Mechanism of Degradation of Methyl Bromide and Propargyl Bromide in Soil

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ABSTRACT

The degradation of methyl bromide (MB) and propargyl bromide (PB) was investigated in soil and water to obtain information on the mechanism of degradation. It has been suggested that primary alkyl halides (including MB and the potential alternatives PB and methyl iodide) can undergo S_N2 nucleophilic substitution with nucleophilic sites on soil organic matter (i.e., $-NH_2$, –NH, –OH, –SH). The pattern of product formation observed in this study provides more direct evidence that fumigants that are primary alkyl halides can alkylate soil organic matter and that this may be a significant mechanism of degradation in soil. Degradation in water samples (hydrolysis) formed Br^- and the corresponding alcohol (propargyl alcohol from PB, methanol from MB) in equimolar amounts. The rate of hydrolysis was not significantly different from the rate of Br^- formation for both MB and PB. Degradation in two soils resulted in the formation of Br^-, but very little production of the corresponding alcohol, indicating that some mechanism other than hydrolysis must be occurring in the soil. Degradation of MB and PB was much more rapid in the higher-organic-matter clay loam soil than in the sandy loam soil. Spiking ^{14}C-labeled MB to soil resulted in the formation of nonextractable (soil-bound) ^{14}C, which increased as the extractable ^{14}C decreased. Microbial oxidation was not significant in these soil samples, which were sterilized through autoclaving and/or treatment with high concentrations of fumigants. These results provide further experimental evidence that MB, PB, and similar compounds can alkylate soil organic matter.

Soil fumigants are widely used in intensively farmed areas and in greenhouses to control nematodes, weeds, fungi, and insects. Methyl bromide, one of the most widely used soil fumigants, is scheduled to be phased out in the USA by 2005 because it has been implicated in the depletion of stratospheric ozone (USDA, 1999). Management practices and low-permeability tarps have been shown to be effective in reducing MB emissions to the atmosphere (Wang et al., 1997a,b). It is possible that even though anthropogenic emissions of MB resulting from soil fumigation can be reduced to insignificant levels, the 2005 phase out will remain (Yates et al., 1998). This has led to a search for a replacement for MB that has focused on identifying alternative chemicals and management practices that would provide adequate pest control at an acceptable cost. Potential chemical alternatives include methyl iodide (MeI) (Ohr et al., 1996) and PB (3-bromopropyne) (Yates and Gan, 1998). These chemicals are structurally similar to MB (primary alkyl halides), but have a low ozone-depletion potential and would not be subject to phase-out under the Clean Air Act.

The lower alkyl halides are broad-spectrum biocides, reacting with nucleophilic groups in amino acids and peptides (e.g., $-NH_2$ and –SH groups) via S_N2 nucleophilic substitution (Ohr et al., 1996). It is generally accepted that degradation of MB in soil can be due to hydrolysis, microbial oxidation, and reaction with soil substituents. Reaction of MB with water (hydrolysis) occurs through S_N2 nucleophilic substitution to form methanol and bromide ion:

$$CH_3\text{–}Br + H_2O \rightarrow CH_3\text{–}OH + Br^- + H^+$$

$$CH_3\text{–}Br + OH^- \rightarrow CH_3\text{–}OH + Br^-$$

It has been suggested that methyl bromide can react with nucleophilic sites on soil organic matter (–SH, –NH, $-NH_2$, –OH) via S_N2 nucleophilic substitution, resulting in the methylation of soil organic matter (Arvieu, 1983; Gan et al., 1994).

$$CH_3\text{–}Br + OM\text{–}NH \rightarrow OM\text{–}N\text{–}CH_3\ Br^- + H^+$$

$$CH_3\text{–}Br + OM\text{–}OH \rightarrow OM\text{–}O\text{–}CH_3 + Br^- + H^+$$

Methylation of organic matter as a MB degradation mechanism is supported by indirect experimental evidence. The rate of degradation of MB in moist or air-dry soils is observed to decrease with decreasing organic matter content (Brown and Jenkinson, 1971; Brown and Rolston, 1980; Gan et al., 1994; Shorter et al., 1995). Correlations between the N content of soil and degrada-

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Abbreviations: GC, gas chromatograph; MB, methyl bromide; MeI, methyl iodide; MeOH, methanol; PB, propargyl bromide; POH, propargyl alcohol.

tion rate have been noted (Arvieu, 1983; Gan et al., 1994). Arvieu (1983) noted that the MB degradation rate (production of Br^-) in peat increased as the exchangeable cation decreased in affinity for carboxylic groups, suggesting that MB was reacting with carboxylic groups on the peat. Gan and Yates (1996) measured the rate of disappearance of MB and MeI in water and in aniline (C_6H_5–NH_2) solution. They observed a decrease of ~90% in half-life for both MB and MeI in aniline solution compared with water. The products of degradation were *N*-methylaniline and *N*,*N*-dimethylaniline, verifying that nucleophilic substitution was occurring in aniline solution. Degradation of MB via nucleophilic substitution was observed in anaerobic sediment slurries (Oremland et al., 1994b): nucleophilic substitution reactions with sulfide in the sediments were indicated by the formation of methanethiol (MeSH) and dimethylsulfide with the concurrent depletion of MB. All known mechanisms of MB degradation in soil result in the release of Br^-, making formation of Br^- in soil a useful indicator of MB transformation. Since multiple degradation pathways (hydrolysis, methylation of organic matter, and microbial oxidation) of MB result in the formation of Br^-, analysis of the ion alone or loss of the parent compound can provide information on the rate and extent of degradation, but not about the mechanism.

To investigate the mechanism by which primary alkyl halides are abiotically transformed in soil, we monitored the formation of the products of MB and PB degradation in soil and water. We measured the production of bromide ion and the corresponding alcohol, MeOH for MB degradation and propargyl alcohol (POH) for PB degradation. Degradation studies were conducted in purified deionized water and two soils of differing organic matter content; experiments were conducted using autoclaved and nonautoclaved soil samples. Additional soil samples were spiked with ^{14}C-labeled MB to monitor the formation of bound ^{14}C residues. The pattern of product formation provided information on possible degradation mechanisms.

MATERIALS AND METHODS

Chemicals

Propargyl bromide (97% purity) and propargyl alcohol (>99% purity) were obtained from Fluka (Ronkonkoma, NY). Methyl bromide (>99% purity) was obtained from Great Lakes Chemical Company (West Lafayette, IN), ^{14}C-labeled MB (3.7×10^6 Bq, specific activity 7.4×10^{10} to 1.8×10^{11} Bq mol^{-1}, purity ≥97%) from New England Nuclear (Boston, MA), and methanol (≥99.9% purity) from VWR Scientific (West Chester, PA). Ethyl acetate was purchased from Fisher Scientific (Pittsburgh, PA). Purified deionized water with a conductance of 5.9×10^{-6} S m^{-1} was prepared using a Millipore (Bedford, MA) Nanopure system.

Soils

Arlington sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf) was collected from the University of California, Riverside Experiment Station in Riverside, CA. Linne clay loam (fine-loamy, mixed, thermic Calcic Pachic Haploxeroll) was collected from a site near Paso Robles, CA. Some soil properties are given in Table 1. Neither site has received application of soil fumigants for at least 20 yr. Soil was collected from the surface ~30 cm (sandy loam) or ~15 cm (clay loam). Soils were sieved to pass through a 2-mm screen. The initial moisture content of the soil was determined, then purified deionized water was added to bring the moisture content (w/w) to 10% (sandy loam) or 24% (clay loam). The moist soil was thoroughly mixed and sieved to 2 mm. Soil samples (10 g dry wt.) were placed in 21.6-mL headspace vials. Half of the soil samples, along with all equipment to be used to spike and crimp cap the vials, were sterilized by autoclaving. Samples to be autoclaved were capped with aluminum foil to minimize water loss during autoclaving. The autoclave cycle was 1 h at 121°C and 0.1 MPa, after which the items were removed, allowed to rest for 24 h, then autoclaved for an additional 1-h cycle. Since autoclaving changed the water content slightly, the moisture content of the soil samples was readjusted after autoclaving using sterile distilled deionized water.

Table 1. Properties of the soils used in this study.

	Arlington sandy loam	Linne clay loam
Organic carbon (g kg^{-1})	9.2	25.1
Inorganic carbon (g kg^{-1})	0.03	5.5
Sand (%)	74.6	36.7
Silt (%)	18.0	32.0
Clay (%)	7.4	31.3
pH	6.73	6.80
CEC ($cmol_c$ kg^{-1})†	5.95	29.86

† Cation exchange capacity.

Hydrolysis

For propargyl bromide samples, nonsterile purified deionized water (≈21 mL) was placed in 21.6-mL headspace vials and the exact amount of water in each vial was determined by weight. Headspace in each vial was minimal (≈0.6 mL). Each vial was spiked with 5 μL of PB by placing the needle of the microsyringe below the water line and injecting the liquid PB into the water; each vial was capped immediately after spiking with an aluminum seal and a Teflon-faced butyl rubber septum. Vials were incubated at room temperature (22°C). At various times, vials were removed and analyzed directly for PB, POH, and Br^-.

For methyl bromide samples, 8.8-mL vials were filled completely with nonsterile purified deionized water and the vials were capped with an aluminum seal and a Teflon-faced butyl rubber septum so that there was no headspace in the vial. Using a gas-tight syringe, 2.0 mL of MB saturated vapor was added to each vial by puncturing the septum and bubbling the MB into the inverted vial. The addition of MB gas produced some pressure in the vial and some liquid and gas escaped when the needle was removed. The vials were incubated inverted at 25 ± 0.1°C. At predetermined times, triplicate vials were removed and analyzed for MB, MeOH, and Br^-. To determine the reaction rate of MeOH in water, vials were prepared, spiked, and incubated in the same manner as for MB, except a microsyringe was used to add 2.0 μL of pure MeOH to each vial.

Aliquots were removed from the vials and transferred to gas chromatograph (GC) autosampler vials for PB, POH, MB, and MeOH determination. Calibration standards of PB, POH, MB, and MeOH were prepared in water in headspace vials and transferred to autosampler vials with minimal headspace. Samples for PB, POH, MB, and MeOH in water were injected

into a GC–mass spectrometer (MS) without extraction. The GC–MS was a Hewlett–Packard (Palo Alto, CA) 5890 GC interfaced with a Hewlett–Packard 7673 mass selective detector. The GC analysis used a Carbowax 20M column (24-m long × 0.2-mm i.d. × 0.2-μm film thickness) (Hewlett-Packard, Wilmington, DE), injection volume 3 μL (split), inlet temperature 230°C, and helium at a flow rate of 0.65 mL min^{-1} as the carrier gas. For PB (selected ion monitoring of m/z 118 and 120) and POH (m/z 32 and 55), the oven temperature program was 40°C held for 1 min, increased at a rate of 10°C min^{-1} to 160°C, and held for 0.1 min. Under these conditions, the retention times of PB and POH were 4.3 and 7.1 min, respectively. For MB (m/z 79, 80, and 94) the oven temperature was 33°C held for 2 min, increased at a rate of 70°C min^{-1} to 150°C, and held for 4.33 min.; the retention time was 1.5 min. For MeOH (m/z 29, 31, and 32) the oven was held at 70°C for 3.5 min, increased at a rate of 70°C min^{-1} to 150°C, and held for 3.36 min.; the retention time for MeOH was 1.6 min. Propargyl bromide and POH were sufficiently resolved to allow concurrent analysis in a single injection; separate injections were required for MB and MeOH determination.

An aliquot of each sample was removed for bromide analysis using ion chromatography. Samples were diluted 5 to 10 times with purified deionized water as necessary to attain concentrations within the calibration range of 0.5 to 25 mg L^{-1}. Samples (50 μL) were injected into a Dionex (Sunnyvale, CA) DX-100 ion chromatograph equipped with a 4-mm AS-14 column. The flow rate was 1.2 mL min^{-1} and the eluant was 3.5 m*M* Na_2CO_3 + 1.0 m*M* $NaHCO_3$. Under these conditions, the retention time of bromide was 5.4 min.

Degradation in Soil

Autoclaved and nonautoclaved soil samples in vials were spiked with either 2 μL of liquid PB, 2.0 mL of MB saturated vapor (sandy loam), or 1.0 mL of MB saturated vapor (clay loam) and the vials capped immediately with Teflon-faced butyl septa. This resulted in PB soil concentrations of 0.31 g kg^{-1} of dry soil and MB concentrations of 0.78 g (sandy loam) or 0.39 g (clay loam) kg^{-1} of dry soil. Assuming no sorption to soil and using a Henry's constant (K_H) of 0.30 for MB (Gan and Yates, 1996), a K_H of 0.051 for PB (Yates and Gan, 1998), and a particle density of 2.65 Mg m^{-3} for both soils, calculated MB soil gas concentrations were approximately 380 g m^{-3} for sandy loam and 160 g m^{-3} for clay loam. The PB soil gas concentrations were 90 g m^{-3} for sandy loam and 50 g m^{-3} for clay loam. Blanks consisted of moist soil that was not spiked. Autoclaved soils were spiked and capped in a laminar flow hood using a sterile syringe and capped with autoclaved septa and caps using a sterilized crimp capper. Autoclaved and nonautoclaved soil samples were incubated at 23.5 ± 0.1°C (PB degradation in sandy loam soil) or 25.0 ± 0.1°C (MB degradation and PB in clay loam soil). Six soil vials were reserved for time zero analysis. At each sampling time, six randomly selected vials were removed and frozen at −20°C until the end of the experiment, when all the soil samples were extracted. Blanks were removed and extracted at the end of the experiment.

Separate soil vials were used for extraction with organic solvent (PB and MB extraction) and with water (POH, MeOH, and Br^- extraction); triplicate samples were extracted at each sampling time. For PB and MB extraction, vials were removed from the freezer, decapped, and 10 mL of ethyl acetate was added, followed by 10 g of anhydrous sodium sulfate to remove residual water in the extract. Samples were decapped and solvent added to frozen samples to minimize fumigant loss from the vials. Vials were capped with Teflon-faced butyl septa and vortexed for 2 min, then placed on a reciprocating shaker table for 1 h. An aliquot of the solvent was withdrawn from each vial and transferred to a GC autosampler vial. For POH, MeOH, and Br^- extraction, vials were removed from the freezer, decapped, and 10 mL of water was added. Vials were capped and vortexed for 2 min, placed on the shaker for 1 h, then transferred to HDPE centrifuge tubes. Samples were centrifuged at 10 000 rpm for 10 min. An aliquot of the extract was transferred to a GC autosampler vial for POH or MeOH analysis. An additional aliquot was removed and diluted 10 times for Br^- analysis. Sample analysis was the same as for the hydrolysis experiment. Calibration standards for PB and MB were prepared in ethyl acetate; standards for POH, MeOH, and Br^- were prepared in purified deionized water.

Table 2. Recovery of compounds of interest from spiked soil samples (10 g dry weight).

Compound	Spiking Level	Recovery	
		Sandy loam	Clay loam
	μmol	%	
Methyl bromide	2.0	110 ± 17	97 ± 11
	12	127 ± 21	111 ± 3
Propargyl bromide	6.6	96 ± 4	102 ± 3
	26	90 ± 2	96 ± 0.6
Methanol	2.0	80 ± 19	Not detected
	12	97 ± 5	68 ± 0.7
Propargyl alcohol	8.5	94 ± 2	69 ± 1
	34	95 ± 1	78 ± 1
Bromide	6.3	94 ± 4	109 ± 0.4
	25	89 ± 5	107 ± 0.7

Recovery studies were conducted by spiking 10 g (dry wt.) of moist sandy loam (10% moisture content) and clay loam (moisture content 17%) soil with pure PB, MB, POH, MeOH, and Br^- in aqueous solution; separate soil samples were spiked at two levels for each analyte (Table 2). Samples were incubated overnight and frozen at −20°C until extraction. Five soil samples were used for each concentration level.

Because POH and MeOH were simultaneously being formed and degraded in soil samples spiked with PB and MB, it was necessary to correct resulting alcohol concentrations for the portion degraded in the course of the experiment. Separate soil samples were spiked with POH and MeOH to determine the rate of degradation of these reaction products. Arlington sandy loam soil (10% moisture) and Linne clay loam soil (24% moisture) were weighed into 21.6-mL vials (10 g dry wt.). Soil samples were spiked with 2 μL of POH or 2 μL of MeOH, mixed, and incubated at 23.5 ± 0.1°C (POH in sandy loam) or 25 ± 0.1°C (MeOH samples and POH in clay loam). Methanol degradation was determined in both autoclaved and nonautoclaved soil samples; POH degradation was measured only in nonautoclaved soil samples. Spiking resulted in soil concentrations of 0.19 g kg^{-1} dry soil for POH and 0.16 g kg^{-1} dry soil for MeOH. At each sampling time, replicate vials were removed and frozen at −20°C until extraction. Blanks (moist soil samples not spiked) were removed at the end of the experiment. Extraction and analysis for POH and MeOH were as described above. The rate of POH and MeOH degradation were determined by fitting a first-order model to the μmol of alcohol remaining. The μmol of alcohol formed in PB- or MB-spiked samples were corrected for degradation at each time point by multiplying the POH or MeOH (μmol) measured in extracts by the dimensionless factor $kt/(1 - e^{-kt})$ where k is the degradation constant for each alcohol (d^{-1}) and t is time (d).

For both hydrolysis and soil degradation, nonlinear regression using a first-order kinetic model was used to determine degradation rates. For the disappearance of the parent prod-

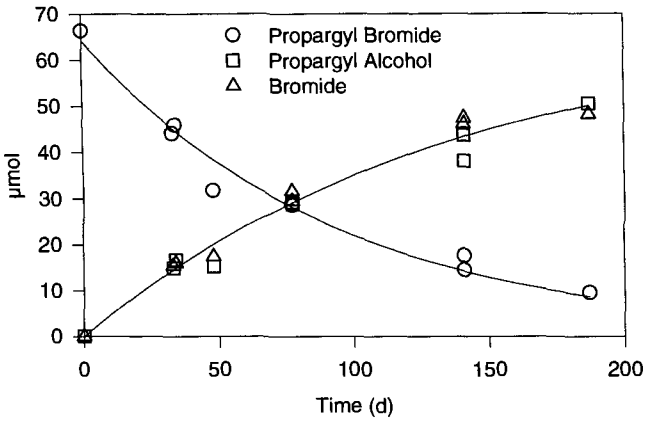

Fig. 1. Hydrolysis of propargyl bromide with concurrent formation of equimolar amounts of propargyl alcohol and Br^- in water.

uct, the model is $C = C_0 \times e^{-kt}$, where C is the µmol of compound remaining, C_0 is the µmol of the compound at time 0, k is the first-order degradation constant, and t is time. For product appearance, $C = C_0(1 - e^{-kt})$. Degradation rates were compared statistically using t-tests.

Degradation of Radiolabeled Methyl Bromide

Samples of Linne clay loam (10 g dry wt., 24% moisture) were prepared and half the samples autoclaved as described above. To prepare the spiking solution, liquid MB was added to ethyl acetate to give a solution containing 308.74 g L^{-1} methyl bromide. The ^{14}C–MB was dissolved in ethyl acetate and a 1-mL aliquot was added to the cold MB solution. The initial activity of this solution was determined and 20 µL spiked to each soil sample. Samples were capped immediately after spiking, mixed, and incubated at 23°C. At each sampling time, replicate soil samples were removed and frozen at −20°C until the end of the experiment, when all the samples were extracted.

Samples were extracted with 10 mL of ethyl acetate and dried with anhydrous sodium sulfate following the procedures described in the previous section. A 1-mL aliquot of the extract was removed from each vial (without decapping) using a gas-tight syringe and transferred into a 20-mL vial containing 19 mL of Liquicent (National Diagnostics, Atlanta, GA) scintillation cocktail. Carbon-14 was determined using a Beckman model LS 5000TD liquid scintillation counter (Beckman Scientific, Fullerton, CA) and corrected for quenching.

After extraction, the soil samples were decapped, air-dried, and the residual ^{14}C remaining in the soil was measured by combusting replicate 0.3-g portions of each sample in a Packard model 306 sample oxidizer (Packard Instruments, Meriden, CT), trapping the CO_2 evolved, and determining the ^{14}C using a Packard 1500 Tri-Carb Liquid Scintillation Analyzer. Activity of $^{14}CO_2$ recovered was corrected for oxidation efficiency and quenching.

RESULTS AND DISCUSSION

Recovery

The extraction and analysis methods used in this study resulted in recoveries near 100% for each compound at various spiking levels (Table 2); results were not adjusted for recovery. Very low concentrations of MeOH spiked to clay loam soil were not recovered; lower recovery of MeOH in unsterilized Linne soil could be partially

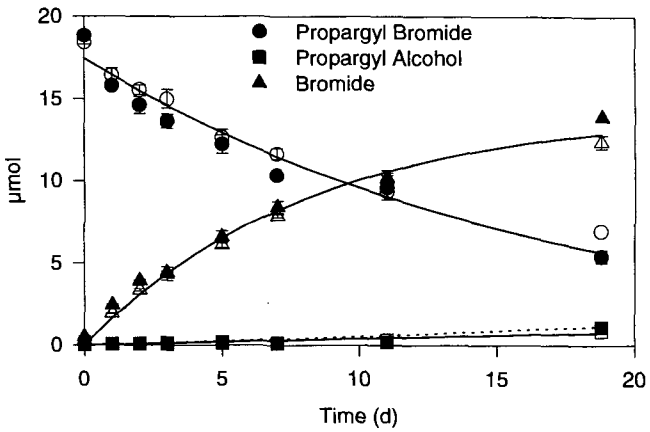

Fig. 2. Degradation of propargyl bromide in Arlington sandy loam soil with concurrent formation of Br^- and propargyl alcohol. Autoclaved soil samples are indicated by closed symbols, nonautoclaved samples by open symbols. Error bars indicate standard error in triplicate samples. Solid lines are first-order fit to data. Dotted line indicates propargyl alcohol after correction for propargyl alcohol degradation in nonautoclaved soil.

due to its very rapid degradation in this soil. All blanks contained undetectable concentrations of all analytes except for small concentrations of Br^-. Background (soil) Br^- concentrations were subtracted from the results for MB- or PB-spiked soil extracts.

Propargyl Bromide

Hydrolysis of PB in water followed first-order degradation with a half-life of 64 d. Hydrolysis of PB resulted in the formation of POH and Br^- in equal molar amounts ($p > 0.01$) (Fig. 1). Bromide and POH production accounted for all propargyl bromide degraded, indicating that there were no other reaction products. The rate of PB hydrolysis was not significantly different from the rate of Br^- production ($p > 0.05$). The hydrolysis $t_{1/2}$ of 64 d is similar to that reported by Yates and Gan (1998), who observed a $t_{1/2}$ of 47 d for PB in distilled water at 25°C.

Soil degradation experiments produced distinctively different results. As PB was degraded in soil, Br^- was produced, but little accumulation of POH was observed in either sandy loam (Fig. 2) or clay loam soil (Fig. 3). Propargyl bromide was degraded in clay loam soil ($t_{1/2}$ = 3.5 d) much more quickly than in sandy loam soil ($t_{1/2}$ = 11.5 d) (Table 3), indicating an increasing rate of degradation with increasing organic matter content. These results are consistent with those of Yates and Gan (1998), who also reported increasing PB degradation rates with increasing soil organic matter content. Autoclaved and nonautoclaved soils exhibited very similar degradation (Fig. 2 and 3, Table 3), and the degradation rates were not significantly different ($p > 0.1$), indicating that the primary degradation mechanism was abiotic. Since autoclaved and nonautoclaved samples were not significantly different, both sets of data were used to fit one first-order model (Fig. 2 and 3).

Propargyl alcohol degradation in nonautoclaved soil followed first-order kinetics with degradation occurring much faster in the higher organic matter (clay loam)

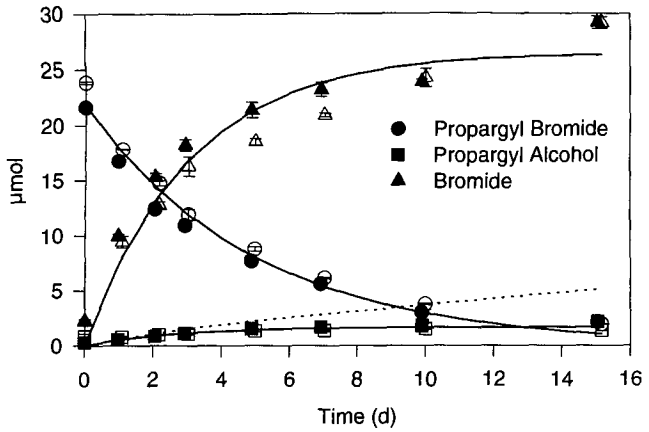

Fig. 3. Degradation of propargyl bromide in Linne clay loam soil with concurrent formation of Br^- and propargyl alcohol. Autoclaved soil samples are indicated by closed symbols, nonautoclaved samples by open symbols. Error bars indicate standard error in triplicate samples. Solid lines are first-order fit to data. Dotted line indicates propargyl alcohol after correction for propargyl alcohol degradation in nonautoclaved soil.

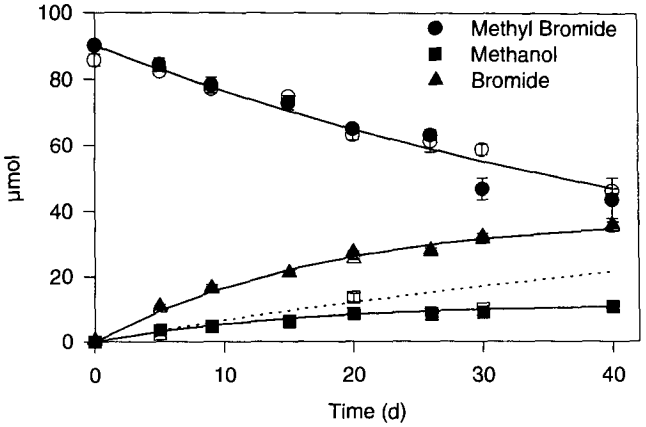

Fig. 4. Degradation of methyl bromide in Arlington sandy loam soil with concurrent formation of Br^- and methanol. Autoclaved soil samples are indicated by closed symbols, nonautoclaved samples by open symbols. Error bars indicate standard error in triplicate samples. Solid lines are first-order fit to data. Dotted line indicates methanol after correction for methanol degradation in autoclaved soil.

soil ($t_{1/2}$ = 3.6 d) than in the sandy loam soil ($t_{1/2}$ = 18 d) (Table 3). Even after correcting for the degradation rate of POH in soil, the production of POH in soil samples spiked with PB was small compared with the production of bromide ion (Fig. 2 and 3). Therefore, some other degradation mechanism that produces bromide ion but does not result in the production of POH (i.e., some mechanism other than hydrolysis) must be occurring in these soils. Alkylation of organic matter is one mechanism that would result in this pattern of degradation products.

Methyl Bromide

Degradation of MB in soil and water produced a pattern of product formation similar to that observed for PB: hydrolysis in water resulted in the production of MeOH and Br^- in equimolar amounts ($p > 0.05$). The rate of MB degradation in water was not significantly different from the rate of Br^- production ($p > 0.01$). The rate of MB hydrolysis ($t_{1/2}$ = 20 d) is consistent with previously reported hydrolysis half-lives for MB in distilled and natural waters (10–50 d) (Mabey and Mill, 1978; Arvieu, 1983; Gentile et al., 1992; Elliott and Rowland, 1995; Gan and Yates, 1996; Jeffers and Wolfe, 1996). Degradation of methanol in water was described by first-order kinetics, with a $t_{1/2}$ of 22 d.

Degradation of MB in soil produced Br^-, but little accumulation of MeOH (Fig. 4 and 5). Degradation rates were not significantly different in autoclaved and nonautoclaved soils ($p > 0.05$ for both sandy loam and clay loam) (Fig. 4 and 5), indicating that the primary degradation mechanism was abiotic. Degradation in sandy loam soil followed first-order kinetics with a $t_{1/2}$ of 42 d (Table 3). Methyl bromide degradation in other soils with similar texture and organic matter and moisture contents exhibited half-lives of 20 to 50 d (Arvieu, 1983; Gan et al., 1994; Gan and Yates, 1996). Methyl bromide degradation in the clay loam soil was much more rapid, with a $t_{1/2}$ of 4.0 d (Table 3). Reported degradation rates for soils with similar organic matter contents indicate half-lives of 4 to 11 d (Arvieu, 1983; Gan et al., 1994; Gan and Yates, 1996). As has been previously observed, the rate of MB degradation was faster in the soil with higher organic matter content.

Methanol degradation in autoclaved soil followed first-order kinetics with degradation occurring faster in the lower-organic-matter sandy loam soil ($t_{1/2}$ = 17 d) than in the clay loam soil ($t_{1/2}$ = 27 d) (Table 3, Fig. 6). Degradation in nonautoclaved soil samples was very rapid in the clay loam soil. In the nonautoclaved sandy loam soil, degradation did not follow first-order kinetics, but appeared to follow a microbially mediated reaction model: a lag period of ~30 h during which no degradation was observed was followed by a rapid consumption of MeOH, with undetectable MeOH measured at 4.5 d (Fig. 6). Methanol formation in MB-spiked soil samples was corrected using the degradation rates for MeOH

Table 3. First-order degradation rates (d^{-1}) for compounds spiked to soil.

Compound	Arlington sand loam		Linne clay loam	
	Autoclaved	Nonautoclaved	Autoclaved	Nonautoclaved
	d^{-1}			
Propargyl bromide	0.065 ± 0.007	0.056 ± 0.004	0.20 ± 0.01	0.20 ± 0.01
Propargyl alcohol	ND†	0.038 ± 0.002	ND	0.19 ± 0.03
Methyl bromide	0.018 ± 0.002	0.015 ± 0.001	0.165 ± 0.006	0.19 ± 0.04
Methanol	0.040 ± 0.002	NA‡	0.026 ± 0.002	0.57 ± 0.05

† ND: Degradation rate not determined.
‡ NA: Degradation did not follow first-order model.

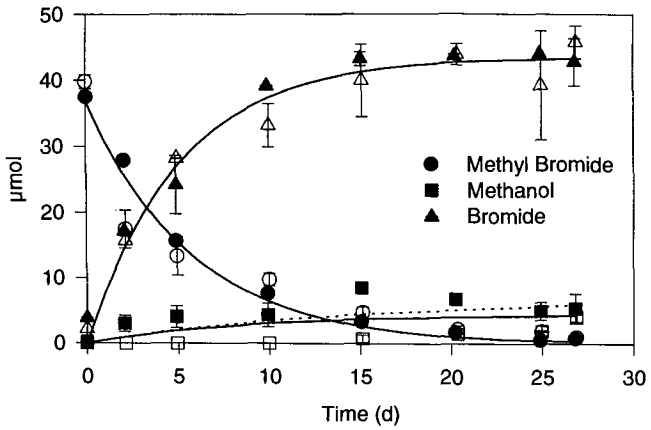

Fig. 5. Degradation of methyl bromide in Linne clay loam soil with concurrent formation of Br^- and methanol. Autoclaved soil samples are indicated by closed symbols, nonautoclaved samples by open symbols. Error bars indicate standard error in triplicate samples. Solid lines are first-order fit to data. Dotted line indicates methanol after correction for methanol degradation in autoclaved soil.

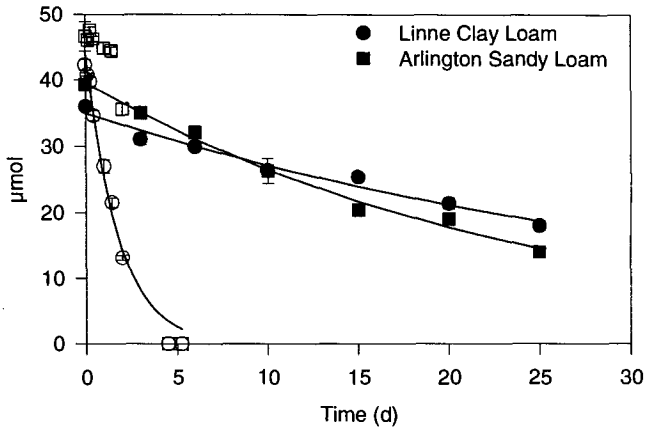

Fig. 6. Degradation of methanol in autoclaved (solid symbols) and nonautoclaved (open symbols) soil samples. Lines indicate first-order kinetics. Methanol degradation in nonautoclaved Arlington sandy loam samples did not follow first-order kinetics.

observed in autoclaved soil samples. Corrected production of MeOH in MB-spiked samples was much less than the production of Br^- (Fig. 4 and 5). For both PB and MB, some mechanism other than hydrolysis was occurring in the soil samples.

Experiments using radiolabeled MB indicate that reaction with the soil may be one mechanism of degradation occurring in these soil samples. Soil-bound ^{14}C increased as the extractable ^{14}C decreased (Fig. 7), and the fraction of ^{14}C associated with the soil increased with time. In this case, extractable ^{14}C residues include MB, MeOH, and any other species that partition into ethyl acetate. The soil-bound component includes nonvolatile residues that remain associated with the soil after extraction. These bound residues represented transformed (not sorbed) MB, as evidenced by the equimolar production of Br^- for each mole of MB lost (Fig. 5). Sorption of MB to this moist soil is expected to be low, with an approximate K_d of 100 kg m^{-3}. (Gan et al., 1996). Mean ^{14}C recovery (relative to time 0) was 102 ± 8%, indicating that all the ^{14}C in the samples was accounted for in the ethyl acetate extracts and soil samples.

Microbial oxidation can be eliminated from consideration as a degradation mechanism for MB and PB in this study because autoclaved and nonautoclaved soils exhibited the same degradation behavior. The soil samples used in this study were exposed to very high concentrations of MB (~100 mL L^{-1}), which may be toxic to an existing microbial population capable of degrading methyl bromide. Therefore, the absence of rapid degradation in nonautoclaved soil samples may not indicate that a degrading population did not exist, only that conditions used in this experiment were not conducive to microbial degradation. Reported rates of degradation of MB (Oremland et al., 1994b; Gan and Yates, 1996; Ou et al., 1997; Gan et al., 1998), MeI (Gan and Yates, 1996), and PB (Yates and Gan, 1998) are similar in sterilized and live soils for several soils under a variety of environmental conditions, indicating that abiotic degradation is the dominant pathway in some soils. Others have reported a large decrease in degradation in sterilized soils compared with live soils, and microbial oxidation of MB has been reported to be significant in some soils (Oremland et al., 1994a; Shorter et al., 1995; Ou et al., 1997, Miller et al., 1997; Hines et al., 1998) and surface water (Connell et al., 1997). Soil microorganisms have been reported to degrade a large range of MB concentrations, ranging from 10^{-12} to 10^{-3} L L^{-1}.

It has been reported that autoclaving soil can alter soil properties, including increasing the measured soil organic matter content (Eno and Popenoe, 1964; Skipper and Westerman, 1973). Treatment of soil with methyl bromide also has been reported to change some soil properties, but had no effect on soil organic matter content (Eno and Popenoe, 1964). In this study, we did not observe differences in the degradation behavior of methyl bromide and propargyl bromide in autoclaved soil compared with fumigant-treated soil; any induced changes in soil properties were not expressed in changes in degradation rates. Previous studies using similar soils also reported small differences in the degradation rate of MB, MeI (Gan and Yates, 1996), and PB (Yates and Gan, 1998) in autoclaved and live soils.

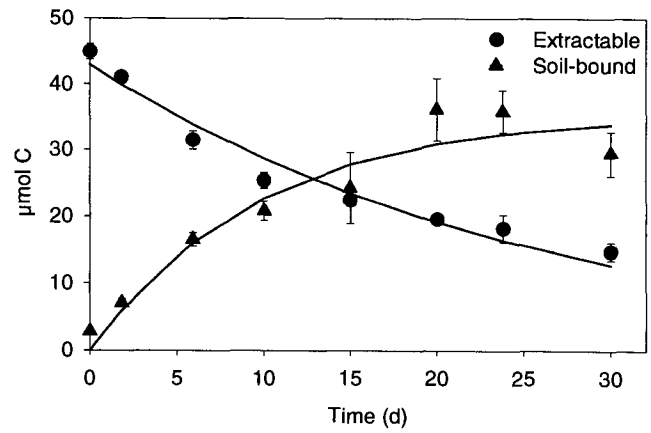

Fig. 7. Degradation of ^{14}C-labeled methyl bromide in Linne clay loam. Data points are means of autoclaved and nonautoclaved samples. Lines indicate first-order kinetics. Extractable C is ^{14}C counted in ethyl acetate extracts, soil-bound C is ^{14}C measured in extracted soil after air drying.

The pattern of reaction products observed in this study lends strong support to the hypothesis that alkyl halides can react with and alkylate soil organic matter. Many of the soil fumigants, including MB, 1,3-dichloropropene (1,3-D), chloropicrin, MeI, and PB contain halogenated alkyl groups. Therefore, this mechanism of degradation is likely to be at least partially responsible for the soil degradation of all these compounds. The importance of this mechanism depends on the molecular structures of the fumigant and soil organic matter, the concentration (and accessability) of both reactants, environmental conditions, and the rate of competing reactions, including biological degradation, which can be very rapid in some soils.

CONCLUSIONS

The results of this experiment indicate that abiotic degradation of MB and PB is significant in these soils and the reaction can be rapid in high-organic-matter soils (with half-lives of only a few days). The pattern of product formation, where one mole of the parent compound degrades to form one mole of bromide ion, but less than one mole of the corresponding alcohol, indicates that the primary abiotic reaction in these moist soils was not hydrolysis. Spiking ^{14}C-labeled MB to soil resulted in the formation of nonextractable (soil-bound) ^{14}C, which increased as the extractable ^{14}C decreased. These results lend additional support to the hypothesis that primary alkyl halides can alkylate soil organic matter via nucleophilic substitution.

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