

Short Communication

A pilot study of methyl chloride emissions from tropical woodrot fungi

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Abstract

Flux chamber measurements made in a rainforest provide evidence that methyl chloride is emitted from rotting wood. However, its net flux was found to be into the soil, probably due to competing production and consumption processes within the soil. Evidence was found for a regional source, possibly vegetation, since its concentration above the canopy was substantially greater than reported average equatorial values.

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1. Background

Methyl chloride (CH_3Cl) is the most abundant chlorine-carrying gas in the atmosphere and is supplied at an estimated rate of $\approx 3.5 \text{ Tg a}^{-1}$. In the unperturbed atmosphere, it would represent an important carrier of chlorine to the stratosphere. Recent work (Keene et al., 1999; Khalil et al., 1999) has confirmed the existence of a major imbalance ($\approx 2 \text{ Tg a}^{-1}$) between the total sources of CH_3Cl and the atmospheric sink through reaction with OH radicals. The ocean, once thought to be the predominant source, has now been shown to balance only 5–12% of the atmospheric sink (Moore, 2000). In compiling the Reactive Chlorine Emissions Inventory (RCEI), best estimates were made of CH_3Cl fluxes from several sources, mostly little studied. An estimate was made of the potential supply from woodrot fungi, based only on laboratory experiments (Harper et al., 1988) since there were no field data.

Tropical regions must be a strong source of CH_3Cl because the atmospheric sink is strongest there and yet the atmospheric concentration is not lower than else-

where. Khalil and Rasmussen (1999) estimated that about 85% of the total atmospheric source comes from between 30°N and 30°S. Production by woodrot fungi is a possible tropical source, laboratory studies having demonstrated that its biosynthesis is a widespread trait in white rot fungi (Watling and Harper, 1998). The potential global contribution to the atmosphere has been estimated from the mass of wood decomposed, its Cl^- content, and the efficiency of conversion of Cl^- to CH_3Cl . The pilot study described here was conducted at a site in Rondonia, Brazil, the focus of forest studies forming a part of the Large Scale Biosphere-Atmosphere experiment (LBA). The objective was to determine whether there is field evidence for a major fungal source from tropical forests.

2. Methods

Measurements were made during the transition period between wet and dry season in April 1999 in the rainforest at Reserva Biológica Jarú, a primary forest ecological reserve located about 90 km north of Ji-Paraná, Rondonia, Brazil. The site is described by Andreae et al. (2002). Air samples were pumped into stainless steel canisters (800 ml) from circular static flux chambers constructed of Perspex (diameter 29 cm,

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internal height 18 cm). The samples were taken as time-series so that concentration changes in the chambers could be used to calculate fluxes between the soil and atmosphere. Four such experiments were conducted within 100 m of a station monitoring soil temperature and moisture at a depth of 0–5 cm using respectively thermistors and time domain reflectory (TDR)—sondes (Trime IT, IMKO, Germany). The chamber was sited with preference for locations where rotting wood was visible, with the exception of Series 1 which was located on moist sandy soil covered with leaf litter. Series 2 was unique in that it was located solely on rotting wood, and not in the presence of any soil. In addition, two air samples were collected from a tower at a height of 36 m (at the top of the forest canopy) to detect any gradient in concentration between the boundary layer and the forest floor, which might indicate local production or loss. The canister samples were measured at Dalhousie University by GC–MS in December 1999. The air sample was carried from a sample loop (207 ml) in a stream of high purity helium through a magnesium perchlorate drier, followed by cryotrap (20 cm steel tube, 0.8 mm i.d.) held at $-150\text{ }^{\circ}\text{C}$. The trap was heated to about $20\text{ }^{\circ}\text{C}$ to desorb the contents into a helium flow and through two DB-624 columns (J&W Scientific Inc.) to a Finnegan Trace MS operating in single ion monitoring mode. A CD_3Cl internal standard was used to correct for any variations in detector sensitivity. Calibration was performed by injecting volumes (50–150 μl) of a gravimetrically prepared CH_3Cl standard using gas-tight syringes. The coefficient of variation of five measurements from a single 15 l canister was 1.9%. Identification

of fungal species is tentative and was done by R. Watling from photographs.

3. Results and discussion

Three flux chamber time-series were measured in the last week of April 1999 either on bare soil (Series 1) or on soil on which rotting wood was visible (Series 3 and 4) at a mean soil temperature of $24\text{ }^{\circ}\text{C}$ and a mean soil moisture of $0.32\text{ m}^3\text{ m}^{-3}$. These time-series all showed a decrease in the concentration of CH_3Cl (Fig. 1). A single set of measurements (Series 2) was made with the chamber placed on a nearly flat portion of a fallen tree (diameter $\approx 1\text{ m}$) that was supporting visible fungal growth (*Rigiporus lignosus* agg., or a species of *Perreniporia*). This series showed an increase in CH_3Cl , from ≈ 700 to 1300 ppt, with most of the change occurring during the first 20 min.

Series 1, comprising measurements made over 1 h, showed an initial steep decrease in CH_3Cl occurring over 20 min, followed by roughly constant concentrations. There are several possible explanations for this result. First, it is known that in spite of the precautions taken to ensure a good seal around the base of the flux chamber, some exchange can occur with outside air: this might result in a steady state concentration being reached. Second, when air is pumped into the canisters, air will be drawn into the chamber from around its edge and perhaps from the underlying substrate, if it is porous. Each sample volume was about 12% that of the chamber. Third, and most probable, the concentrations

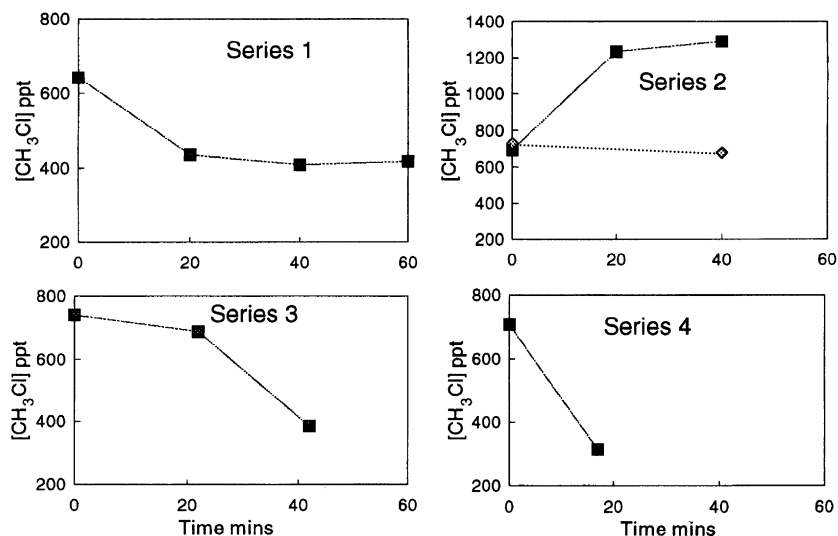


Fig. 1. Concentrations of CH_3Cl (ppt) in air samples from four static flux chamber experiments plotted against time. Series 1 was measured on bare soil, Series 2 on a rotting log, and Series 3 and 4 on soil with rotting wood. Diamond symbols in Series 2 represent measurements made on air samples from an enclosed control chamber. Note the different concentration range for Series 2.

of CH_3Cl in the chambers could result from competing processes of production and consumption in the underlying substrate. If the compensation concentration of the soil (the equilibrium concentration resulting from simultaneous production and consumption) were reached, the concentration gradient between soil and air, and thus the flux, could be reduced to 0.

In Series 3 and 4 CH_3Cl was initially in the range of 700 ± 20 ppt and finally in the range 310–371 ppt. Controls were run using a separate, totally enclosed chamber having a Perspex base. Time-zero samples were taken with the chamber lid removed. One of the canisters containing air from a control experiment was apparently contaminated, having levels of CH_2Cl_2 , CHCl_3 and C_2Cl_4 that were typically three times higher than any other canister. The single remaining control (Series 2) showed a decrease of 53 ppt in CH_3Cl over 40 min. The declines seen in three of the four series were 223, 344 and 394 ppt, much greater than the change in the control.

As shown in Fig. 1, the pattern of decreasing concentration varied between the three series. For consistency, fluxes have been calculated from the initial and final concentrations and the total duration of the experiment. Each measurement has been corrected for the rate of change of CH_3Cl in the control chamber. This yields an average uptake rate by the soil of $77 \text{ pmol m}^{-2} \text{ min}^{-1}$ (range 18–161). The lower end of this range is an underestimate because the decreasing concentration in the chamber over time causes the flux into the soil to decrease. Also, any competing processes of production and consumption in the soil would tend to maintain a balanced level of CH_3Cl : its value is indicated by Series 1 to be around 400 ppt.

The single experiment showing an efflux of CH_3Cl was that conducted on the surface of rotting wood. The efflux rate over the 40-min experiment was $120 \text{ pmol m}^{-2} \text{ min}^{-1}$, but faster during the first 20 min ($210 \text{ pmol m}^{-2} \text{ min}^{-1}$). The higher initial rate might better represent the true flux to the atmosphere because it is reported that woodrot fungi consume CH_3Cl as well as produce it (Harper, 1993), so the apparent leveling of the concentration with time may result from enhanced consumption as ambient levels climbed.

In view of the evidence from Series 2, as well as from laboratory experiments indicating that certain woodrot fungi produce CH_3Cl (e.g. Harper, 1985), it is important to realize that the observed fluxes into the rainforest soils are likely to be the net result of microbial processes in the soil (a sink) and wood rotting by fungi (a source). The co-existence of sources and sinks in soils may have important implications for the isotopic composition of atmospheric CH_3Cl even where no net flux is evident. This is relevant in view of recent efforts to elucidate the global sources and sinks of CH_3Cl through $\delta^{13}\text{C}$ measurements for the various sources (Harper et al., 2001; Czapiński et al., 2002).

Because this study was intended only as a very limited field exploration of the potential importance of fungal emissions, we will not attempt to extrapolate these results to a global scale. However, it is necessary to compare these measurements, at least on a local scale, with other processes that control atmospheric CH_3Cl concentrations. The fluxes have therefore been quantified by their effect on the local column inventory of CH_3Cl . The soil uptake fluxes are equivalent to a lifetime with respect to this process of 5 years (range 2.3–21 years). For comparison, its loss by reaction with atmospheric OH has a global average of 1.4 years, with a range from 0.8 year in the tropics to 12 years at the poles (Harper and Hamilton, 2003). For the single measurement that showed a net supply of CH_3Cl , its lifetime with respect to this source is 3.1 years (1.8 years if the initial, higher rate of emission is used). But because the fraction of the forest floor characterized by rotting wood alone must be vastly outweighed by that which is represented by our soil-only and soil-plus-wood sampling spots, this work suggests that soil consumption is very likely to outweigh the woodrot fungal production. It has not been possible to even estimate fungal emissions from standing trees.

There are very few other studies of CH_3Cl fluxes between forest soils and the atmosphere. A limited study by Khalil and Rasmussen (2000) that presented flux chamber measurements for several ecosystems, including a forest site in Brazil, showed soil uptake at all sites. A study by Dimmer et al. (2001) reported significant efflux from the floor of a temperate conifer plantation in the West of Ireland. The median annual flux was $33.4 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$, from which the global contribution of conifer forest floor of 85 (range 39–131) Gg a^{-1} was estimated. The authors suggested that this estimate is highly uncertain and may be too large on account of possible seasonal variations and the effect of snow cover being ignored.

In addition to the chamber samples, two CH_3Cl measurements were made from a tower above the forest canopy at a height of 36 m, and a third in ground level air. The tower samples averaged 785 ppt (761 and 809 ppt) while the ground level sample had a concentration of 673 ppt. These values are consistent with a downward flux of CH_3Cl indicated by the chamber experiments. The single ground level sample may be compared with all the time zero values for the flux chambers: the average of eight such samples is 687 ppt (min 639, max 725). This supports the evidence for higher concentrations in and above the forest canopy than at ground level.

One other single air sample was taken at a height of ≈ 2 m close to a growth of woodrot fungi (*Hydnopolyporus palmatus*) on a standing tree in order to determine whether CH_3Cl is enhanced in the immediate vicinity of woodrot fungi. Its concentration of 843 ppt

was well in excess of all the samples taken near the forest floor (excluding non-time-zero samples from the flux chambers).

Theoretical estimates (Watling and Harper, 1998; Khalil et al., 1999) of CH_3Cl production by woodrot fungi have assumed that its yield will depend on the Cl^- content of wood. A more detailed study should include areas where potentially higher concentrations of Cl^- occur in soils, particularly coastal regions. It is reported that there are higher concentrations of Cl^- in foliage, bark and litter, though not in wood, in coastal forests in comparison to those inland (Lobert et al., 1999). Recent publications have pointed to CH_3Cl emissions from coastal land sites. Yokouchi et al. (2000) showed that atmospheric CH_3Cl was elevated near low latitude, island sites. Rhew et al. (2000) reported substantial emissions from salt marshes. It was apparently produced by plants, and there is potential for saltmarsh plants to account for up to 10% of the global supply to the atmosphere. Some common tropical forest plants, including tree ferns and some Dipterocarpaceae species, are reported to be strong sources of CH_3Cl (Yokouchi et al., 2002), an observation consistent with reported elevated CH_3Cl at low latitudes. The same study also reported a low rate of uptake by tropical soils.

The tower samples (785 ppt) and average ground levels samples (687 ppt) all substantially exceed the background equatorial concentration of about 570 ppt reported by Yokouchi et al. (2002), suggesting that the rain forest may represent an important source, though perhaps via emissions from vegetation rather than fungi. The observed CO and aerosol concentrations during the campaign and published emission ratios for CH_3Cl , CO , and aerosols, show that biomass burning could not account for more than ≈ 30 – 40 ppt of the observed CH_3Cl excess (Andreae and Merlet, 2001; Artaxo et al., 2002).

4. Conclusions

Flux chamber measurements of CH_3Cl made in a natural tropical forest provide evidence for emission from rotting wood and indicate that the forest soil, including areas with substantial rotting wood, acts as a sink. Considering the forest floor, the relative areas represented by rotting wood and forest soil would suggest that the balance of the processes leads to removal of CH_3Cl from the atmosphere (though quantification of emissions from standing wood could alter this conclusion). However, the observation that atmospheric CH_3Cl concentrations both at ground level and over the canopy were substantially in excess of background equatorial values suggests that the tropical rain forest may be a source, perhaps from vegetation.

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