

# Depleting Methyl Bromide Residues in Soil by Reaction with Bases

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Despite generally being considered the most effective soil fumigant, methyl bromide (MeBr) use is being phased out because its emissions from soil can lead to stratospheric ozone depletion. However, a large amount is still currently used due to Critical Use Exemptions. As strategies for reducing the postfumigation emissions of MeBr from soil,  $\text{Ca}(\text{OH})_2$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{NH}_3$  were assessed as means of promoting MeBr degradation. Ammonia aqueous solution ( $\text{NH}_4\text{OH}$ ) was the most effective, because MeBr can be degraded by both hydrolysis and ammonolysis. At 20 °C, the half-lives ( $t_{1/2}$ ) of MeBr were 18.0, 2.5, and 1.3 h in 0.1, 1.0, and 2.0 M  $\text{NH}_4\text{OH}$ , respectively. In 1.0 M  $\text{NH}_4\text{OH}$ , increasing the solution temperature to 40 °C reduced the half-life of MeBr to 0.23 h. Ammonia amendment to moist soil also promoted MeBr transformation, and the MeBr degradation rate increased with increasing soil temperature.  $\text{NH}_4\text{OH}$  (30%, 16 M) very effectively reacted with MeBr that was contained under plastic film. Under Hytibar (a virtually impermeable film, VIF), over 99.5% of the MeBr could be destroyed by 30%  $\text{NH}_4\text{OH}$  in 8 h at 20 °C. On the basis of these results, good management practices (i.e., VIF plus  $\text{NH}_4\text{OH}$ ) could be developed for continued use of MeBr as a soil fumigant under Critical Use Exemptions, without significant emissions.

## Introduction

Methyl bromide (MeBr) has a wide spectrum of action for control of nematodes, weeds, and fungi and has been used for several decades as a highly effective agricultural fumigant. As early as 1990, the world usage of methyl bromide reached over 67 million kilograms, with about 77% used as a soil fumigant (1). In 1991, MeBr was identified as a potential ozone-depleting compound (2) and in 1992 was officially added to the list of ozone-depleting chemicals. Countries participating in the Montreal Protocol agreed that use of MeBr would be eliminated by the year 2010 in industrial countries and at an unspecified later date in developing countries. In 1993, the USEPA announced that MeBr was scheduled for phase out in the United States by the year 2001 (3).

However, an economic assessment by the USDA showed that there would be at least \$1.5 billion production lost

annually in the United States if MeBr use was restricted immediately (4, 5). Because MeBr was so important agriculturally and no other chemicals were considered adequate replacements, the phase out date in the United States was later changed to the year 2005 (6). Nevertheless, since 2005, a considerable amount of MeBr has been used under Critical Use Exemptions. For example, 1 191 815 kg of MeBr is requested for use in 2010 for preplant soil use in open-field strawberry production (7). In 2008, MeBr was the third most highly used fumigant in California (8).

The issue of whether MeBr should be phased out has proved controversial for two reasons. First, natural sources dominate the atmospheric MeBr budget; natural sources contributed 11% to the total tropospheric burden of ozone-depleting halogenated gases, while the anthropogenic source contributed only 3% (other halogenated gases contributed the remaining 86%) (9). Second, and more importantly, emission of MeBr from soil could probably be considerably reduced with new technology or methodology. A key theme with this approach is to deplete the residual soil MeBr before it enters the atmosphere.

Covering the fumigated soil with plastic film is a conventional approach to reduce the emissions of MeBr into the atmosphere. Munnecke et al. showed that using gastight films led to very high concentrations of MeBr within the soil, whereas under the more permeable low-density polyethylene (LDPE) covers, MeBr rapidly dissipated to the atmosphere (10). Several other field-scale experiments with high-density polyethylene (HDPE) plastic films have shown that 27–78% of applied MeBr was lost to the atmosphere after soil fumigation (11–19) because of the HDPE's partial permeability to MeBr (22). The virtually impermeable film (VIF) Hytibar has been shown to effectively trap MeBr within the soil for extended periods. For example, only 0.9–1.9% total emissions of MeBr were observed when the soil surface was covered with Hytibar over 15 days. This is compared to 64–67% total emissions with HDPE (20). Because a soil's ability to degrade MeBr is usually low, MeBr's half-life in soils generally ranges from 5 to 28 days (21). Consequently, a large proportion of MeBr could penetrate LDPE or HDPE films before it becomes decomposed. Even if MeBr is trapped in soil by a VIF, such as Hytibar, a long time is needed for MeBr's complete degradation. This is problematic since films are usually removed or cut for crop planting, resulting in the potential for significant MeBr emissions to the air.

In order to promote the degradation of MeBr, several methods have been tested but none of them are considered highly practicable. Though organic materials, such as composted steer manure and biosolid–manure mix, could enhance MeBr degradation, the quantity of these materials required to facilitate degradation is likely too high to be of practical value (22). Similarly, although sodium thiosulfate (STS) or ammonium thiosulfate (ATS) can efficiently reduce MeBr volatilization from fumigated soils (23), in order to promote MeBr degradation at an application rate of 112 kg  $\text{ha}^{-1}$ , a large amount (660 kg  $\text{ha}^{-1}$ ) of ATS was needed. Also, ATS must be sprayed on the soil surface before fumigation, meaning that the timing of the chemical reaction is not easily manipulated.

Research on the mechanism of MeBr degradation in soil has shown that MeBr is hydrolyzed via  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions under natural conditions and forms methanol and bromide (24). At low pH (pH 3–8) in natural fresh water, the dominant mechanism of hydrolysis was a  $\text{S}_{\text{N}}1$  reaction (25). However, at higher pH values (>8) the faster  $\text{S}_{\text{N}}2$ -type reaction was dominant (25).

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In agriculture, several alkaline substances are widely used and it is considered likely that such substances may be effective in promoting MeBr degradation. For example, agricultural lime is used as a soil additive to increase the pH of soil, provide a source of calcium for plants, and improve water penetration in acid soil. Plant ash, the residue of burned plants, which includes CaO, K<sub>2</sub>O, and K<sub>2</sub>CO<sub>3</sub>, is used for soil liming and for pest control. Ammonia can be used as a general fertilizer in the form of water solution.

Using such substances, the objective of this study was to find a feasible approach for quickly decomposing residual MeBr in soils. The work aimed to (a) determine which of Ca(OH)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, and NH<sub>4</sub>OH was the most effective base for degradation of MeBr, (b) investigate the effect of temperature on MeBr degradation, and (c) explore possible ways to quickly deplete residual MeBr in fumigated soil while maintaining its pesticide efficacy.

## Experimental Section

**Chemicals, Soil, and Other Materials.** A cylinder of methyl bromide 100 (active ingredient 100%) was donated by Soil Chemical Co. (Hollister, CA). CaO (Certified) was purchased from Fisher Chemical Inc. Ammonium hydroxide (28–30%) was purchased from EMD Chemicals Inc. K<sub>2</sub>CO<sub>3</sub> (Reagent-plus, 99%) was purchased from Sigma-Aldrich. Diethyl ether (certified A.C.S., anhydrous), *n*-hexane (95%), and NaBr (certified A.C.S., anhydrous) were purchased from Fisher Scientific (Fair Lawn, NJ).

Arlington sandy loam soil was obtained from the University of California, Riverside Agricultural Experiment Station. Fresh soil was passed through a 2 mm sieve without air drying, packed in a plastic bag, and stored in a 4 °C refrigerator until use. The contents of moisture and organic matter were 6.43% and 1.08%, respectively. The pH was 7.2.

Three kinds of plastic films, i.e., clear HDPE film, black Blockade (Pliant, Corp.) film, and the VIF Hytibar (Klerk's Plastics, Inc.), were used in the permeability cell experiment. These films have mass transfer coefficients (e.g., permeability), respectively, of 2, 0.2, and less than 0.01 cm h<sup>-1</sup> (31).

**MeBr Degradation in Ca(OH)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, and NH<sub>3</sub> Solutions.** Saturated Ca(OH)<sub>2</sub>, 1.0 M K<sub>2</sub>CO<sub>3</sub>, and 0.1, 1.0, and 2.0 M NH<sub>3</sub> aqueous solutions were prepared using deionized water. The pH values of these solutions were measured with an UltraBasic pH Meter (Denver Instrument Co.) at 20 ± 1 °C.

MeBr (5.538 g) was dissolved in about 15 mL of anhydrous diethyl ether, and its concentration was measured using a standard calibration curve. MeBr analysis was performed using a Hewlett-Packard HP 6890 gas chromatograph (GC) equipped with a microelectron capture detector ( $\mu$ ECD). A DB-VRX capillary column (30 m × 250  $\mu$ m × 1.4  $\mu$ m, J&W Scientific, Folsom, CA) was used with the following conditions: 1.0 mL min<sup>-1</sup> carrier gas flow rate, 240 °C inlet temperature, and 290 °C detector temperature. The oven was held at 90 °C. Under these conditions, the retention time of MeBr was 2.42 min.

At 20 ± 1 °C, 10.0  $\mu$ L of 50 mM MeBr in Et<sub>2</sub>O solution was transferred into 500  $\mu$ L of each alkaline solution in an inverted 2.1 mL GC vial using a gastight syringe. At predetermined time intervals, 1.0 mL of *n*-hexane was injected into the GC vial to extract the unreacted MeBr, and the water solution was then removed from the vial with a gastight syringe. The content of MeBr in *n*-hexane extract was analyzed, as above, on GC- $\mu$ ECD. Triplicate samples were tested.

**MeBr Degradation in NH<sub>4</sub>OH at Differing Temperatures.** Into a 2.1 mL GC vial containing 500  $\mu$ L of 1.0 M NH<sub>4</sub>OH (previously equilibrated in an incubator at 4, 10, 20, 30, 40, or 50 ± 1 °C), 10.0  $\mu$ L of 50 mM MeBr solution was injected, before the vial was returned to the incubator. As a control, 500  $\mu$ L of water was used instead of 1.0 M NH<sub>4</sub>OH at 20 ±

1 °C. At predetermined time intervals, vials were removed from the incubator and placed in a freezer (−20 °C) to allow cooling for 20 min before 1.0 mL of *n*-hexane was injected to extract the residual MeBr. The water phase was immediately removed by a gastight syringe after extraction, and the remaining *n*-hexane MeBr solution was analyzed on GC- $\mu$ ECD (as above).

**MeBr Degradation Kinetic Analysis in Different Bases Aqueous Solutions.** To compare the potential of the three bases, Ca(OH)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, and NH<sub>4</sub>OH, in promoting MeBr degradation, it was assumed that all the MeBr was dissolved in aqueous solution and that the nominal concentration was C (micromolar). Regression analysis of C with reaction time *t* (h) indicated that in each case the reaction was fitted well with the first-order kinetic model (eq 1), and the apparent reaction rate constant *k* was obtained

$$C = C_0 \cdot e^{-kt} \quad (1)$$

The half-life of MeBr in the reaction system could be calculated according to the following equation

$$t_{1/2} = \ln 2 / k \quad (2)$$

However, as MeBr is volatile and the vials were not completely filled with liquid, its reaction rate constant in solution should be corrected as follow (*k*<sub>corr</sub>)

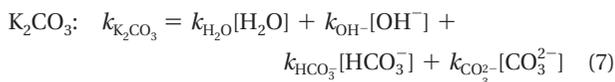
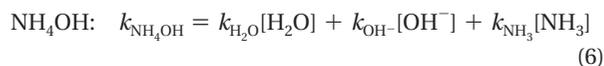
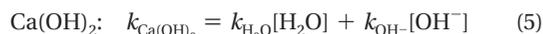
$$k_{\text{corr}} = k[1 + K_H(V_G/V_L)] = k[1 + K_H(1.59/0.51)] \quad (3)$$

where *K*<sub>H</sub> is the dimensionless Henry's Law constant of MeBr at temperature *t* (0.21 at 20 °C) (26) and *V*<sub>G</sub> and *V*<sub>L</sub> are headspace and aqueous solution volumes in the reaction system, respectively.

The half-life of MeBr in the reaction solution could then be calculated according to the following equation

$$t_{1/2, \text{corr}} = \ln 2 / k_{\text{corr}} \quad (4)$$

Additionally, and in common with MeBr degradation in seawater (26, 27), MeBr degradation constants for each system, *k*<sub>Ca(OH)<sub>2</sub></sub>, *k*<sub>NH<sub>4</sub>OH</sub>, and *k*<sub>K<sub>2</sub>CO<sub>3</sub></sub>, could be described in more detail as follows



where *k*<sub>H<sub>2</sub>O</sub>, *k*<sub>OH<sup>-</sup></sub>, *k*<sub>NH<sub>3</sub></sub>, *k*<sub>HCO<sub>3</sub><sup>-</sup></sub>, and *k*<sub>CO<sub>3</sub><sup>2-</sup></sub> represent the rate constants for neutral, base-catalyzed hydrolysis, ammonolysis, HCO<sub>3</sub><sup>-</sup>-promoting MeBr degradation, and CO<sub>3</sub><sup>2-</sup>-promoting MeBr degradation. [NH<sub>3</sub>] is ammonia concentration in solution, as its Henry's Law constant (*K*<sub>H</sub> = 0.00126 at 40 °C) indicates that 99.6% of the NH<sub>3</sub> in the GC vial was in solution. Therefore, *k*<sub>NH<sub>3</sub></sub> did not need correction when temperature < 40 °C.

**MeBr Degradation in Ammonia-Amended Soil.** Into 21.8 mL headspace vials, which were filled with 10.65 g of fresh soil (containing moisture of 6.43%) and sealed with Teflon-faced butyl rubber septum and an aluminum seal, 7.0  $\mu$ L of 0.35 M MeBr ether solution was injected through the septum using a gastight syringe. In this case, the initial MeBr concentration was 23.3 mg kg<sup>-1</sup> dry soil, which approximated the concentration of surface soil during the first few days following a typical MeBr fumigation under tarp conditions

**TABLE 1. Model-Fitting Parameter Values and MeBr Half-Lives in Different Alkaline Solutions**

solution	pH value	$k$ (h <sup>-1</sup> )	$r^2$	$t_{1/2}$ (h)	$k_{\text{corr}}$ (h <sup>-1</sup> )	$t_{1/2,\text{corr}}$ (h)
saturated Ca(OH) <sub>2</sub>	12.50	0.016 ± 0.002	0.90	44.1	0.026	26.2
1.0 M K <sub>2</sub> CO <sub>3</sub>	11.08	0.087 ± 0.002	0.99	8.0	0.14	4.8
1.0 M KHCO <sub>3</sub>	8.42	0.011 ± 0.001	0.92	63.0	0.018	38.1
0.10 M NH <sub>4</sub> OH	11.00	0.038 ± 0.001	0.99	18.0	0.063	11.0
1.0 M NH <sub>4</sub> OH	11.65	0.27 ± 0.01	0.99	2.5	0.45	1.6
2.0 M NH <sub>4</sub> OH	11.86	0.52 ± 0.01	0.99	1.3	0.86	0.81

(28, 29). The mixture was shaken to evenly distribute the MeBr within the soil, and the vial was placed at  $-20 \pm 1$  °C for 30 min, after which the septum (pierced) was replaced.

The vials were equilibrated in incubators at differing temperatures (4, 10, 20, 30, 40, and  $50 \pm 1$  °C) before 40  $\mu\text{L}$  of 30% NH<sub>4</sub>OH or water (as a control) was injected into each with a gastight syringe. Under these conditions, the (non-control) concentration of ammonia in soil–water was 1.0 M. The samples were then moved back to the incubators, and at certain time intervals the samples were removed to a freezer ( $-20$  °C) and kept there until all the samples were collected. Into the headspace vial, 10 mL *n*-hexane was injected using a syringe through the septum, to extract unreacted MeBr. The soil–solvent mixture was warmed to room temperature and vortexed for 2 min. An aliquot (1.5 mL) of the *n*-hexane extract was then transferred into a 2.1 mL GC vial with a gastight syringe for analysis on GC- $\mu\text{ECD}$  (as above).

**MeBr Degradation under Plastic Film in the Presence of NH<sub>4</sub>OH.** Cylindrical stainless steel permeability cells of dimensions 12 cm diameter by 8 cm depth (30) were used to determine the degradation of MeBr under three plastic films: clear HDPE film, black Blockade film, and Hytibar film. The sealed cell was separated into two chambers (source and receiving) of equal volumes of 452 mL by the plastic film.

MeBr gas was first introduced into a vacuumed Teflon gas sampling bag from the stock cylinder. Then 75.0 mL of MeBr gas was transferred into a 1.0 L glass cylinder using a syringe. After 30 min, 25.0 mL of gas from the glass cylinder was injected into the source chamber of the permeability cell via a sealable port in the wall of the chamber. This was followed by injection of 7.5 mL of 30% NH<sub>4</sub>OH.

Experiments were conducted at  $20 \pm 1$  °C. At predetermined time intervals, 250  $\mu\text{L}$  of gas was taken from the receiving chamber and transferred into a 12.1 mL headspace vial using a gastight syringe. The same was done for the source chamber. Each vial was immediately capped with a Teflon-faced butyl rubber septum and an aluminum seal. The syringe was flushed 4 times with fresh air between samplings. Samples were analyzed using an Agilent Technologies G1888 Network Headspace Sampler interfaced with an HP6890 GC- $\mu\text{ECD}$ . The headspace sampler conditions were as follows: 80 °C equilibration temperature; 5.0 min equilibration time; 1000  $\mu\text{L}$  sample loop. The GC was equipped with a DB-VRX column: 30 m long  $\times$  0.25 mm i.d.  $\times$  1.4  $\mu\text{m}$  film thickness fused silica capillary column (J&W, Folsom, CA). GC conditions were as follows: helium carrier gas at a flow rate of 1.4 mL min<sup>-1</sup>; 240 °C injector temperature; 280 °C detector temperature. Oven temperature program: 45 °C held for 1 min, increasing at 2.5 °C/min to 80 °C. Under these conditions, the retention time of MeBr was 2.70 min. Calibration standards for this GC analysis were prepared in *n*-hexane at seven concentrations and analyzed at the beginning of each set of samples.

**Quantification of Residual MeBr and Bromide Anion from MeBr Reaction with NH<sub>4</sub>OH.** To determine residual MeBr following reaction, experiments were carried out in 1.0 M NH<sub>4</sub>OH as for the alkaline solution experiments (above). To quantify the Br<sup>-</sup> in the reaction mixture, 1.0 mL *n*-hexane

was injected into the vial containing MeBr and 500  $\mu\text{L}$  of 1.0 M NH<sub>4</sub>OH. The mixture was shaken for 2 min to extract the unreacted MeBr before the *n*-hexane solution was removed. The remaining water solution was diluted with 1.50 mL of deionized water, and 1.2 mL of this solution was transferred into an ion chromatography (IC) tube for analysis. A 861 Advanced Compact IC equipped with a Dionex column (IonPac, AS14, 4  $\times$  250 mm) and AS40 automated sampler was used to determine concentrations of Br<sup>-</sup>. The mobile phase consisted of 0.75 mM Na<sub>2</sub>CO<sub>3</sub> and 0.25 mM NaHCO<sub>3</sub> water solution. The flow rate was 1.0 mL min<sup>-1</sup>.

The concentration of Br<sup>-</sup> was measured by a standard calibration curve. Calibration standards for IC analysis were prepared with NaBr in deionized water. Eight different concentration solutions were prepared with stock solution and deionized water.

## Results and Discussion

**MeBr Degradation Kinetics in Ca(OH)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, and NH<sub>4</sub>OH Solutions.** According to eqs 1–4, MeBr apparent degradation rate constants ( $k$ ), apparent half-lives ( $t_{1/2}$ ), corrected degradation rate constants ( $k_{\text{corr}}$ ), and half-lives ( $t_{1/2,\text{corr}}$ ) in different base solutions at 20 °C are shown in Table 1.

Though the pH value of the saturated Ca(OH)<sub>2</sub> solution was the highest among all these solutions, the degradation rate of MeBr in this solution was the lowest. At 1.0 M concentration, NH<sub>4</sub>OH was more effective at promoting MeBr degradation than K<sub>2</sub>CO<sub>3</sub> solution. The results can be further interpreted by eqs 5–7 and using the following. At 20 °C,  $k_{\text{H}_2\text{O}} = 1.30 \times 10^{-5} \text{ M}^{-1} \text{ h}^{-1}$  (second order) [calculated from Jeffers and Wolfe (27),  $k_{\text{H}_2\text{O}}(1\text{st}) = (5.7 \pm 0.6) \times 10^{11} \text{ e}^{-(12455 \pm 240)/T} \text{ s}^{-1}$ ],  $k_{\text{OH}^-} = 0.81 \text{ M}^{-1} \text{ h}^{-1}$ ,  $k_{\text{NH}_3} = 0.44 \text{ M}^{-1} \text{ h}^{-1}$ ,  $k_{\text{HCO}_3^-} = 0.0070 \text{ M}^{-1} \text{ h}^{-1}$ ,  $k_{\text{CO}_3^{2-}} = 0.16 \text{ M}^{-1} \text{ h}^{-1}$  [calculated from Table 1 for saturated Ca(OH)<sub>2</sub>, 1.0 M NH<sub>4</sub>OH, 1.0 M K<sub>2</sub>CO<sub>3</sub>, and 1.0 M KHCO<sub>3</sub> data]. Equations 5–7 can then be described as follows

$$k_{\text{Ca(OH)}_2} = 7.25 \times 10^{-4} + 0.81[\text{OH}^-] \text{ h}^{-1} \quad (8)$$

$$k_{\text{NH}_4\text{OH}} = 7.25 \times 10^{-4} + 0.81[\text{OH}^-] + 0.44[\text{NH}_3] \text{ h}^{-1} \quad (9)$$

$$k_{\text{K}_2\text{CO}_3} = 7.25 \times 10^{-4} + 0.81[\text{OH}^-] + 0.0070[\text{HCO}_3^-] + 0.16[\text{CO}_3^{2-}] \text{ h}^{-1} \quad (10)$$

It should be noted that in eq 8, although OH<sup>-</sup> has the highest reaction rate constant  $k_{\text{OH}^-}$ , [OH<sup>-</sup>] in saturated Ca(OH)<sub>2</sub> solution was limited (the maximum [OH<sup>-</sup>] = 0.032 M). The maximum  $k_{\text{Ca(OH)}_2}$  was therefore 0.026 h<sup>-1</sup>. Comparing this to eq 9 (NH<sub>4</sub>OH) shows that even though the pH was lower in NH<sub>4</sub>OH than in saturated Ca(OH)<sub>2</sub> solution,  $k_{\text{NH}_3}$  was as much as one-half of  $k_{\text{OH}^-}$  and [NH<sub>3</sub>] (0.1–2.0 M) was much higher than [OH<sup>-</sup>] in saturated Ca(OH)<sub>2</sub> solution. Therefore  $k_{\text{NH}_4\text{OH}}$  had the potential to be larger than  $k_{\text{Ca(OH)}_2}$ . Similarly, in eq 10, although 1.0 M K<sub>2</sub>CO<sub>3</sub> solution had a lower pH than saturated Ca(OH)<sub>2</sub> solution, because  $k_{\text{CO}_3^{2-}}$  was as one-fifth of  $k_{\text{OH}^-}$  and [CO<sub>3</sub><sup>2-</sup>] was much higher than [OH<sup>-</sup>] in saturated

**TABLE 2. Fitting Results of MeBr Degradation and MeBr Half-Lives in 1.0 M Ammonia Aqueous Solution at Differing Temperatures**

temp. (°C)	<i>k</i> (h <sup>-1</sup> )	<i>r</i> <sup>2</sup>	<i>t</i> <sub>1/2</sub> (h)	<i>k</i> <sub>corr</sub> (h <sup>-1</sup> )	<i>t</i> <sub>1/2,corr</sub> (h)
4	0.042 ± 0.002	0.99	16.3	0.058	12.0
10	0.078 ± 0.003	0.99	8.9	0.11	6.1
20	0.28 ± 0.00	0.99	2.5	0.46	1.5
30	0.60 ± 0.03	0.99	1.2	1.1	0.61
40	1.35 ± 0.18	0.99	0.51	3.0	0.23

**TABLE 3. Regression Models and Parameter Values of MeBr Degradation and Br<sup>-</sup> Formation in 1.0 M Ammonia Aqueous Solution<sup>a</sup>**

	regression model	<i>k</i> (h <sup>-1</sup> )	<i>r</i> <sup>2</sup>
Br <sup>-</sup> formation	$c = c_0 \cdot (1 - e^{-kt})$	0.25 ± 0.01	0.99
MeBr degradation	$c = c_0 \cdot e^{-kt}$	0.26 ± 0.00	0.99

<sup>a</sup> *C* is the concentration of Br<sup>-</sup> (or MeBr) at time *t*, *C*<sub>0</sub> is the initial MeBr concentration in solution, and *k* is the rate constant of the reaction.

Ca(OH)<sub>2</sub> solution, *k*<sub>K<sub>2</sub>CO<sub>3</sub></sub> had the potential to be larger than *k*<sub>Ca(OH)<sub>2</sub></sub>. Because NH<sub>4</sub>OH has a higher pH than K<sub>2</sub>CO<sub>3</sub> solution at the same concentration and *k*<sub>NH<sub>3</sub></sub> is 2.75 times *k*<sub>CO<sub>3</sub><sup>2-</sup></sub>, NH<sub>4</sub>OH was more effective than K<sub>2</sub>CO<sub>3</sub> in promoting MeBr degradation. For these reasons, overall, NH<sub>4</sub>OH was the most effective of the bases in promoting MeBr degradation.

In eq 9, *k*<sub>NH<sub>4</sub>OH</sub> is a result of both [OH<sup>-</sup>] and [NH<sub>3</sub>]. Although *k*<sub>OH<sup>-</sup></sub> is 1.8 times *k*<sub>NH<sub>3</sub></sub>, [NH<sub>3</sub>] is much higher than [OH<sup>-</sup>] in NH<sub>4</sub>OH, and as a consequence, MeBr is mainly degraded by ammonolysis. At 20 °C, MeBr ammonolysis rates were 54, 122, and 151 times MeBr hydrolysis rates and the half-lives of MeBr were 11.0, 1.6, and 0.80 h in 0.1, 1.0, and 2.0 M NH<sub>4</sub>OH, respectively.

#### MeBr Degradation in NH<sub>4</sub>OH at Differing Temperatures.

In studying the effect of temperature on MeBr degradation in 1.0 M NH<sub>4</sub>OH, the relationship between the nominal MeBr concentration and time could again be fitted with the simple first-order kinetic model (eq 1). The regression parameters of MeBr degradation are shown in Table 2. MeBr is highly stable in deionized water, and there was no significant degradation in the control samples during 48 h incubation at 20 °C. By comparison, in 1.0 M NH<sub>4</sub>OH, MeBr was degraded relatively quickly, with half-lives ranging from 0.23 to 12.0 h (Table 2). The higher the temperature of NH<sub>4</sub>OH, the higher the rate of MeBr degradation. The half-life of MeBr at 40 °C was 52 times shorter than at 4 °C and 6.5 times shorter than at 20 °C.

**Mechanism of MeBr Degradation in NH<sub>4</sub>OH.** As described above, MeBr was quickly degraded in 1.0 M NH<sub>4</sub>OH. It was observed that the decreasing concentration of MeBr was accompanied by an increase in the concentration of Br<sup>-</sup>. The decrease in the nominal MeBr concentration and increase in Br<sup>-</sup> concentration in 1.0 M NH<sub>4</sub>OH could both be fitted with simple first-order kinetic models (Table 3), and the two rate constants were very similar. This similarity indicates that MeBr was completely degraded to Br<sup>-</sup> and that no other volatile organic or inorganic bromide compounds were formed. These results suggest that the release of MeBr from fumigated soil could be significantly reduced by reacting MeBr with NH<sub>4</sub>OH to form water-soluble Br<sup>-</sup> within the soil system.

**MeBr Degradation in Ammonia-Amended Soil.** After incubation at 50 °C for 1.5 h, 39% of added MeBr was degraded in NH<sub>3</sub>-amended soil, but no degradation was observed in nonamended soil. Previous work showed that the half-life of MeBr was 21 days in this nonamended soil at 25 °C (28).

**TABLE 4. Model-Fitting Parameter Values and MeBr Half-Lives at Differing Temperatures in Soil**

temp. (°C)	<i>k</i> (h <sup>-1</sup> )	<i>r</i> <sup>2</sup>	<i>t</i> <sub>1/2</sub> (h)
4	0.0053 ± 0.0004	0.97	130.8
10	0.015 ± 0.001	0.98	45.3
20	0.045 ± 0.002	0.99	15.6
30	0.088 ± 0.006	0.99	7.9
40	0.32 ± 0.02	0.99	2.2
50	0.41 ± 0.03	0.99	1.7

However, in the present work, MeBr half-lives were only 15.6 h at 20 °C and 7.9 h at 30 °C (Table 4) in the NH<sub>3</sub>-amended soil. Therefore, NH<sub>3</sub> had a significant effect on MeBr degradation in soil.

The degradation of MeBr in NH<sub>3</sub> amended soil at differing temperature could be fitted well with the first-order kinetic equation (eq 1; values of parameters shown in Table 4).

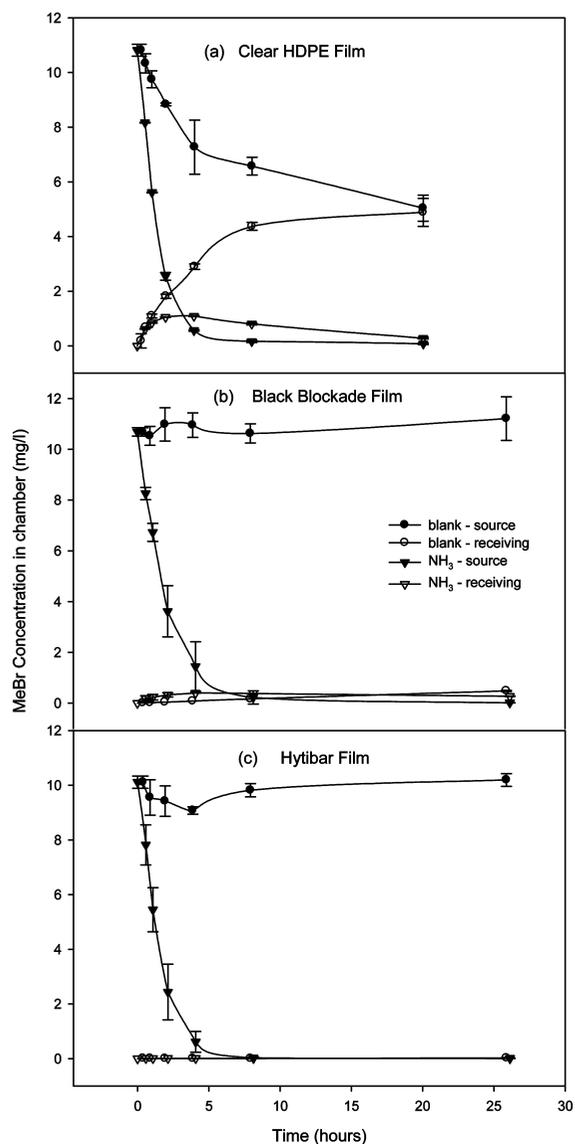
Compared to that in NH<sub>4</sub>OH, the degradation rate of MeBr in soil was much lower, even though the ammonia concentration (based on the soil moisture) was the same as in the water solution (1.0 M). The soil moisture could be regarded as a buffer solution, i.e., once NH<sub>3</sub> was added, it became partially neutralized and ammonium could then be absorbed onto soil surfaces (e.g., clay minerals) by cation exchange. Thus, the actual concentration of ammonia in the water phase in the soil would likely have been much lower than 1.0 M. In soil, increasing temperature promoted the reaction between MeBr and NH<sub>4</sub>OH. The reaction rate increased 78 times from 4 to 50 °C. At 50 °C, the MeBr half-life time was reduced to 1.7 h.

**MeBr Degradation under Plastic Film in the Presence of NH<sub>4</sub>OH.** Through the clear HDPE film a high rate of MeBr transfer was observed in the absence of NH<sub>4</sub>OH, with around 30% and 45% of the total MeBr passing through the film in 4 and 8 h, respectively. With 30% NH<sub>4</sub>OH added under this kind of film, nearly 85% of the total MeBr was degraded in 4 h and about 10% of the MeBr passed through the film (Figure 1a). With the less permeable black Blockade film, less than 5% of the MeBr passed through the film over 26 h in the absence of NH<sub>4</sub>OH. In this case, the degradation rate of MeBr by NH<sub>4</sub>OH was similar to that with clear HDPE film (about 83% of the total MeBr disappeared in the initial 4 h) but only about 3.8% passed through the film (Figure 1b). As shown in Figure 1c, the Hytibar film exhibited very low permeability to MeBr with or without NH<sub>4</sub>OH in the chamber. Indeed, less than 0.2% of the MeBr passed through the film in 26 h in the absence of NH<sub>4</sub>OH. In the presence of NH<sub>4</sub>OH, 96% of the total MeBr degraded under Hytibar film in 4 h, and less than 0.1% of total MeBr passed through the film. In 8 h, 99.5% of the total amount of MeBr was degraded under the Hytibar film.

Because NH<sub>4</sub>OH only occupied 1.7% of the space in the chamber (7.5 mL of solution in 452 mL chamber) and NH<sub>4</sub>OH was highly concentrated, the reaction kinetics between NH<sub>4</sub>OH and MeBr become complicated and could not be described by a simple model. However, overall, 30% NH<sub>4</sub>OH promoted MeBr transformation under plastic film, especially under the highly impermeable Hytibar film.

**Environmental Implication.** NH<sub>4</sub>OH can quickly react with MeBr and convert it to MeNH<sub>2</sub>, MeOH, and Br<sup>-</sup>. Overall, we believe this approach may be effectively used to destroy residual MeBr in soil after agricultural fumigation and thus mitigate MeBr emissions to the atmosphere.

To reduce the emission of MeBr from fumigated soil, only covering the field surface with conventional polyethylene (PE) films is apparently not sufficient. Up to 65% (16) and 87% (13) of applied MeBr could escape to the atmosphere because of the film's permeability. The research suggests



**FIGURE 1.** MeBr degradation in permeability cell with (a) clear HDPE film, (b) black Blockade film, and (c) Hytibar film. "blank" indicates no ammonia in the cell. "receiving" and "source" indicate "receiving chamber" and "source chamber", respectively.

that an improved approach would be to use a more impermeable film, such as VIF (e.g., Hytibar film), instead of conventional PE film (e.g., clear HDPE film), since VIF would more effectively retard MeBr emission and improve MeBr's efficacy as a fumigant (17). To enhance its efficacy before it reacts with ammonia, the MeBr should be maintained under the film and ammonia added only after pesticide efficacy is achieved. In order to provide favorable conditions for the reaction, it seems that adequate surface soil moisture (in this experiment soil moisture was around 7%) is required. In California, a common use of MeBr, under Critical Use Exemptions, is in raised bed strawberry production. In such systems, the raised beds are often covered with plastic film and irrigated via drip lines buried close to the soil surface. This system provides ideal conditions for the use of ammonia to destroy MeBr and reduce emissions. For example, VIF could be used to cover the raised beds and the drip line used to administer water and, after sufficient time for pest kill to be achieved, the ammonia. Although  $\text{NH}_3$  is volatile it can be trapped under VIF without emissions and immediately absorbed by the condensed water known to collect on the under side of plastic films and by the soil moisture. As the

research shows, higher temperatures can enhance MeBr degradation in  $\text{NH}_4\text{OH}$  and  $\text{NH}_3$ -amended soil. Under agricultural film, the temperature of surface soil (up to 5 cm depth) in Southern California has been shown to approach  $43^\circ\text{C}$  and in the air space below the plastic to exceed  $60^\circ\text{C}$  (14). Therefore, the timing (with respect to soil temperature) of soil amendment with ammonia could be controlled to effectively degrade MeBr. For example, addition of ammonia at the time of maximum soil temperature (typically late afternoon) would likely deplete the residual MeBr within a short period, (i.e.,  $t_{1/2}$  2.2 h at  $40^\circ\text{C}$ ). Moreover, any excess  $\text{NH}_3$  could be washed into the soil via irrigation water where it would likely serve as an additional source of plant nutrient. Overall, with such an approach, more than 99.5% of the MeBr which diffuses to the soil surface could be destroyed prior to its potential release into the atmosphere. However, such an approach requires further testing under large-scale field conditions. If proved successful, current and continued MeBr use under Critical Use Exemptions could be managed more effectively and its potential impact on stratospheric ozone depletion substantially limited.

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