



EFFECT OF SOIL PROPERTIES ON DEGRADATION AND SORPTION OF METHYL BROMIDE IN SOIL

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ABSTRACT

Methyl bromide (CH_3Br) is currently the most widely used soil fumigant, and its emission into the atmosphere after application reportedly contributes to ozone depletion in the stratosphere. Irreversible degradation and partially reversible sorption reactions affect the quantity of this fumigant reaching the soil surface and escaping into the atmosphere. Incubation studies in closed headspace vials under controlled conditions showed that degradation of CH_3Br was highly dependent on soil organic matter content, and to a lesser extent, on the moisture level in the soil. Methylation of CH_3Br on organic matter was suggested to be the major reaction that CH_3Br undergoes in the soil environment. Other soil constituents such as clay did not contribute to the degradation under moist or air-dried conditions, though enhanced degradation was observed on oven-dried montmorillonite and kaolinite clays. Within soil profiles, degradation of CH_3Br decreased with soil depth mainly due to the reduction of soil organic matter content with depth. In both Greenfield and Wasco sandy loams, the degradation rate of CH_3Br in soil layers from 0 to 270 cm could be estimated from soil organic matter content. Sorption of CH_3Br on moist soils was generally limited, and varied with soil depth. The degree of sorption could be predicted from soil moisture alone or soil moisture and organic matter content.

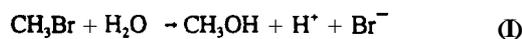
INTRODUCTION

Methyl bromide (bromomethane, CH_3Br) is the most widely used fumigant in crop production, and commodity and structure preservation (1). Its use in soil fumigation is currently vital for the economic viability of crops including strawberries, tomatoes, peppers, eggplants, tobacco, ornamentals, nursery stock, vines and turf (1,2). The production and sales of this fumigant in 1990 reached 63,000 tons world-wide, approximately 80% of which was used as a soil fumigation agent prior to planting (1). CH_3Br along with other halogenated organic compounds, however, have been reported to cause ozone depletion in the stratosphere. Extensive concerns have been raised about the environmental impact from the continuing use of CH_3Br (1).

Due to its extremely high vapor pressure (1420 mm Hg at 20°C) and low boiling point (3.56°C), CH_3Br

disperses rapidly from the injection point in soil and it is suspected that 30-90% of the injected CH_3Br may reach the soil surface and escape into the atmosphere (1). The emission rate depends on the use of a soil cover and injection depth, as well as on soil conditions such as soil texture, moisture content, organic matter content and temperature (3-5). Brown and Rolston (6) classified the processes involved in the behavior of CH_3Br in the soil environment as reversible and irreversible sink processes. Reversible sink processes include physical adsorption-desorption, reversible chemical adsorption-desorption, and dissolution-distillation from the soil water. Irreversible sink processes include irreversible chemical bonding and degradation leading to the production of Br^- . Degradation and sorption of CH_3Br in the soil profile are the two most important processes governing the amount of CH_3Br reaching the soil surface and, consequently, the quantity emitted into the atmosphere.

Degradation of CH_3Br in soil after fumigation is evidenced by the accumulation of Br^- in the soil profile and in the groundwater (7-9). Soil covers, usually plastic sheets, are often applied to increase the residence time of CH_3Br in soil and therefore increase the extent of degradation after application. Though numerous studies have evaluated the movement and efficiency of CH_3Br in the soil after application, the significance and mechanisms of environmental degradation of this fumigant have not been adequately studied independent of other processes. The absence of this information could be due to the high toxicity of CH_3Br and the difficulties in confining it. As a result of its extremely diffusive and mobile nature, results reported from field trials only indicate the overall behavior of CH_3Br and do not account for the contribution of each individual process *in situ*. It is generally accepted that hydrolysis and methylation are the two main degradation pathways for CH_3Br in the soil environment. CH_3Br undergoes nucleophilic substitution according to an SN_2 reaction:



Both H_2O and a nucleophilic group on soil organic matter (OM) interact with the C-center, resulting in the substitution of OH or OM for Br (reactions I and II, respectively).

In soils of low organic matter content, degradation could be expected to be primarily a consequence of hydrolysis in soil solution. In organic matter rich soils, methylation by CH_3Br has been suggested as the main reaction responsible for the degradation of CH_3Br (10). Both N and S have been suggested as possible nucleophilic moieties on the vaguely-defined OM species in reaction II, though experimental evidence is lacking. Little information is available on the sorption behavior of CH_3Br gas on soil under controlled conditions. Arvieu (10) indicated that soils of low organic matter content may adsorb CH_3Br via chemical binding.

After application, CH_3Br diffuses rapidly throughout the soil profile from 0 to 3-4 meters of depth, depending on the soil conditions and injection depths (11,12). Since many edaphic parameters such as soil texture, organic matter content and moisture level may change drastically with depth, it is expected that CH_3Br at different depths has different patterns of degradation and sorption behavior. However, the relationships between degradation

and sorption of CH_3Br and soil depth have not been investigated.

In this study, extent and rate of degradation of CH_3Br were determined in 4 selected surface soils of different properties under controlled conditions in an effort to quantify the controlling factors. Attempts were also made to establish correlations between degradation and sorption of CH_3Br and soil depth from 0 to 270 cm from two locations in Southern California where CH_3Br is commonly used. The information will be useful in providing the parameters required for mathematical modelling of the behavior of CH_3Br in soil, and to assess the importance of these processes in the loss of CH_3Br to the atmosphere after agricultural applications.

MATERIALS AND METHODS

Soils and Clay Materials

Four soils, Greenfield sandy loam, Wasco sandy loam, Linne clay loam and Carsetas loamy sand, were selected for this study. A sample of Greenfield sandy loam was taken from the surface layer (O-30 cm) at the University of California Moreno Valley Experimental Station near Riverside, California; Wasco sandy loam (O-30 cm) was taken near Shafter, California; and Carsetas loamy sand (O-30 cm) was taken from the University of California Coachella Valley Experimental Station near Indio, California. For the Greenfield sandy loam and Wasco sandy loam, samples of subsurface soils from 61-90, 121-150, 181-210 and 241-270 cm depths were also taken using a hand auger. All the soils were kept in closed glass jars at room temperature to maintain the original moisture content, and remixed to reincorporate and redistribute moisture within the sample just before use in experiments. Aged Linne clay loam, obtained from the soil bank at the University of California, Riverside, was air-dried. Soils were subject to different handling to modify the moisture content before use. Air-dried soils were prepared by air-drying, grinding, then sieving (2mm). Oven-dried soils were prepared by drying the air-dried soils at 115°C for 18h. Soils directly from the jars, except Linne clay loam, were defined as “moist” soils. Moist Linne clay loam was prepared by adding deionized water equivalent to 5% of the soil weight to the air-dried soil and equilibrating for at least one week before use. Montmorillonite K_{10} and kaolin were obtained from Aldrich Chemical Co. (Milwaukee, WI). Clays directly from the original bottles were used as air-dried clays. Moist montmorillonite and kaolin were prepared by equilibrating the materials for one week in a closed desiccator containing a small amount of water. Oven-dried clays were prepared by drying air-dried materials at 115°C for 18h before use.

Some of the physico-chemical properties of the soils and clays used in the study are given in Table 1. Total carbon content (TC%) in oven-dried soils (115°C for 18h) was measured using the dry-combustion method on a NA 1500 CNS Analyzer (Carlo Erba, Italy). Total inorganic carbonates (TIC%) in the oven-dried soils was determined by reacting the soil with HCl and measuring the *change* of pressure in a closed vessel due to the release of CO_2 (13). Organic carbon content (OC%) was estimated by subtracting TIC% from TC%, and *organic* matter content (OM%) was derived from OC% by using the formula: $\text{OM}\% = 1.724 \times \text{OC}\%$. Texture was

Table 1. Some Properties of Soils Used

Soil	Depth (cm)	OM (%)	Clay (%)	Surface ^b Area(m ² g ⁻¹)	pH(H ₂ O)
Greenfield SL	0 - 30	0.921	9.5	14.4	7.39
	61 - 90	0.427	14.7	19.8	8.16
	121-150	0.238	4.9	12.7	7.93
	181-210	0.118	3.0	6.2	8.25
	241-270	0.131	3.7	8.0	7.97
Wasco SL	0 - 30	0.646	4.3	12.0	6.98
	61 - 90	0.234	4.0	11.9	8.03
	121-150	0.225	4.2	15.4	8.52
	181-210	0.161	7.4	13.9	8.00
	241-270	0.109	17.5	25.4	8.07
Linne CL	0 - 30	2.989	25.1	19.8	7.23
Carsetas LS	0 - 30	0.222	0.1	2.0	8.02

^a SL=sandy loam; CL=clay loam; LS=loamy sand.

^b External surface area measured as N₂ adsorption.

determined by the hydrometer method (14). External surface area was estimated by the adsorption of N₂ on oven-dried materials with a Flow Sorb II 2300 (Micromeritics, GA) (15). Moisture contents in all soil and clay materials determined at the termination of each experiment by drying at 115°C for 18h are given in Table 2.

CH₃Br Gas and He&space Vials

CH₃Br with a purity of 99.5% was purchased in a lecture bottle from Matheson Gas Products Inc. (East Rutherford, NJ)[†]. CH₃Br gas was introduced via a needle valve, teflon tubing and hydraulic needle into a 500-mL Teflon sampling bag (Fisher Scientific Inc.) in a fume hood and used as the stock gas for all the treatments. The CH₃Br gas in the sampling bag had a vapor density of 3.97 mg mL⁻¹ at 25°C under normal atmospheric pressure. All studies were conducted in 21.6-mL headspace vials (Supelco Inc., Bellefonte, PA). Introduction of CH₃Br gas into vials (with or without soil) was made with a direct delivery of a known volume of CH₃Br gas from the stock bag into the deep pan of the vials using gas-tight syringes (Hamilton Co., Reno, NV). The treated vials were sealed immediately with aluminum seals lined with PTFE-faced butyl rubber septa (Supelco Inc., Bellefonte,

[†] Names of products are included for the benefit of the reader and do not imply endorsement or preferential treatment by USDA.

Table 2. Moisture contents of moist, air-dried and oven-dried soil and clay materials

Matrix'	Depth (cm)	Moisture Content (% , wt/wt)		
		Moist	Air-dried	Oven-dried
Greenfield SL	0 - 30	6.49	1.88	0
	61- 90	11.63		
	121-150	9.83		
	181-210	4.64		
	241-270	6.13		
Wasco SL	0 - 30	8.81	1.64	0
	61 -90	8.21		
	121-150	9.16		
	181-210	9.41		
	241-270	12.20	-	
Linne CL	0 - 30	11.34	5.14	0
Carsetas LS	0 - 30	5.56	0.43	0
Montmorillonite				0
Kaolin				0

*SL= sandy loam; CL=clay loam; LS=loamy sand.

PA) using a hand crimper. In preliminary tests, these vials did not leak significantly over a time period of 3 weeks ($4.5 \pm 2.4\%$ of amount spiked, $n=20$). Spiking with CH_3Br gas directly instead of using CH_3Br dissolved in an organic solvent eliminated possible interferences from the carrier solvent.

Degradation in Soil and Clay Minerals

Ten grams (oven-dry weight) moist, air-dried, or oven-dried surface soil were placed in headspace vials and $500\text{-}\mu\text{L}$ CH_3Br gas (1.99 mg or $20.9\ \mu\text{mol}$) was added to each vial. The vials were sealed immediately and incubated in the dark at room temperature ($25 \pm 1^\circ\text{C}$). A set of vials not treated with CH_3Br was used as soil-only controls. At predetermined time intervals, two vials from each treatment and the controls were opened and the residual CH_3Br in the vials was vented in a fume hood for 15 min. All the soil was then transferred into a 125-mL beaker, and 50 mL deionized water and 0.5 mL 5.0 M sodium nitrate (ion activity adjustor) were added. The soil-water mixture was stirred thoroughly with a glass rod and the soil particles allowed to settle for 15 min before Br^- concentration in the supernatant was measured. Measurement of Br^- was conducted with an Accumet model 25 pH/ISE meter (Fisher Scientific Co., Pittsburgh, PA) coupled with a bromide ion specific electrode and a double junction reference electrode. Readings were taken 2 min after the immersion of electrodes. Standard curves

consisting of at least 4 concentration points were prepared each time just prior to the analysis of samples. Soil-less vials were also treated and kept under the same conditions, and CH_3Br in the headspace was analyzed on the gas chromatograph (GC) periodically to monitor and correct for the loss of CH_3Br in the vials due to leakage.

In a separate study, 10.0 g (oven-dry weight) of moist Greenfield sandy loam or Wasco sandy loam from 0-30, 61-90, 121-150, 181-210 or 241-270 cm below the surface was weighed into the headspace vials, and 500 μL CH_3Br gas was added. The treated vials were closed immediately and kept in the dark at room temperature ($25 \pm 1^\circ\text{C}$). Two duplicate vials were removed from each treatment and analyzed for the production of Br^- at different time intervals after treatment. Blank vials containing the same amount of CH_3Br were analyzed periodically to monitor the loss of CH_3Br due to leakage in the containers during the experiment. The same procedures were used as described above for preparing and measuring Br^- concentration in the samples.

In a study to evaluate the capacity of clay minerals to degrade CH_3Br , 2.0 g (oven-dry weight) of moist, air-dried, or oven-dried montmorillonite K_{10} or kaolin was weighed into the headspace vials, and 500 μL CH_3Br gas was added. The treated vials were sealed immediately, and kept in the dark at room temperature ($25 \pm 1^\circ\text{C}$). Duplicate samples were analyzed for Br^- periodically using the same procedures as described for soil samples. Blank controls were prepared and analyzed in the same way to monitor the recovery of CH_3Br in the containers.

Sorption on Surface and Subsurface Soils

Sorption isotherms of CH_3Br on surface and subsurface soils with moisture maintained at the original field water content were obtained using the batch equilibration method in the headspace vials. Similar headspace methods were used by Garbarini and Lion (16) and Rao et al. (17) in their studies of sorption of other volatile compounds in soil. Vials containing 10.0 g (oven-dried weight) of moist Greenfield sandy loam or Wasco sandy loam from different depths were spiked with approximately 20, 60, 200, and 600 μL of CH_3Br gas, and the vials were closed immediately. Control vials without soil were also spiked with the same amount of CH_3Br and the actual amount of CH_3Br added for each concentration point was determined by analyzing CH_3Br in these vials. Three replicates were used for each concentration level. All the vials were equilibrated for 24 hr in the dark at room temperature ($25 \pm 1^\circ\text{C}$). To determine the concentration of CH_3Br in the vapor phase, 100 μL of the headspace atmosphere was injected into the GC by hand using a gas-tight syringe. Preliminary studies showed that equilibrium was completed within 24 hr in these soils under the experimental conditions. The free headspace volume in the vials containing soil was measured by weighing the vials before and after filling with water, and was estimated to be 16.8 to 17.2 mL for vials containing 10.0 g Greenfield sandy loam, and 16.9 to 17.2 mL for vials containing 10.0 g Wasco sandy loam. The difference in headspace vapor concentrations of CH_3Br between the soil-less controls and vials containing soil at equilibrium was assumed to be the amount of CH_3Br sorbed on soil (adsorbed on soil plus that dissolved in soil water).

Analysis of CH₃Br

CH₃Br in the headspace of the vials in the sorption experiment was determined on a Hewlett Packard HP5890 GC with an electron capture detector (Hewlett Packard Co., San Fernando, U.S.A.). The GC conditions were, as follows: RTX-624 capillary column (30 m × 0.25 mm × 1.4 μm, Restek Corp., Bellefonte, PA); carrier gas: helium at 1.1 mL min⁻¹ column flow rate; detector gas: 5% methane + 95% argon; oven temperature: 35 °C; injection port temperature: 85 °C; and detector temperature: 240 °C. **CH₃Br** was eluted 2.30 min after the injection under these conditions. Calibration curves of **CH₃Br** generated with various known amounts of **CH₃Br** were found slightly non-linear over a concentration range of 3 orders of magnitude, and a 2nd-order fitting was therefore used for the quantitation.

RESULTS AND DISCUSSION

Degradation as a Function of Organic Matter Content

Of the 4 selected surface soils, Linne clay loam was the highest in organic matter content, while Carsetas loamy sand was the lowest (Table 1). Degradation of **CH₃Br** to Br⁻ depended on the soil type, and followed the first-order reaction in all the soils under moist conditions ($r = 0.945 - 0.995$) (Figure 1 and Table 3). The most extensive degradation was found in Linne clay loam and the least in Carsetas loamy sand under both air-dried and moist conditions. However, a similar pattern was not noted for the oven-dried soils. Based on the production of Br⁻, the degradation rate constant (k) of **CH₃Br** in each soil was calculated, assuming first-order kinetics (Table 3). Correlation analysis between the k values and the selected soil properties revealed that the degradation of **CH₃Br** in moist and air-dried soils was highly dependent on soil organic matter content (OM%), as described respectively in equations 1 and 2:

$$k_{\text{air-dried}} = 0.0090 + 0.0174(\text{OM}\%) \quad (r = 0.999, n=4) \quad (1)$$

$$k_{\text{moist}} = 0.0116 + 0.0364(\text{OM}\%) \quad (r = 0.989, n=4) \quad (2)$$

However, similar correlation did not exist between the degradation rate constant k and soil OM% in oven-dried soils, as indicated with the poor r value for equation 3:

$$k_{\text{oven-dried}} = 0.0206 - 0.0023(\text{OM}\%) \quad (r = 0.454, n=4) \quad (3)$$

Dependence of **CH₃Br** degradation on soil organic matter content agreed well with the work reported previously (10). In a displacement experiment using soil columns under laboratory conditions, Brown and Rolston (6) found that the rate of Br⁻ production was greatest with muck, intermediate with loam, and least with sand, decreasing in the order of the decrease of soil organic matter content. The mechanisms involved in the

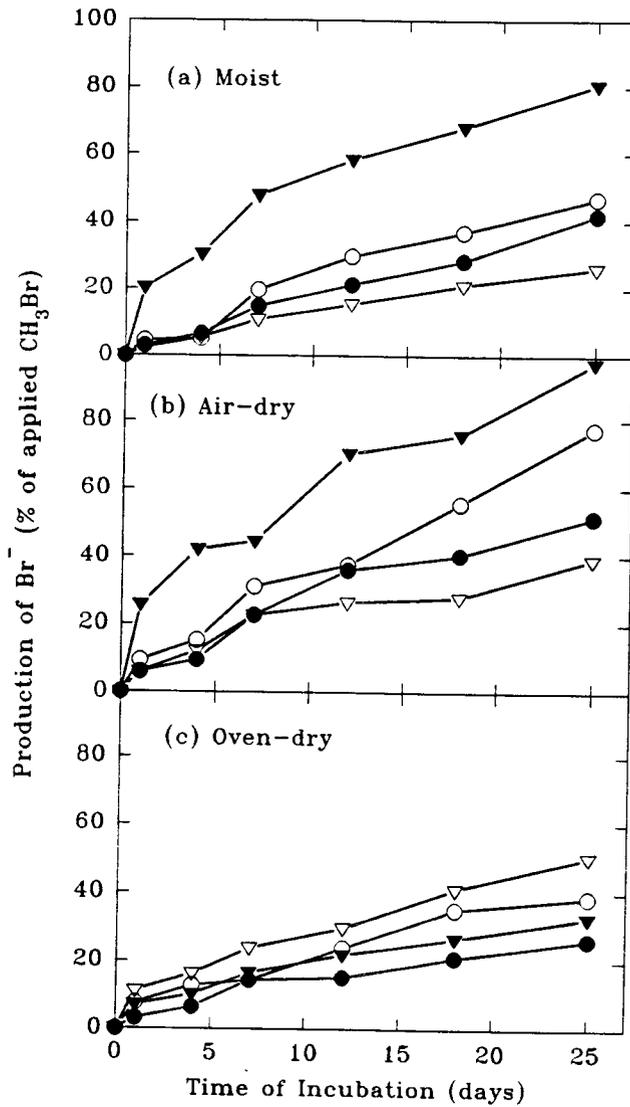


Figure 1. Degradation of CH₃Br in (a) moist, (b) air-dried, and (c) oven-dried soils

(○ = Greenfield sandy loam; ● = Wasco sandy loam; ▽ = Carsetas loamy sand; ▼ = Linne clay loam)

Table 3. Degradation rate constant k (day⁻¹) of CH_3Br in 4 selected surface soils under different moisture conditions

Moisture level	Soil ^a	k	r(n=12)
Moist	Greenfield SL	-0.0256	0.991
	wasco SL	-0.0207	0.994
	Carsetas LS	-0.0121	0.991
	Linne CL	-0.0608	0.991
Air-dried	Greenfield SL	-0.0548	0.977
	wasco SL	-0.0287	0.988
	Carsetas LS	-0.0179	0.962
	Linne CL	-0.1189	0.944
Oven-dried	Greenfield SL	-0.0193	0.991
	wasco SL	-0.0117	0.979
	Carsetas LS	-0.0259	0.982
	Linne CL	-0.0148	0.985

^a SL= sandy loam; LS- loamy sand; CL= clay loam.

effect of soil organic matter in the degradation of CH_3Br are not well understood. It is likely that the methyl group on CH_3Br is transferred by nucleophilic substitution to nucleophilic amino groups (-NH₂) or mercapto groups (-SH) which are usually abundant in humic substances in soil. This same type of alkylation is also responsible for the toxicity of CH_3Br and other toxic alkylating agents (such as mustard gas) in living organisms. This assumption is supported by the significant correlation between degradation rate and total nitrogen content (N%) in the moist and air-dried soils:

$$k_{\text{air-dried}} = 0.0073 + 0.3424(\text{N}\%) \quad (r = 1.000, n=4) \quad (4)$$

$$k_{\text{moist}} = 0.0080 + 0.7158(\text{N}\%) \quad (r = 0.987, n=4) \quad (5)$$

Production of Br⁻ in all the soils except Carsetas loamy sand was reduced when the free soil water was removed by oven-drying. However, degradation in oven-dried Carsetas loamy sand increased, and was the greatest among all the oven-dried soils. Different mechanisms from those in moist and air-dried soils were apparently involved in the degradation of CH_3Br in oven-dried soils.

Degradation as a Function of Moisture

Response of CH_3Br degradation to soil moisture was dependent on the types of soil (Figure 1). Among

all the soils except Carsetas loamy sand, greatest degradation of CH_3Br was found in the air-dried soils, and least in oven-dried soils. In Linne clay loam, degradation in oven-dried soils was greatly reduced compared to that in air-dried and moist soil. In Carsetas loamy sand, however, degradation followed the order: oven-dried > air-dried > moist soil.

In soils containing water, three phases - solid, water and air - are involved in governing the distribution of CH_3Br . In soils containing organic matter, the presence of a minimum amount of water, such as in the air-dried Linne, Greenfield and Wasco soils, seems to be necessary for CH_3Br to be partitioned into the organic matter phase and for the methylation of organic matter to proceed. However, as the amount of water increases, dissolution of CH_3Br into the soil water becomes important, which consequently lowers the proportion of CH_3Br distributed into the organic matter phase and therefore the methylation of CH_3Br , as seen with the reduced CH_3Br degradation in moist Linne, Greenfield and Wasco soils. Partitioning of volatile organic molecules into soil organic matter has been suggested as the major mechanism for adsorption in moist soils (18,19). It is reasonable to hypothesize that different reaction velocities exist for CH_3Br methylation on organic matter and its hydrolysis in soil water. In soils containing organic matter, it appears that degradation caused by methylation was more important than that caused by hydrolysis, as evidenced with the reduced degradation in moist soils. The stereoconfiguration of soil organic matter substantially changes when thoroughly oven-dried, and this may also account for the observed differences in degradation between oven-dried and moist or air-dried soils. The effect of soil water on the CH_3Br degradation in organic matter-poor Carsetas loamy sand, however, was opposite from the other three soils. Degradation decreased with increases of soil water content. Surface-induced transformation of CH_3Br may be responsible for this phenomenon.

Degradation on Clay Surfaces

As discussed above, degradation of CH_3Br in oven-dried soils indicated the possibility of surface-induced catalytic decomposition. To confirm this, degradation of CH_3Br on moist, air-dried and oven-dried montmorillonite and kaolin surfaces was studied for 25 days at room temperature (Figure 2). Enhanced degradation of CH_3Br was observed on oven-dried kaolin and montmorillonite clays. The existence of free water on clay surfaces, however, effectively suppressed the degradation, as indicated by the proportional decrease in degradation with the increase of moisture on both materials. For example, when the moisture content changed from 0 on the oven-dried kaolin to 2.65% on the moist kaolin, the production of Br^- decreased from 29.8% to 0.12% during the 25 days of incubation. More degradation occurred on oven-dried and air-dried kaolin than on montmorillonite K_{10} , though the latter had a surface area 9 times that of the former. It seems that it is the type of surface rather than the area that determines the rate of reaction. Suppression of degradation by water may be attributed to the competitive displacement of CH_3Br on the adsorption sites by water molecules. Water molecules showed much higher affinity than the molecules of many organic compounds for mineral surfaces (20-25). Based on these observations, adsorption likely led to the degradation of CH_3Br on oven-dried mineral surfaces.

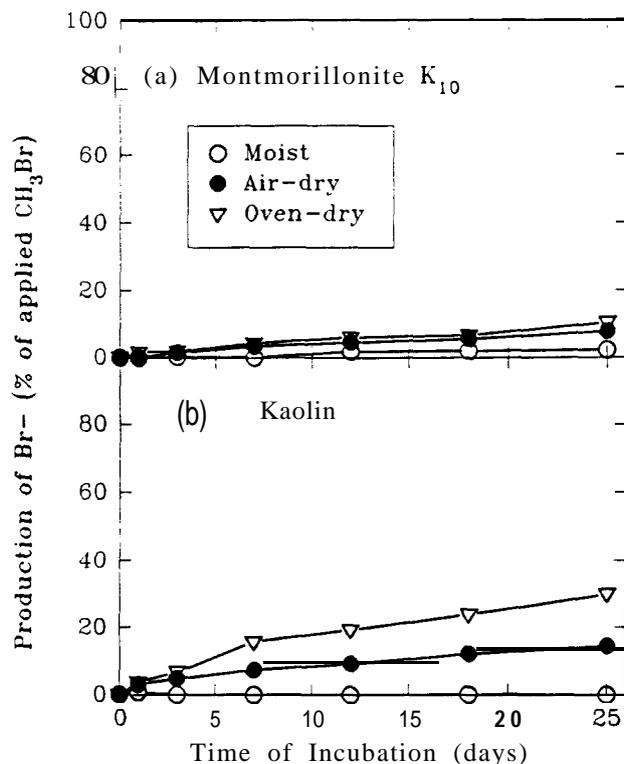


Figure 2. Degradation of CH_3Br in moist, air-dried and oven-dried (a) montmorillonite K₁₀, and (b) kaolin

The catalytic conversion of organophosphorus insecticides in the adsorbed state has been extensively studied (26-28). Hydrolysis of the weak phosphate ester bond has been proposed as the pathway for the surface-related degradation of most organophosphate esters studied. The reaction requires specific adsorption sites, and is highly dependent on the moisture content and cation type (26). It is appropriate to point out, nevertheless, that in soils under most field conditions, since a significant amount of water is always present on the mineral surfaces, the contribution of surface catalyzed degradation to the overall degradation of CH_3Br should be negligible.

Degradation as a Function of Depth

The physico-chemical properties of Greenfield and Wasco sandy loams vary with depths at which the soils were sampled (Table 1). The organic matter content in Greenfield sandy loam decreased continuously with depth from 0 to 210 cm. In Wasco sandy loam, the organic matter content decreased sharply from 0 to 60 cm, followed by a decline at a lesser rate from 60-270 cm. The moisture content appeared to vary with clay content in both soils. Degradation of CH_3Br in all the soils followed the first-order reaction, and the calculated r fell between

Table 4. Degradation rate constant k , k_f (day⁻¹) and estimated half-degradation time ($T_{1/2}$) of CH₃Br in soils from different depths

Soil	Depth(cm)	k	k_f	$T_{1/2}$	r(n= 12)
Greenfield SL	0 - 30 cm	-0.0253	-0.0878	7.9	0.987
	61- 90 cm	-0.0212	-0.0864	8.0	0.994
	121-150 cm	-0.0133	-0.0537	12.9	0.986
	181-210 cm	-0.0066	-0.0254	27.3	0.990
	241-270 cm	-0.0084	-0.0328	21.1	0.987
wasco SL	0 - 30 cm	-0.0177	-0.0625	11.1	0.997
	61- 90 cm	-0.0093	-0.0369	18.8	0.986
	121-150 cm	-0.0106	-0.0422	16.4	0.996
	181-210 cm	-0.0096	-0.0385	18.0	0.995
	241-270 cm	-0.0100	-0.0418	16.6	0.994

*SL- sandy loam.

0.986 - 0.997 (Table 4). Degradation of CH₃Br in both Greenfield sandy loam and Wasco sandy loam changed with depth (Figure 3). While correlating the estimated degradation rate constant (k) and the selected soil properties, significant dependence of degradation on soil organic matter content (OM%) was again observed. Degradation rate constants in Greenfield and Wasco sandy loams may be predicted from equations 6 and 7, respectively, based only on the organic matter content:

$$k = 0.0068 + 0.0224(\text{OM}\%) \quad (r = 0.923, n=5) \quad (6)$$

$$k = 0.0071 + 0.0159(\text{OM}\%) \quad (r = 0.956, n=5) \quad (7)$$

Assuming the degradation rate of CH₃Br is proportional to the soil/air ratio in a closed system and the typical soil bulk density is 1.5 g cm⁻³ for the top layer (0-30 cm) and 1.7 g cm⁻³ for the lower layers (61-270 cm), the degradation rate constant (k) under field conditions was estimated from k (Table 4) which was determined at a soil/air ratio of approximately 0.22. The half-degradation time ($T_{1/2}$) in the field was then calculated from the k_f values by using the formula: $T_{1/2} = 0.693/k$, (Table 4). As shown in Table 4, CH₃Br would become more persistent in the deeper soil layers, and its half-life of degradation would be generally between 1-4 weeks. With these degradation rates, it is necessary to confine CH₃Br for at least 1-2 months in the soil profile to assure a near-complete degradation. In practice, since covers are only used for a short period, e.g., 5-7 days, and most of the tarping materials are not effective in retarding CH₃Br, less degradation and higher emission are likely. To reduce

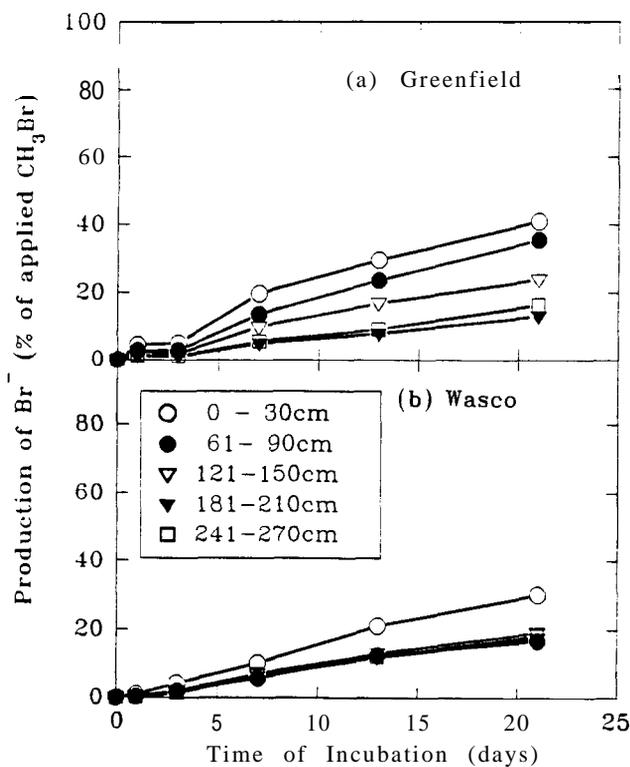


Figure 3. Degradation of CH_3Br in surface and subsurface soils of (a) Greenfield sandy loam and (b) Wasco sandy loam

the emission of CH_3Br into the atmosphere from soil applications, it is necessary to use more effective covers and longer covering time, or other management strategies which may increase the residence time of CH_3Br in the soil profile and hence its degradation.

Sorption as a Function of Depth

“Sorption” of CH_3Br on moist soils as measured herein is a combination of dissolution and adsorption. Sorption isotherms derived from the batch equilibration experiments showed that the isotherms were near-linear over the entire concentration range for all the Wasco soils and over the low part of the concentration range for the Greenfield soils (Figure 4). Sorption on Greenfield sandy loam was greater than that on Wasco sandy loam for all depths. However, sorption was very limited on both soils. Using the measured vapor concentration of CH_3Br in the headspace and Henry’s constant, the proportion of CH_3Br dissolved in the soil water was estimated. Dissolution of CH_3Br into the soil water accounted for 38-72% of the CH_3Br sorbed on Greenfield soils, and near

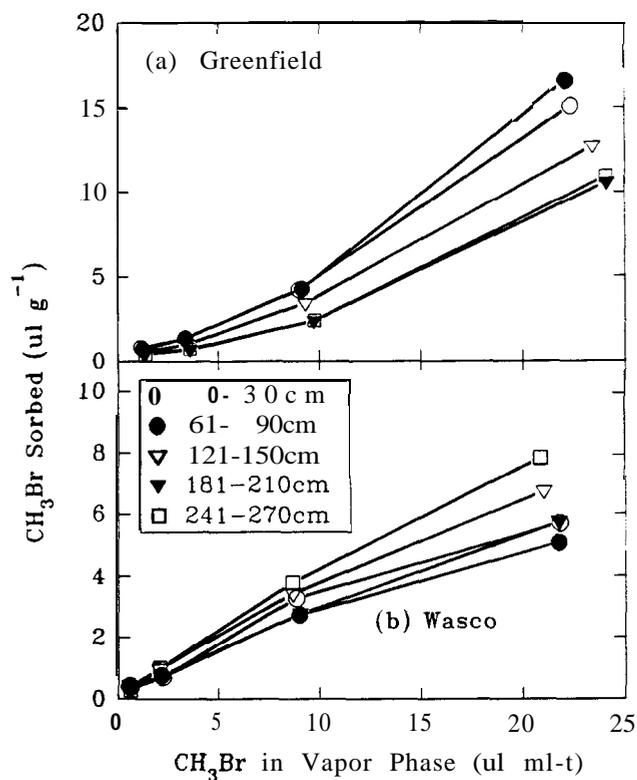


Figure 4. Sorption isotherms of CH_3Br on surface and subsurface soils of (a) Greenfield sandy loam and (b) Wasco sandy loam

100% of the sorbed CH_3Br on the Wasco soils. Direct adsorption of CH_3Br on the Wasco soils was so low that the slopes of the linearized sorption isotherms could be well predicted by using moisture content alone:

$$S = 2.68 + 0.244(M\%) \quad (r = 0.917) \quad (8)$$

where: S = slopes of the linearized sorption isotherms; and $M\%$ = moisture content in percentages. This indicates that the measured sorption was mainly due to the dissolution of CH_3Br in the soil water. Suppression of adsorption of other volatile compounds on soils by water have been extensively reported (19-24). In Greenfield sandy loam, a similar relationship with moisture content could not be established. However, when both soil moisture and organic matter content were included, the following expression was obtained:

$$S = 0.262(\text{OM}\%) + 0.031(M\%) + 0.256 \quad (9)$$

From equation 9, it is clear that both soil moisture and organic matter contributed to the sorption behavior of CH_3Br in Greenfield surface and subsurface soil.

CONCLUSIONS

Degradation of CH_3Br to Br^- in soil was highly dependent on the organic matter content in air-dried and moist soils. More degradation occurred in organic matter-rich Linne clay loam than in the other three soils. In oven-dried Carsetas loamy sand and montmorillonite and kaolinite clays, degradation of CH_3Br was significantly enhanced and surface-catalyzed decomposition of CH_3Br was suggested as the mechanism involved. However, methylation of soil organic matter by CH_3Br may be the predominant pathway for the degradation of CH_3Br in most soils under moist and air-dried conditions, and surface-catalyzed decomposition should be of little importance in the field due to the effective suppression of this reaction by soil water. Within soil profiles, degradation of CH_3Br decreased with depth, following the decrease in soil organic matter content with depth. Sorption of CH_3Br on the moist soils was generally very limited, and dissolution into soil water accounted for the majority of the measured sorption. This investigation of soil constituents affecting CH_3Br degradation and sorption indicates that substantial retention and degradation of CH_3Br within soil profiles of agricultural soils is unlikely, and that CH_3Br applied to the soil may readily diffuse to the soil surface and escape into the atmosphere. Prudent management practices to retard volatilization may minimize such risks, however study of these field management practices is outside of the scope of this investigation.

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