positive fluxes represent production, the negative values represent consumption.

Very little methyl bromide activity existed in all chambers during the summer. Production had a very small presence in nearly all chambers (1.26 nmol/m^2/d). Methyl bromide consumption was minor (.945 nmol/m^2/d), with a couple chambers consuming no detectable amount of methyl bromide. As seen in Figure 2, consumption and production of methyl halides during the summer was inconsistent and relatively weak.

Winter Behavior Plot 1 produced more methyl chloride as the day progressed, beginning with no production and linearly increasing to 74.36 nmol/m^2/d. Methyl chloride consumption peaked during midday and had a considerably higher value (635.6 nmol/m^2/d) than production (37.0 nmol/m^2/d). Plot 2 had a very strong initial methyl chloride production (135.16 nmol/m^2/d) but fell dramatically later in the day. Consumption was also highest during midday for plot 2, and was similar to plot 1 in this respect but plot 2 had a higher consumption flux (760.1 nmol/m^2/d). Plot 3 had no production in FC 3 and FC 9, with small production in FC 6. Methyl chloride consumption gradually increased in plot 3 over the day, averaging 711.2 nmol/m^2/d.

Winter methyl bromide fluxes were considerably stronger (19.2 nmol/m^2/d) than summertime fluxes for the two compounds (Fig. 2), with consumption approximately ten times greater. Methyl bromide consumption was stronger in the sunny plots compared to the site shaded by the oak tree. Production of methyl bromide was very minor (1.48 nmol/m^2/d) and almost identical to production seen during the summer.

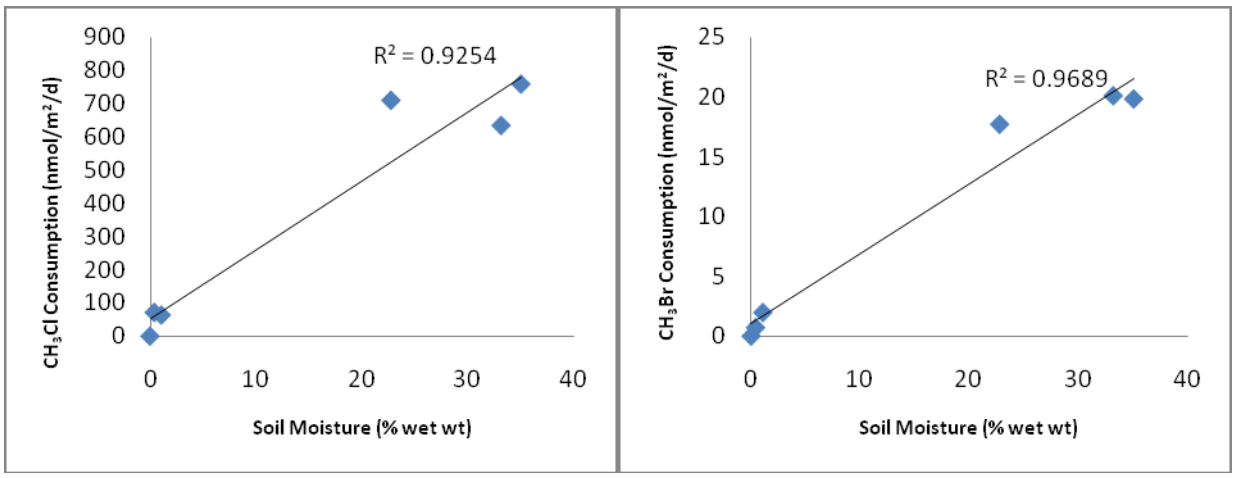

Figure 3. Correlation between soil moisture and the consumption flux for methyl chloride and methyl bromide respectively.

Field Variables Methyl bromide and methyl chloride concentrations were too sporadic to discern any diurnal trend within each plot during the summer and winter. Soil temperature did not have any correlation with consumption fluxes. Air temperature had a very weak positive relationship with consumption (R^2=0.19). Consumption flux values became larger as soil moisture level increased for both methyl chloride and methyl bromide (Fig. 3).

Concentrations of $^{13}CH_3Cl$ (isotopic form of methyl chloride) gradually decreased throughout the time span of most flux chambers, signifying that consumption is occurring within the soil. A very moderate decrease in CFC-113, a methyl halide neutral compound added to the flux chamber to track the loss of compounds from the chamber, signifies that part of the decline in concentration of $^{13}CH_3Cl$ and $^{13}CH_3Br$ is purely due to loss to the atmosphere. This loss means that some of the $^{13}CH_3Cl$ and $^{13}CH_3Br$ loss was due to leakage or the compounds entering the soil air space, but it only partially contributed to the entire $^{13}CH_3Cl$ decline. Because $^{13}CH_3Cl$ and $^{13}CH_3Br$ loss from the chamber did not compensate for all of the decrease, this confirms that consumption is actually occurring.

Discussion

Tonzi Ranch methyl halide concentrations suggest that woodland soils are not likely a major producer of methyl chloride and methyl bromide. Tonzi Ranch exhibits a net methyl halide consumption presence during the winter time due to a fairly strong consumption rate. The soils were very weak net producers of methyl halides during the summer, with little consumption present. The summer fluxes have a very minor role in the net Tonzi Ranch flux due to the considerably stronger winter consumption fluxes. The net consumption at Tonzi Ranch suggests that woodlands are likely methyl halide consumers, which is consistent with claims by previous research that soil is a consumer (Shorter *et al.* 1995; Serca *et al.* 1998). This result conflicts with other preceding research, which has indicated that woodlands may in fact be a net emitter despite occasionally high uptake rates (Dimmer *et al.* 2001; Drewer *et al.* 2008). Winter consumption was ten to twenty times greater than summer values. Production existed in only a few chambers and the production fluxes were fairly similar for summer and winter. The methyl chloride production at Tonzi Ranch is lower compared to production rates at other ecosystems such as salt marshes (Rhew *et al.* 2000) and shrublands (Rhew *et al.* 2001).

The production and consumption of both methyl halides at the three summer plots were variable and inconsistent with each other. The erratic concentrations may be due to the very low microbial activity and porous nature of the soil. These qualities in the soil may make it more susceptible to inconsistent fluxes, especially with production and consumption at such a small scale. With such small fluxes, another possible reason is the GCMS may have not been able to accurately provide consistent data.

I expected a diurnal pattern from each plot over the course of the day but all plots for summer and winter did not display this behavior. This makes sense upon examining the soil and air temperature data. An increase in soil temperature would theoretically lead to more microbial activity (Ding *et al.* 2007), but the soil temperature did not significantly increase or decrease over the course of the day. With no strong patterns in temperature throughout the day, it is a reasonable result to have no discernable trend between production or consumption with temperature over time.

Winter methyl halide consumption fluxes were considerably larger and more consistent than summer data, which may be due to the fact that biological activity is occurring (Hines *et al.* 1998). The winter methyl chloride consumption ranged from 550 to 850 nmol/m^2/d, which was

over one order of magnitude larger than the methyl chloride production presence during winter. While the increase in biological activity in the soil resulted in significantly higher consumption levels, the methyl chloride production level for the summer was similar to winter methyl chloride production despite the differences in conditions. I found no literature that links a strong microbial presence with production, so the more aerobically active winter soils should not make an impact on production fluxes. The weak and similar production during winter and summer confirms that microbially rich soils are not related to production. Production has been shown to correlate with fungal presence (Harper 1985) or certain methyl halide emitting plants (Rhew 2000), but no significant amount of fungi was observed and the grasses are not a producer as seen through the low production rate.

The high consumption rate of both halomethanes during winter was consistent with past studies indicating that soil moisture contributed to higher consumption rates due to a more highly aerobic soil. Wetter soils have more microbial activity (Barros *et al.* 1995), and as a result, this leads to more consumption. This supports the theory that methyl halides are primarily biologically mediated because the wetter and microbial-rich soils of the winter consume far more methyl halides. At the very least, past research has indicated that higher moisture correlates with higher consumption rates, and the results seen here corroborate this past trend (Rhew and Abel 2007).

Tonzi Ranch's overall weak production follows the trend of shrubland (Rhew *et al.* 2001) and grassland fluxes (Rhew and Abel 2007) because these two terrestrial ecosystems did not appear to contribute to the atmospheric budget of methyl halides and only had a moderate consumption rate. Shrublands and grasslands both were weak emitters that lacked the high production of ecosystems such as salt marshes (Rhew *et al.* 2000). Tonzi Ranch is also not a strong producer of methyl chloride and methyl bromide, which may hint that most woodlands are not important emitters and that it may harbor some similarities with grasslands and shrublands.

Temperate forest methyl halide behavior data has not been published yet, but shrubland data exists for comparison with Tonzi Ranch. The shrubland ecosystem measurements occurred in Southern California and had a Mediterranean climate (Rhew *et al.* 2001). Tonzi Ranch experiences fairly similar climatic conditions, making the comparison between the two ecosystems apt. The methyl chloride production at Tonzi Ranch ranged from 0 to 227

nmol/m^2/d. This is smaller than existing shrubland production data, which ranged from 100 to 1000 nmol/m^{-2}/d^{-1}. Methyl bromide production at Tonzi Ranch was between 0 to 5 nmol/m^2/d, while shrubland production was higher than 100 nmol/m^2/d in a couple instances. In terms of production, the Tonzi Ranch woodland has smaller fluxes than shrublands.

Tonzi Ranch displayed stronger consumption of both halomethanes compared to the shrublands. The shrublands ranged between 0 and 10 nmol/m^2/d, while Tonzi Ranch averaged 19.2 nmol/m^2/d during the winter. Methyl chloride uptake at the shrubland sites were mostly lower than 200 nmol/m^2/d, with some sites reaching up to 400 nmol/m^2/d (Rhew *et al.* 2001). Tonzi Ranch, while having weak consumption during the non-growing season, ranged between 550 to 850 nmol/m^2/d during the wet season. As seen here, production at Tonzi Ranch was much weaker but the consumption presence was significantly higher than the shrublands. The consumption and production rates of Tonzi Ranch during winter and from shrubland data do differ from each other but not enough to suggest that the two ecosystems should be grouped independently. This result contradicts my hypothesis that these ecosystems should be evaluated separately when creating halomethane consumption models. The shrublands and Tonzi Ranch had similar behavior; both had weak consumption during summer and stronger consumption during the wetter winters.

The methyl bromide consumption observed at Tonzi Ranch is not consistent with the net emissions from woodlands observed by Drewer *et al.* (2008). This discrepancy is likely due to the presence of organisms such as fungus in these other woodlands that are not present in Tonzi Ranch. Evidence exists that fungi are moderate producers of methyl bromide (Harper 1985), which may account for a net emission instead of the consumption seen at Tonzi Ranch. Another possible reason for this difference may be the variation in woodland ecosystems. Tonzi Ranch contained many oak trees compared to sycamore, ash, and beech trees dominating the Scottish woodlands (Drewer *et al.* 2008). Any given woodland has diverse characteristics and the differences in flora, climate, and soil conditions may lead to varying methyl halide behavior.

While soil uptake occurred, methyl bromide uptake at Tonzi Ranch did not fit the current methyl bromide soil consumption model but was much lower than the model predicted. Summer soil consumption at Tonzi Ranch was 45 times less than the 42 nmol/m^2/d projected for woodlands by a previous study (Shorter *et al.* 1995). Winter consumption was considerably

higher, reaching up to 20 nmol/m^2/d, which was still less than half of the projected value. When examining shrubland and woodland production, and assuming temperate forests are not significantly different than the other two, it does not seem correct to allocate half of the global methyl bromide soil consumption within these ecosystems. These comparisons are based only on Tonzi Ranch, which is not an indicator of all woodlands but does help illuminate the fact that current methyl bromide models may need revising. Based on existing data on shrublands and this study, evidence seems to point towards revising downwards the current soil consumption budget for shrublands, temperate forests, and woodlands.

The sample and data analysis ran into a couple obstacles, which led to error in portions of the data. All flux chambers should have started with approximately 1000 ppt of isotopic methyl chloride, and have a gradual downward trend. A couple chambers had a much lower initial isotopic methyl chloride value than expected, which may have meant a small leakage at the initial spiking. Also, each flux chamber was run twice to ensure consistency, but some of the point couplets were significantly different from each other. This may have led to the possibility of skewed trends because an average is taken, while the possibility exists that one of the points was considerably inaccurate. One factor to this was machine daily drift, where samples analyzed later in the day have a slightly lower value than earlier runs in the day due to declining sensitivity. The GCMS also has erratic values at the beginning of the day, so the first run of the day was always tossed. The inconsistencies in the GCMS make the data liable to vary slightly between each run. Methyl chloride is difficult to measure, and this issue came up when analyzing the data. All the other compounds measured (methyl bromide, F-113, F-11) were stable and fairly consistent, signifying that irregular methyl chloride numbers are not due to errors in analysis or laboratory work. Another factor is the correction factors used on the data points. The daily standards, which determined the correction factor applied for a given day, had sporadic values. The standard concentrations have known values so the amount of error occurring at any given time may be quantified by running a standard. The daily drift error usually did not have a definable trend, which made correcting more complicated. Some samples may have been corrected excessively, or did not need to be corrected as much as they were.

Sampling from the Tonzi Ranch woodland ecosystem revealed a methyl bromide consumption rate that was far lower than previous budgets suggest (Shorter *et al.* 1995). The

observed methyl bromide consumption was consistent with past research on terrestrial ecosystems, which detected smaller consumption fluxes than expected (Rhew *et al.* 2001; Rhew *et al.* 2007). This consistently smaller consumption value hints that the methyl bromide consumption budget for terrestrial ecosystems may be overestimated. The production and consumption of both measured methyl halides was weak and inconsistent during the summer season, likely due to a lack of biological activity in the soil. Production of halomethanes during the wet season was also weak, suggesting that halomethane production does not have a strong connection with microbial activity in the soil. Consumption of methyl halides during winter was considerably larger than any of the other fluxes observed, and helped characterize Tonzi Ranch as a net consumer of methyl halides.

The research shown here samples only one woodland ecosystem. Methyl halide behavior in soils may vary in different woodlands, and it is important to collect samples from other woodlands around the world to obtain a fuller understanding of woodland soils and methyl halides overall. This paper provides a basis for woodland halomethane behavior, but it is not enough to make firm conclusions about the role woodland ecosystems play. Many gaps in understanding still exist in terms of methyl halide budgeting and behavior such as all the sources and sinks of the compounds. Ecosystems still exist that have none or very few studies yet such as coniferous forests, deserts, and even agricultural lands. We know that most halide production is biologically mediated, but with gaps in the global budget still existing, it is important to discover how these processes work and which organisms are the most significant producers. Abiotic processes are also poorly understood with some believing their importance is understated, and research in this subject may lead to important shifts in perspective. Research on methyl halides is a relatively young field in need of much more examination. This paper only fills a tiny portion of the vast holes of knowledge that still subsist in the subject of methyl halides.

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