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An estimate of the uptake of atmospheric methyl bromide by agricultural soils

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Abstract. Published estimates of removal of atmospheric methyl bromide (CH_3Br) by agricultural soils are 2.7 Gg yr^{-1} (Gg = 10^9 g) [*Shorter et al.*, 1995] and 65.8 Gg yr^{-1} [*Serça et al.*, 1998]. The *Serça et al.* estimate, if correct, would suggest that the current value for total removal of atmospheric CH_3Br by all sinks of 206 Gg yr^{-1} (based on *Shorter et al.*, 1995) would be 30% too low. We have calculated a new rate of global agricultural soil uptake of atmospheric CH_3Br from a larger sampling of cultivated soils collected from 40 sites located in the United States, Costa Rica, and Germany. First order reaction rates were measured during static laboratory incubations. These data were combined with uptake measurements we reported earlier based on field and laboratory experiments [*Shorter et al.* 1995]. Tropical (10.2°-10.4°N) and northern (45°-61°N) soils averaged lower reaction rate constants than temperate soils probably due to differing physical and chemical characteristics as well as microbial populations. Our revised global estimate for the uptake of ambient CH_3Br by cultivated soils is 7.47 ± 0.63 Gg yr^{-1}, almost three times the value that we reported in 1995.

Introduction

Methyl bromide (CH_3Br), a widely utilized soil and structural fumigant, is a potential source of stratospheric ozone depleting bromine [*Wofsy et al.* 1975; *McElroy et al.* 1986]. Bromine has been determined to destroy ozone 50 times more efficiently than chlorine [*Yung et al.* 1980; *Solomon et al.* 1992; *WMO*, 1992; *Mano et al.* 1994]. Due to this potential detrimental effect and CH_3Br' s relatively large ozone depletion potential (ODP), the reduction and eventual cessation of the industrial production and use of CH_3Br was scheduled for 2001 by the 1995 Montreal Protocol [*UNEP*, 1995].

The current understanding of the tropospheric budget for CH_3Br implies a significant discrepancy between sinks and sources [*Yvon-Lewis and Butler*, 1997]. Sources equaling approximately 137 Gg/yr of atmospheric CH_3Br include biological production and release from the ocean [*Khalil et al.* 1993; *Yvon-Lewis and Butler*, 1997], emission from fumigation of cultivated land, structures, and perishables [*Yates et al.* 1996, 1997], combustion of leaded gasoline [*Penkett et al.* 1995; *Baker et al.* 1998], biomass burning [*Blake et al.* 1993; *Cicerone et al.* 1994; *Mano and Andreae*, 1994], and production from terrestrial higher plants [*Gan et al.*, 1998].

The principal sinks of atmospheric CH_3Br include loss to the ocean [*Butler et al.* 1994; *Lobert et al.* 1995; *Yvon and Butler*,

1996], reaction with OH [*Penkett et al.* 1995; *Prinn et al.* 1995], uptake by soils [*Shorter et al.* 1995; *Serça et al.* 1998], and possibly uptake by green plants [*Jeffers and Wolfe*, 1997; *Jeffers et al.* 1998]. The sinks total approximately 206 Gg/yr [*Yvon-Lewis and Butler*, 1997] with the soil sink contributing 21% [*Shorter et al.* 1995].

The *Shorter et al.* [1995] report was our first attempt to estimate the global uptake of ambient CH_3Br by soils. Our research involved measuring the uptake of CH_3Br by selected soils from a New Hampshire forest, cornfield, and grass covered site, a Costa Rican forest, and a Canadian boreal forest. We determined that the uptake was microbially mediated by the use of sterilization and various antibiotics [*Hines et al.* 1998]. We then extrapolated these measurements to obtain a global soil sink estimate. Recently, *Serça et al.* [1998] reported flux measurements with a new estimate of uptake by all soils that is more than twice the one we obtained. The major disparity between these two estimates is the agricultural uptake values. Uptake by agricultural soils made up approximately seven percent of our total estimate whereas it makes up approximately 70 percent of *Serça et al.* [1998]. In both cases, uptake estimates were based on a limited number of laboratory and/or field experiments utilizing only agricultural soils from New Hampshire or Colorado. To get a more accurate estimate of the uptake of CH_3Br due to agricultural soil, we expanded our measurements to include cultivated sites from across the United States, Costa Rica, and Germany.

Experimental Procedure

Since it is not economically or logistically feasible to conduct field experiments at locations around the world, laboratory incubations of soils collected around the world were completed. We determined that laboratory incubations of soils yield similar results as field flux measurements. The work discussed in this paper is the result of these laboratory incubations. Soil samples from 0-5 cm and 10-15 cm depths were collected from 40 sites including an east-west transect of agricultural soils across the mid-northern United States, agricultural and pasture sites in Costa Rica, and cultivated sites in Germany. The sampling sites consisted of pastures, fallow fields, and agricultural fields. The pastures and fallow fields were mostly bare ground with scattered grass cover while the planted fields varied from a bare surface to crop cover. The crop types included corn, alfalfa, palmheart, tomatoes, soybeans and various grains. Soil classifications for each sampling site were obtained either during sample collection or from United State Geological Survey soil maps. Soils were stored in doubled plastic bags at 0°C and were incubated within 4 weeks of sampling. Experiments completed to determine loss of activity in soils during 6 months of

storage after collection revealed that there was a loss of less than one third the original activity over the time period.

Laboratory incubations entailed placing 5 to 20 grams of soil into twelve, 200 ml glass vials which were sealed and suspended in a 25°C water bath. The vials were injected with 3 ml of 270 parts per billion by volume (ppbv) CH_3Br to obtain an initial head space mixing ratio of approximately 4 ppbv. The vial head space was evacuated at specified time intervals with Ultra High Purity Nitrogen (UHP N_2) into a sample loop immersed in a dry ice/isopropanol bath. The sample loop contained a plug of Poropak Q (Alltech) packing and quartz wool to allow the head space sample to be immobilized on the plug. The sample loop was immersed in boiling water and connected to an electron capture detector gas chromatograph (8A GC-ECD, Shimadzu). The oxygen (O_2) doped N_2 carrier gas flowed through the sample loop carrying the volatilized head space sample into the pre-column, through the analytical column and then to the detector. Details of the sampling and analytical procedures can be found in *Kerwin et al.* [1996].

The resulting peak areas were compared to daily standard curves and concentrations calculated. The daily standard curves included replicates of the following 5 volumes of standard: 1.0, 0.5, 0.25, 0.1 and 0.05 ml of 270 ppbv CH_3Br. The average r^2 of the linear regression fit of peak area versus nmoles of CH_3Br for the 6 month period of sampling was 0.9998. Replicate head space samples for each of the six time segments were completed. A reaction rate constant, k, was determined as the slope of the regression fit of the natural log of nmoles of CH_3Br versus time. This k, in min^{-1}, was then divided by the grams of dry soil (ds) in the vial resulting in a measured reaction rate constant with the units of $min^{-1}g^{-1}_{ds}$.

The soil pH, water content, and organic matter were measured for all of the incubated agricultural soils. pH was measured using a combination electrode and 10 g of air dried soil in a 0.01 M $CaCl_2$ solution. Soil moisture content was determined in a drying oven at 70°C for 24 hours. Soil organic matter content was measured by ashing 3 to 7 g of oven dried soil in a muffle furnace at 450°C for 24 hours. Details of the measurement procedures can be found in *Carter*, [1993].

Results

The average reaction rate constants and standard errors are presented in Table 1 according to approximate latitudinal location and depth of sampling site . The temperate zone (40°-43°N) had the most rapid uptake of CH_3Br while the northern and tropical zones were approximately 10% less active. Surface soils were on average more active than deeper soils by approximately 50%. In a few isolated cases the deeper soils were more active.

On average, the surface soils tend to be only slightly drier than the deeper soils in the tropical samples, whereas in the temperate

Table 2. Estimate of Global Ambient CH_3Br by Agricultural Soils with Different Land Area Estimates

Cultivated Land References	Land Area x 10^6 km^2	Uptake Estimate Gg yr^{-1}
Matthews, 1983	17.56	8.17 ± 0.69
Born, 1990	14	6.52 ± 0.55
Guenther *et al.*, 1995	19.4	9.03 ± 0.76
DeFries *et al.*, 1995	13.28	6.18 ± 0.52
Average		7.47 ± 0.63

None of the references separated out the cultivated areas by latitude except Guenther *et al.*, 1995 which only specified warm and cold regions. Therefore, the uptake estimate calculations were completed with an average reaction rate constant from all the soil incubations.

and northern samples the moisture content at the two depths were almost equal. The organic matter content varied more with depth than the moisture content. The greatest organic matter content was measured in the surface layer, and it was generally higher than that in the deeper layer with about 7% less in the 10-15 cm tropical soils, 26% less in the 10-15 cm temperate soils, and about 23% less in the 10-15 cm northern soils. As expected, pH varied considerably between climatic zones from an average of 7.28 in the northern areas to 4.97 in the tropics.

Estimate of the global uptake by agricultural soils

The flux of tropospheric CH_3Br into the soil was calculated from the measured reaction rate constants obtained in the laboratory incubation experiments. By taking the same approach as *Bender and Conrad*, [1993]:

$$\text{Flux} = k * V * d * \text{b.d.} * [CH_3Br]$$
$$* 1440 \text{ min/day} * 94.94 \text{ g } CH_3Br/ \text{ mol} * 10^4 \text{ cm}^2/\text{m}^2$$

where Flux is in g m^{-2} day^{-1}, k is in min^{-1} g^{-1}_{ds} (average of all soil incubations performed), V is the vial head space of 200 cm^3 for the laboratory experiments, d is the depth of uptake in cm (assumed to be 1 cm because the uptake is the fastest in the surface soils), b.d. is the bulk density of the soil in g cm^{-3} (1.5 g cm^{-3}, average of those measured), and [CH_3Br] is 4.5 x 10^{-16} moles cm^{-3} (ambient CH_3Br equal to 11.1 pptv for the Northern Hemisphere where most of the agricultural land is located [*Lobert et al.* 1995]).

To estimate the global sink of tropospheric CH_3Br to agricultural soils we extrapolated cultivated land areal extent using global estimates [*Matthews*, 1983; *Born*, 1990; *Guenther et al.* 1995; *DeFries et al.* 1995]. Flux, in g m^{-2} day^{-1}, was multiplied by the areal extent of cultivated land and by the number of days in the growing season (240 days for agricultural soils). It is assumed that

Table 1. Summary of Laboratory Incubations

Climatic Regime (Latitude)	Depth, cm	Reaction rate constant k, min^{-1} g^{-1}_{ds}	Moisture Content, %	Organic Matter, %	pH	n
Tropical	0 - 5	0.0092 ± 0.0038	61.4 ± 6.2	22.4 ± 3.5	4.97 ± 0.08	3
(10.2°-10.4°N)	10 - 15	0.0057 ± 0.0005	63.6 ± 5.3	20.8 ± 2.0	4.59 ± 0.17	4
Temperate	0 - 5	0.011 ± 0.0018	19.1 ± 2.2	5.68 ± 0.6	6.33 ± 0.10	25
(40°-43°N)	10 - 15	0.0058 ± 0.0008	18.5 ± 1.7	4.17 ± 0.4	6 29 ± 0.12	25
Northern	0 - 5	0.0095 ± 0.0042	24.9 ± 7.9	9.88 ± 4.5	7.28 ± 0.57	8
(45°-61°N)	10 - 15	0.0067 ± 0.0033	24.8 ± 7.1	7.6 ± 2.8	7.39 ± 0.56	10

Estimated errors are standard error of the mean for the samples.

since the uptake is a microbial process, this activity is insignificant when the soil is frozen. Table 2 contains the results of these calculations.

Discussion

We find a global uptake of ambient CH_3Br by agricultural soils of 7.47 ± 0.63 Gg yr^{-1}. This is a far improved estimate than our previous one for the agricultural soil sink because we sampled a wide variety of soil types with a range of soil properties from many crop types across a broad latitudinal extent. Our estimate in 1995 was 2.7 Gg yr^{-1}, almost three times smaller than our new estimate [Shorter et al. 1995]. This difference is most likely attributed to the greatly increased data base of soil uptake rate measurements.

Many studies have examined CH_3Br consumption in soil when it is added at fumigant levels [Oremland et al. 1994; Miller et al. 1998]. Some studies have related uptake dynamics to environmental factors such as temperature, moisture content, and/or organic matter content [Gan et al. 1994; Rice et al. 1996]. The soil uptake of ambient CH_3Br appears to be microbially mediated [Hines et al. 1998]. The greatest uptake rates were measured in temperate zone soils even though they had the lowest average moisture and organic matter content. This may be because all the soil incubations were performed at 25°C which is closer to the average ambient temperature for the temperate soils than it is for tropical and northern soils. There should be an optimum moisture and organic matter content where the microbes responsible for uptake reside, but because of the variation of soil properties the individual effects of these factors are difficult to isolate.

A temperature manipulation study was performed on two agricultural soil samples from Iowa and Illinois, USA. The soils were incubated at 5, 15, 25, 35 and 45°C and the reaction rate constants determined. The results reveal a specific response to temperature that is typical of a microbial population (Figure 1) [Madigan et al. 1997].

The only other published research on the uptake of ambient CH_3Br by soils gives an estimate for cultivated soils of 65.8 ± 29.2 Gg yr^{-1} [Serça et al. 1998]. Their observed deposition velocities for CH_3Br were measured at an agricultural field site in Colorado (n=7). The discrepancy between these estimates are probably due to differences in measurement technique, sampling location and flux calculation method. Their field measurements were completed in a recently plowed agricultural field that had not received rainfall since plowing. Both studies reveal that microbially mediated uptake is common but that sampling in one location, as we did in 1995, will give an estimate that is restricted to sites with similar physical characteristics.

Conclusions

The uptake of ambient CH_3Br by agricultural soils is a ubiquitous process that varies with location. The rate of uptake is dependent on soil physical properties as well as sampling location with specific controls hard to isolate. Further work must be undertaken to determine the physical, chemical and biological controls on uptake by agricultural soils.

Our estimate of the global uptake rate for agricultural soils is almost three times what we reported in 1995. This is because we have broadened our database to include agricultural soils from 40 new sites from across the U.S., Costa Rica, and Germany. By sampling at so many sites we believe that this is a more representative estimate for uptake by agricultural soils than our previous one. Though this new estimate is significant, it does not significantly affect the lifetime of CH_3Br in the atmosphere.
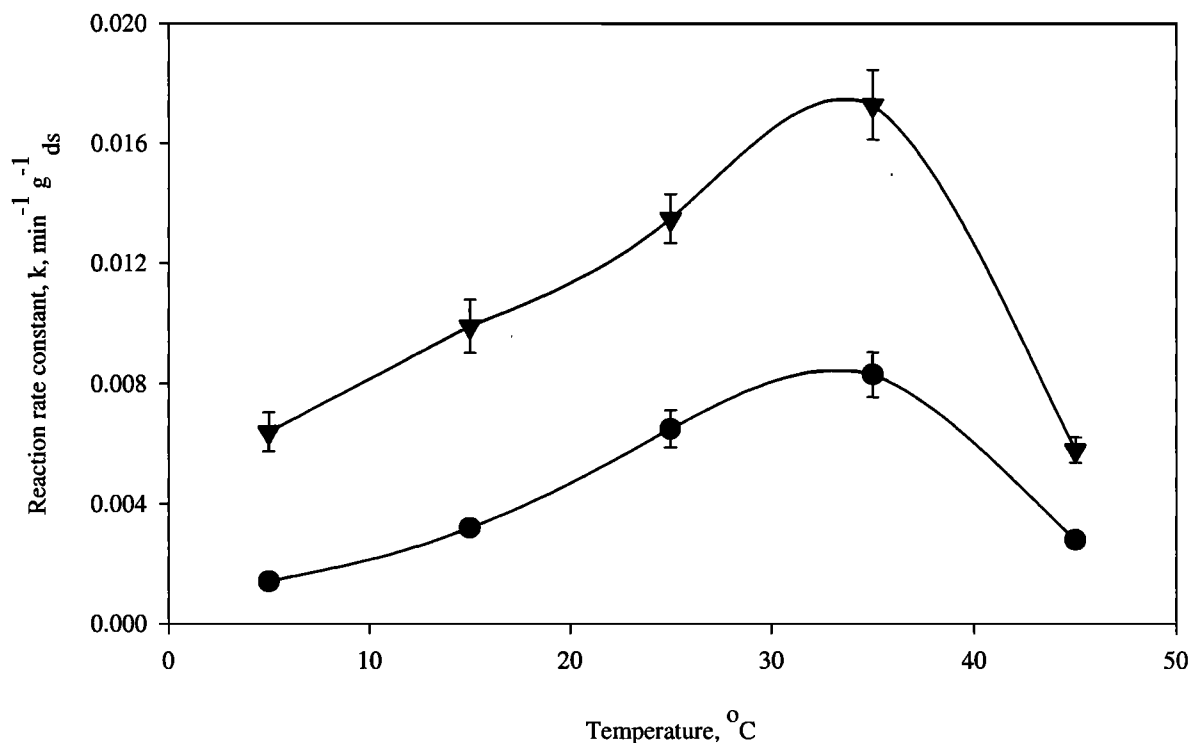

Figure 1. Temperature manipulation experiment utilizing two Mid-western United States agricultural soils. ● - Illinois soil, ▼- Iowa soil. (Each point is the linear regression fit of 10 to 12 points of the ln of nmoles of CH_3Br measured during soil incubations versus time normalized to grams of dry soil. The error bars are the standard error of the slope of the linear regression also normalized to grams of dry soil.)

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