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Characterization of propargyl bromide transformation in soil†

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Abstract: Propargyl bromide is being investigated for its potential as a soil fumigant. Characterization of the fate of propargyl bromide in soil is important in determining both efficacy and the threat of environmental contamination. These experiments investigated some of the factors affecting the rate of propargyl bromide degradation in soil and quantified some of the products formed as a result of propargyl bromide degradation in four soils of differing composition and at three initial propargyl bromide concentrations. In all soils at all initial propargyl bromide concentrations, equimolar formation of Br^- was observed during propargyl bromide degradation, but little propargyl alcohol (product of hydrolysis) was formed. The apparent first-order degradation coefficient (k) increased with decreasing initial propargyl bromide concentration in all soils, but the mass degraded per unit time increased with increasing propargyl bromide concentration. The rate of propargyl bromide degradation increased with increasing soil organic matter content, and the k value was correlated to the organic carbon content of the soil (correlation coefficient >0.97 for all concentrations). Repeated application of propargyl bromide did not increase the rate of propargyl bromide degradation in soil. Addition of Br^- did not affect the rate of propargyl bromide transformation in soil, so accumulation of Br^- in the soil is not expected to impede propargyl bromide degradation.
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1 INTRODUCTION

Soil fumigants are used for broad-spectrum pest control in high-value crops. Concerns of stratospheric ozone depletion have mandated the discontinuation of a popular soil fumigant, methyl bromide.[1] The prescriptions of the Montreal Protocol require that methyl bromide be phased out in participating developed countries incrementally, with the phase-out to be completed in 2005. Several fumigant compounds, including 1,3-dichloropropene (1,3-D), chloropicrin and methyl isothiocyanate are currently available as partial replacements for methyl bromide. However, these compounds lack the broad-spectrum activity of the latter, leading to a search for additional fumigant compounds. Propargyl bromide (3-bromopropyne) is being investigated for its potential to serve as an additional methyl bromide alternative. Initial evaluations of propargyl bromide efficacy indicate that it is effective against nematodes, weeds and fungi.[2] Evaluations of the efficacy and environmental fate of propargyl bromide are required to determine its value as a soil fumigant.

Transformation in soil can affect both efficacy and environmental fate of pesticides. A compound must not degrade so rapidly as to render it ineffective, nor be so persistent as to generate environmental pollution problems. The rate of degradation of fumigant compounds in soil has been observed to vary with environmental conditions such as temperature,[3–7] soil moisture[3,4,8] and soil type,[2,5,8–16] as well as with the initial fumigant concentration.[3,6,11,17] The history of fumigation of the soil may also impact the degradation rate, and increased rates of degradation have been observed in soils with repeated applications.[18–20] These and other results indicate the importance of biological degradation for some fumigant compounds under some conditions,[3–5,17,19,21–23] particularly at low concentrations. Adaptation of a microbial community to fumigant compounds may accelerate the degradation rate to such an extent as to compromise efficacy.[18,19] Experiments investigating the impact of propargyl bromide on soil microbial communities indicated that at an application rate of 10 mg kg^{-1}, little impact on the soil microbial community activity was observed.[24] At propargyl bromide concentrations of 100 and 500 mg kg^{-1}, suppression of soil microbial community activity was observed, accompanied by a reduction in the population of dominant microorganisms and the diversity of the soil microbial community that lasted up to 12 weeks following

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propargyl bromide application.[24] In many assays, propargyl bromide had a stronger impact on the soil microbial community than did 1,3-D.

Little information is available on the degradation of propargyl bromide in soil. Previous results indicated little biodegradation of propargyl bromide at initial concentrations of ~20 and ~300 mg kg^{-1} and first-order half lives that ranged from ~1 day to ~12 days.[15,16] In the same soil, propargyl bromide degraded more rapidly than methyl bromide.[15,16] These compounds are structurally similar, and both are primary alkyl halides. Analysis of some products of propargyl bromide and methyl bromide degradation in soil suggested that both may degrade in soil abiotically by alkylation of soil organic matter:[16] hydrolysis formed propargyl alcohol and Br^- in equimolar amounts. Degradation in soil produced Br^-, but very little propargyl alcohol. Other potential intermediates, including propiolic acid, have not been monitored.

The objective of the present experiments was to further characterize the rate and mechanism of transformation of propargyl bromide in soil. This information is required for a more extensive evaluation of propargyl bromide's potential to serve effectively as a soil fumigant. The potential for biotic degradation at low propargyl bromide concentrations and the effect of environmental conditions, soil type and initial concentration needs to be assessed to better predict soil concentrations that may occur following soil fumigation. Analysis of degradation products and the relative rate of degradation in autoclaved and non-sterilized soil provides some insight into the mechanism of propargyl bromide transformation in soil.

2 MATERIALS AND METHODS

2.1 Chemicals

Propargyl bromide, (80% purity in toluene) was provided by Albemarle Corporation (Baton Rouge, LA). Propargyl alcohol (>99% purity) was purchased from Fluka Chemical (Ronkonkoma, NY) and propiolic acid (96% purity) was purchased from Sigma–Aldrich (Milwaukee, WI). Sodium bromide (99.6% purity) was purchased from Fisher Scientific (Pittsburgh, PA). A standard solution of propargyl bromide (5.0 mg ml^{-1}) in deionized water + methanol (90 + 10 by volume) was prepared and used to spike soil samples for the highest propargyl bromide concentration. This concentration is ~30% of the reported aqueous solubility of propargyl bromide in water.[15] Spiking standards for other initial propargyl bromide concentrations were prepared by diluting this solution with deionized water. Calibration standards of sodium bromide for quantitation were prepared in ultrapure water; calibration standards of propargyl bromide, propargyl alcohol and propiolic acid were prepared in dichloromethane.

2.2 Soils

Arlington sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf) was collected from the University of California, Riverside Agricultural Experiment Station in Riverside, CA. Coachella fine sand (sandy mixed hyperthermic Typic Torrifluvent) was collected from the University of California, Riverside Coachella Valley Agricultural Research Station in Thermal, CA. Chualar loam (fine-loamy, mixed, thermic Typic Argixerroll) was collected from an agricultural field near Salinas, CA, and Florida muck (Euic, hyperthermic Lithic Meisaprists) was collected from the Everglades Research and Education Center near Belleglade, FL and express shipped to Riverside, CA. These soils have widely varying properties (Table 1) representing a range of soils typically used in fumigated production agriculture. Soil was collected from the surface ~30 cm, and all soils were collected fresh for these experiments. Soils were sieved to pass through a 2-mm screen and then stored at 4 °C. Experiments were initiated within 2 weeks of soil collection. The initial moisture content of the soil was determined, then purified deionized water was added to bring the moisture content to that listed in Table 1. The moist soil was thoroughly mixed and sieved to 2 mm mesh size. The organic carbon content of these soils ranged from 3 to 460 g kg^{-1} (Table 1).

2.3 Degradation in soil

For Arlington sandy loam, Coachella fine sand, and Chualar loam, soil (10 g dry weight) was transferred to 21.6-ml headspace vials. For the Florida muck, 2.2 g

	Coachella fine sand	*Arlington sandy loam*	*Chualar loam*	*Florida muck*
Organic carbon[a] (g kg^{-1})	3.2	6.3	8.0	460
Sand (%)	84.2	74.6	55.4	NA[b]
Silt (%)	12.8	18.0	28.0	NA
Clay (%)	2.9	7.4	16.6	NA
pH	7.31	6.73	8.04	7.16
CEC (meq 100 g^{-1})	8	3.8	9.3	NA
Water content (g g^{-1})	0.10	0.10	0.10	1.25
Moisture at 1/3 bar (ml ml^{-1})	0.11	0.19	0.22	NA

[a] Total carbon and inorganic carbon determined coulometrically; organic carbon content determined by difference.
[b] NA: not available for organic soil.

Table 1. Some properties of the soils used in this study

of soil (dry weight) was added to 21.6-ml headspace vials, which resulted in approximately the same ratio of soil to headspace as was present in the vials containing the other soils. Half the samples were sterilized by autoclaving. The autoclave cycle was 1 h at 121 °C and 0.1 MPa, after which the items were removed, allowed to stand for 24 h and 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 deionized water. Vials were spiked with propargyl bromide aqueous solution to result in three initial concentrations ranging from ~0.7 to ~70 mg propargyl bromide per kg dry soil. Vials were capped immediately after spiking with aluminum seals and Teflon-lined butyl rubber septa, which produces a gas-tight seal. Samples were incubated in the dark at 25 (±0.1) °C. Six vials were removed at each sampling time and stored at −78 °C until extraction.

Spiking with propargyl bromide in toluene resulted in toluene concentrations of 1.3–130 μg ml^{-1} for the Arlington sandy loam, Chualar loam and Coachella fine sand, assuming all toluene was present in the soil water. For samples spiked with the two lowest propargyl bromide concentrations, the toluene concentration in the soil water was below that demonstrated to have no observable effect on soil microbial community population, function, or activity.[25] Soil samples spiked with the highest concentration of propargyl bromide may have been impacted by the microbial toxicity of toluene as well as by propargyl bromide: toluene concentrations of this magnitude (130 μg ml^{-1}) have been shown to impact soil microbial functional diversity (Biolog assay), but not the number of culturable bacteria or overall soil respiration.[25] For the Florida muck, toluene concentrations in the soil water ranged from 0.1 to 10 μg ml^{-1}, owing to its higher water content (Table 1), and all toluene concentrations were below the level for which there was no observable impact on the soil microbial community.[25]

Triplicate samples were extracted with dichloromethane for propargyl bromide, propargyl alcohol and propiolic acid analysis. Frozen samples were decapped, 10 ml of dichloromethane and 10 g of anhydrous sodium sulfate were added, and the vials were recapped, vortexed, and placed on a shaker table for 1 h. An aliquot of the extract was transferred to a GC vial for determination of propargyl bromide (GC-ECD), propargyl alcohol and propiolic acid (GC–MS). For propargyl bromide, an HP 6890 GC with a μECD detector was used with a DB 624 column (Restek, Bellefonte, PA). Propargyl alcohol and propiolic acid were quantified using a HP 5890 GC with a 5971 MSD detector in selected ion monitoring mode. For propargyl alcohol analysis, a Carbowax column (Alltech, Deerfield, IL) was used, and ions with *m/z* 28, 39 and 55 were monitored. Analysis of propiolic acid used direct injection to a Stabilwax-DB column (Restek, Bellefonte, PA), and ions with *m/z* 44.05, 44.9, 45.9 and 59.15 were monitored.

An additional set of triplicate vials was extracted with water for analysis of Br^- by ion chromatography. Frozen samples were decapped, 10 ml of ultrapure water added, and the vials recapped, vortexed and placed on a shaker table for 1 h. An aliquot of the water extract was transferred to an IC vial for determination of Br^- using a Dionex DX-100 with an AS14 column.

Recovery of each compound was assessed at concentrations similar to those encountered in the degradation experiment. Recovery of propargyl bromide was measured at 75, 7.5 and 0.75 mg kg^{-1}, Br^- recovery was measured at 0.5, 5 and 50 μg g^{-1} and propargyl alcohol recovery was measured at 7.2 mg kg^{-1}. Samples (five replicates) were spiked with an aqueous solution of propargyl bromide, Br^- or propargyl alcohol, and placed on a reciprocating shaker for 1 h. Samples were then transferred to a freezer maintained at −78 °C overnight, then extracted and analyzed as described above.

A first-order degradation kinetic model ($C = C_0 e^{-kt}$) was fitted to the concentration C (μmol) of propargyl bromide remaining in soil as a function of time (t); k is the apparent first-order degradation constant and C_0 is the concentration (μmol) of propargyl bromide in the soil at time 0. The rate of production of Br^- and propargyl alcohol (μmol) was fitted to a first-order exponential increase model ($C = C_0(1\text{-}e^{-kt})$).

The effect of repeated propargyl bromide treatment on the rate of propargyl bromide degradation was investigated in non-autoclaved Arlington sandy loam. In these experiments, the rate of propargyl bromide degradation was determined following an initial spike with propargyl bromide and after one, two and three additional treatments with propargyl bromide. Soil samples were prepared and spiked as in the initial experiment, with initial propargyl bromide concentrations of about 0.7 and 7 mg propargyl bromide per kg dry soil. Vials were capped immediately after spiking and samples were incubated at 25 (±0.1) °C. Triplicate vials were removed at each sampling time and stored at −78 °C until extraction. Following the final sampling time (11 days), all remaining vials were decapped and allowed to vent in the hood for 3 days, after which the water content was readjusted and the samples respiked with the same concentration of propargyl bromide (spiking interval 14 days). Additional samples were collected to characterize the degradation rate after respiking. Degradation rates were determined after spiking with propargyl bromide once, two, three and four times. Samples were extracted using ethyl acetate (10 ml) and extraction and analysis procedures were as described above.

The effect of the initial Br^- concentration on the rate of propargyl bromide degradation in soil was assessed in Florida muck and Arlington sandy loam. Florida soil samples (2.6 g dry weight) were spiked with 17, 240 and 5800 μmol Br^- as an aqueous solution of sodium bromide. Arlington soil samples (10 g dry weight) were spiked with 60 μmol Br^- as an aqueous solution of sodium bromide. All samples were

then spiked with ~8 μmol propargyl bromide and incubated, extracted, and analyzed as described above.

3 RESULTS AND DISCUSSION

3.1 Pattern of product formation from propargyl bromide degradation

Propargyl bromide degradation resulted in the formation of one mole of Br^- for each mole of propargyl bromide degraded, but little formation of propargyl alcohol (Fig 1). This pattern of product formation was observed for all soils at all initial propargyl bromide concentrations, and in both autoclaved and non-sterilized soil samples. As was observed previously,[16] hydrolysis was not the primary mechanism of propargyl bromide degradation in these soils. Autoclaving had little effect on the rate of propargyl bromide degradation in soil at concentrations $\geqslant 7\,mg\,kg^{-1}$ (Fig 1, Table 2), indicating that propargyl bromide degradation in these samples was dominated by abiotic processes. Formation of Br^- indicated that the observed propargyl bromide loss in all soils was not due to sorption.

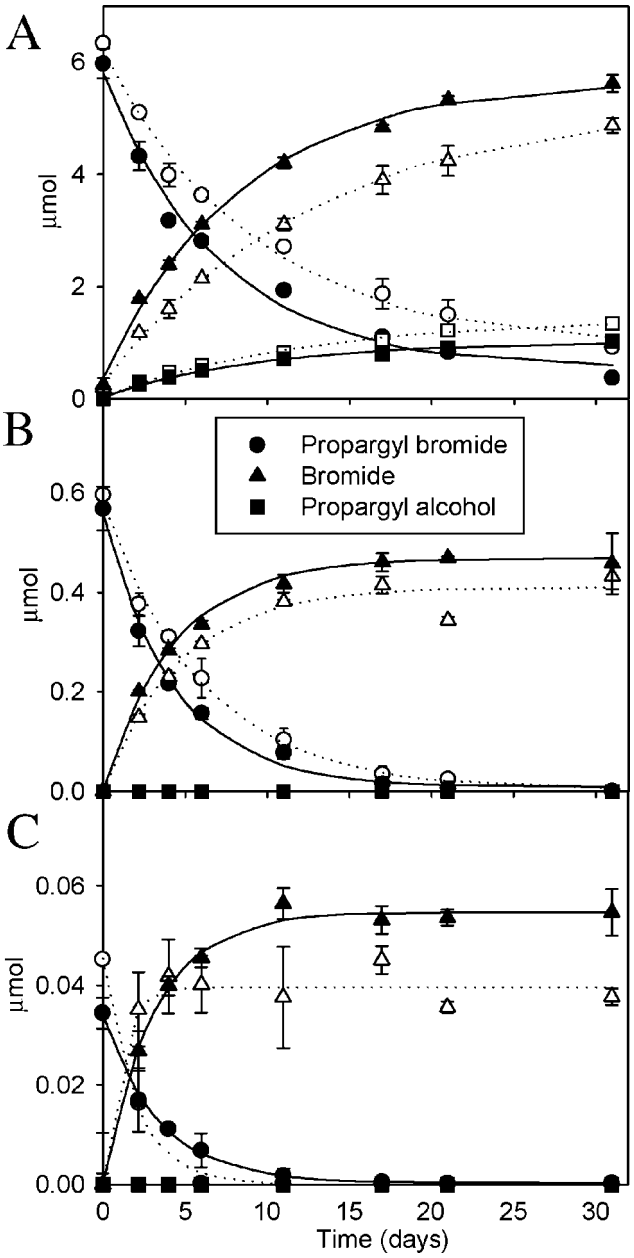

Figure 1. Propargyl bromide degradation with concurrent formation of bromide and propargyl alcohol in Coachella fine sand at initial propargyl bromide concentrations of approximately (A) 70, (B) 7 and (C) 0.4 mg propargyl bromide kg^{-1} dry soil. Closed symbols and solid lines indicate autoclaved soil samples; open symbols and dotted lines indicate non-sterilized samples. Error bars indicate variability between triplicate samples.

In both autoclaved and non-sterilized soil samples, the rate of propargyl bromide degradation was equal to the rate of Br^- formation (Figs 1 and 2(A)). Since degradation of propargyl bromide resulted in equimolar formation of Br^-, the maximum molar concentration of Br^- was similar to the initial molar concentration of propargyl bromide (Figs 1 and 2(B)). Molar concentrations of propargyl alcohol were only 10–20% of the initial propargyl bromide concentration (Figs 1 and 2(B)). Very low concentrations of propargyl alcohol and Br^- were not detectable (instrument limits of detection were ~0.03 ng for propargyl bromide, 0.5 ng for propargyl alcohol and 5 ng for Br^-). Recovery of all compounds was generally 90–105%. Results for samples exhibiting recoveries >80% were not corrected for recovery. Samples showing <80% recovery (Br^- in Arlington sandy loam at lowest two concentrations; propargyl alcohol in Salinas soil) were corrected using the mean recovery measured in five replicate samples. No propiolic acid was detected in any sample (limit of detection ~1.7 ng). Little accumulation of propargyl alcohol during propargyl bromide degradation in soil is advantageous because propargyl alcohol has high toxicity, similar to that of propargyl bromide (oral LD_{50} in rats, ~70 mg kg^{-1} for both propargyl bromide and propargyl alcohol).[26] In soil, propargyl alcohol degrades at a rate similar to propargyl bromide.[16]

3.2 Effect of soil and application conditions on the rate and mechanism of propargyl bromide degradation in soil

3.2.1 Effect of soil type and initial propargyl bromide concentration

The rate of propargyl bromide degradation increased with increasing soil organic matter content, with half-lives ranging from $\leqslant 1$ day for the Florida muck to >1 week for the low-organic sandy soils (Table 2). These results are consistent with previous results, where an increase in propargyl bromide degradation rate was observed with an increase in soil organic matter content.[2,15,16] The rate of propargyl bromide degradation was correlated to the organic carbon content of the soil and, at each concentration, correlation coefficients were >0.97 for the autoclaved samples and >0.99 for the non-sterile samples. A very high rate of degradation in high-organic soils may impact efficacy, where higher propargyl bromide application rates may be required in heavy soils compared to sandy

Initial PrBr	Apparent first-order degradation rate (day^{-1}) (±SE)[a] ~0.7 mg kg^{-1}	~7 mg kg^{-1}	~70 mg kg^{-1}
Coachella fine sand			
Non-sterile	0.2 (±0.1) [0.99]	0.17 (±0.01) [0.99]	0.08 (±0.01) [0.97]
Autoclaved	0.29 (±0.01) [0.99]	0.22 (±0.01) [0.99]	0.11 (±0.01) [0.97]
Arlington sandy loam			
Non-sterile	1.8 (±0.2) [0.99]	0.19 (±0.01) [0.99]	0.09 (±0.01) [0.99]
Autoclaved	0.29 (±0.02) [0.99]	0.15 (±0.01) [0.98]	0.10 (±0.01) [0.97]
Chualar loam			
Non-sterile	1.9 (±0.1) [0.99]	0.25 (±0.02) [0.95]	0.15 (±0.01) [0.99]
Autoclaved	0.68 (±0.02) [0.99]	0.23 (±0.02) [0.94]	0.20 (±0.01) [0.99]
Florida muck			
Non-sterile	15 (±0.7) [0.99]	1.63 (±0.04) [0.99]	0.64 (±0.01) [0.99]
Autoclaved	1.85 (±0.05) [0.99]	0.98 (±0.02) [0.99]	0.60 (±0.03) [0.98]

[a] Values in square brackets are r^2 for curve fit.

Table 2. Apparent first-order degradation rates for propargyl bromide in four soils

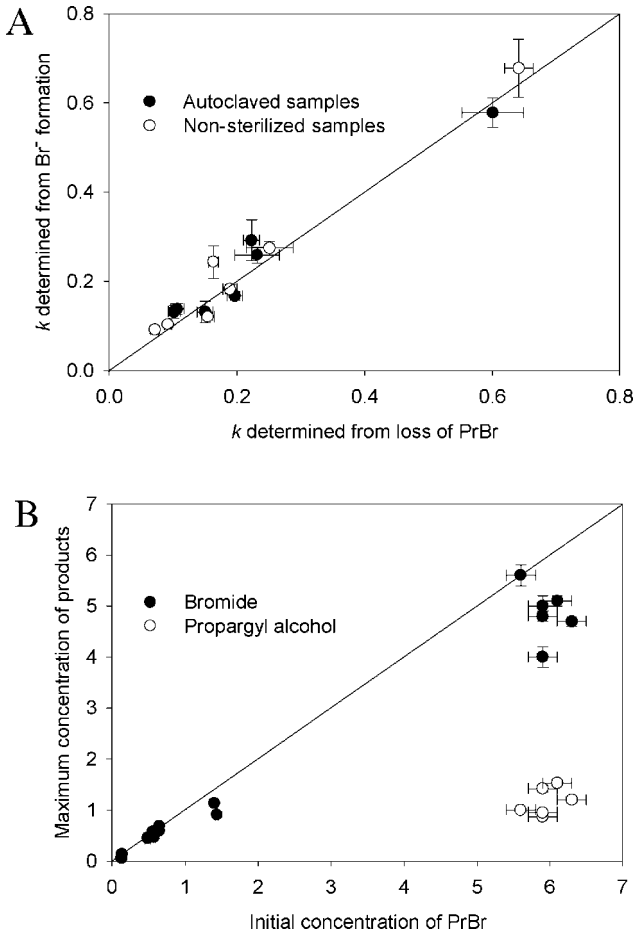

Figure 2. (A) First-order rate coefficients (*k*) determined from loss of propargyl bromide and from the increase in bromide concentration were generally not significantly different. (B) Degradation of propargyl bromide resulted in equimolar formation of Br^- but little propargyl alcohol; the maximum concentration of Br^- (μmol) formed was similar to the initial concentration of propargyl bromide (μmol) but formation of propargyl alcohol accounted for only 10–20% of the initial propargyl bromide. Graphs show *k* and maximum concentration values for the two highest initial concentrations of propargyl bromide; at the lowest spiking concentration, Br^- concentrations near the detection limit precluded an accurate measurement of *k* and C_{max}. Propargyl alcohol was only detected in samples spiked with the highest concentration of propargyl bromide.

soils to compensate for rapid propargyl bromide degradation.[2] However, rapid degradation generally reduces emissions of fumigant compounds, because the fumigant is degraded during its residence time in the soil, reducing the mass volatilized from the soil surface.

The apparent first-order rate coefficients for propargyl bromide degradation in each soil increased as the initial propargyl bromide concentration decreased (Table 2). In autoclaved soil samples, the first-order *k* increased by a factor of 3 for a decrease in concentration from ~70 to ~0.7 mg kg^{-1} (Table 2). Dependence of *k* on the initial concentration of propargyl bromide indicates that the degradation reaction is not simple first order, even in autoclaved soil samples.

In non-sterilized soils, there was generally a greater increase in *k* at low concentrations. A component of biological degradation was evident at the lowest concentration (0.7 mg kg^{-1}). Based on the first-order degradation constants in Table 2, there was no evidence of biological degradation in Coachella fine sand, while biological degradation accounted for ~30% (Chualar loam) to 80–90% (Arlington sandy loam and Florida muck) of the total degradation in the other soils at the lowest spiking level. At the higher two concentrations, there was not an appreciable difference in the rate of propargyl bromide degradation in sterilized and non-autoclaved soil for Coachella fine sand, Arlington sandy loam and Chualar loam (Table 2). For Florida muck, some component of biological degradation was evident at 7 mg kg^{-1}, accounting for ~40% of the total degradation. For all soils, propargyl bromide degradation at concentrations $\geqslant$7 mg kg^{-1} appeared to be primarily via abiotic transformation. An investigation of the impact of propargyl bromide on soil microbial communities indicated that Arlington sandy loam spiked with 100 mg kg^{-1} and higher concentrations of propargyl bromide had a dramatic effect on the structure of the soil microbial community, which was sustained for several weeks following propargyl bromide treatment. A much less severe impact on microbial activity was observed at

10 mg kg^{-1} propargyl bromide.[24] No information on the impact of lower concentrations of propargyl bromide on soil micro-organisms is available.

While the first order k values indicate that proportionally more propargyl bromide is degraded at low concentrations, the propargyl bromide mass degraded per unit time still increased with increasing initial propargyl bromide concentration. In 4 days, approximately 0.03, 0.3 and 3 μmol of propargyl bromide were degraded in samples with initial propargyl bromide concentrations of 0.7, 7 and 70 mg kg^{-1}, respectively, in the Arlington sandy loam, Coachella fine sand and Chualar loam. In the Florida muck, approximately 0.01, 0.06 and 0.4 μmol propargyl bromide were degraded in 0.5 days at initial propargyl bromide concentrations of 0.7, 7 and 78 mg kg^{-1}, respectively. Although higher concentrations result in a longer propargyl bromide half-life in these soils, it is likely that more propargyl bromide mass will be degraded near the injection source where the highest concentrations occur. This may result in the accumulation of Br^- near the injection points.

3.2.2 *Effect of repeated propargyl bromide application*

The rate of propargyl bromide degradation was determined in non-autoclaved Arlington sandy loam after repeated application of propargyl bromide. Arlington sandy loam was chosen because of the high component of biological degradation observed at the lowest spiking level in this soil (Table 2). At the higher propargyl bromide concentration (7 mg kg^{-1}), there was essentially no difference in the rate of propargyl bromide degradation following the first spike and the rate observed in subsequent spikes (Table 3). At the lower propargyl bromide concentration (0.7 mg kg^{-1}), degradation was fastest following the initial propargyl bromide spike, and the degradation rate remained relatively constant in subsequent spikings (Table 3). From these results, it appears that micro-organisms capable of rapidly degrading propargyl bromide were not enriched with repeated application of the compound. Although there was some evidence of biological degradation in this soil at the lowest spiked concentration (Table 2), propargyl bromide degradation did not become more efficient with additional exposure to the compound. At an initial propargyl bromide concentration of 0.7 mg kg^{-1}, the rate of degradation in spikes two through four was only about half of that in the first spike (Table 3), although the rate was still greater than that observed in autoclaved samples at the same initial concentration (Table 2). From these results, it appears that the initial spike may have suppressed biodegrading micro-organisms, but that some component of biological degradation remained active after the first exposure to propargyl bromide and remained constant in subsequent spikes. The impact of repeated application of propargyl bromide at longer time scales requires further investigation. Accelerated degradation of the fumigants 1,3-D and methyl isothiocyanate has been observed in soils receiving repeated applications at bimonthly to yearly intervals.[27–29] There was no evidence of biological degradation in any of the Arlington sandy loam samples spiked with 7 mg kg^{-1} propargyl bromide (Table 3), indicating complete suppression of biodegrading micro-organisms at this concentration.

Table 3. Apparent first-order degradation rates propargyl bromide in non-autoclaved Arlington sandy loam after repeated spiking with propargyl bromide

Initial propargyl bromide	Apparent first-order degradation rate (± SE)[a]	
	~0.7 mg kg^{-1}	~7 mg kg^{-1}
Spike 1	1.2 (±0.1) [0.99]	0.13 (±0.01) [0.98]
Spike 2	0.68 (±0.03) [0.99]	0.10 (±0.00) [0.99]
Spike 3	0.67 (±0.04) [0.98]	0.11 (±0.01) [0.98]
Spike 4	0.50 (±0.02) [0.99]	0.08 (±0.01) [0.98]

[a] Values in square brackets are r^2 for curve fit.

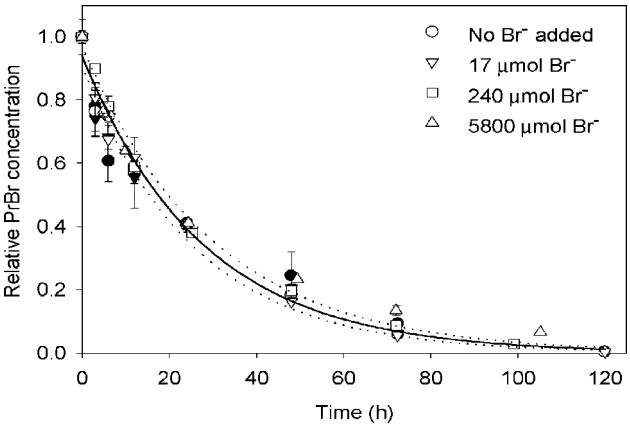

Figure 3. No inhibition of propargyl bromide degradation was observed in Florida muck soil samples with initial concentrations of Br^- approximately 2, 30 and 2600 times higher than the maximum Br^- concentration accumulated as a result of propargyl bromide degradation. Solid symbols indicate autoclaved soil samples; open symbols indicate non-sterilized samples. Solid line indicates first-order fit to pooled data; dotted lines indicate standard error in C_0 and k.

3.3.3 *Effect of high initial Br^- concentrations*

Degradation of propargyl bromide in soil by all known and proposed mechanisms results in the formation of Br^-. In these soil samples, degradation at initial propargyl bromide concentrations $\geqslant$7 mg kg^{-1} was primarily abiotic. This abiotic transformation is postulated to be a nucleophilic substitution reaction with nucleophilic sites on soil organic matter, resulting in the alkylation of soil organic matter.[16] In pure S_N1 nucleophilic substitution reactions, the rate of reaction is slowed by high concentrations of the reaction products. Initial Br^- concentrations thousands of times higher than the maximum Br^- formed as a result of propargyl bromide degradation did not inhibit the rate of propargyl bromide degradation in Florida muck (Fig 3). Likewise, no inhibition of the propargyl bromide degradation rate was observed in Arlington sandy loam with initial Br^- concentrations ~7.5 times

the maximum Br^- formed as a result of propargyl bromide degradation. Accumulation of Br^- in the soil, which may occur as a result of degradation of high concentrations of propargyl bromide near the injection source, is not expected to inhibit the rate of propargyl bromide degradation. The absence of a dependence of the rate of propargyl bromide depletion on the initial concentration of the product (Br^-) suggests that the reaction may not be purely S_N1.

4 CONCLUSIONS

In these experiments, the observed half-life of propargyl bromide in soil ranged from a few hours to 10 days (Table 2), depending on the soil type and initial propargyl bromide concentration. Transformation of propargyl bromide was primarily abiotic at concentrations $\geqslant 7\,mg\,kg^{-1}$, and some component of biological degradation was observed in samples spiked with $0.7\,mg\,kg^{-1}$. Biological degradation was not enhanced with repeated application of propargyl bromide at short (14-day) intervals. The proposed abiotic transformation mechanism is alkylation of soil organic matter. Since there is the potential for a wide variety of reactive sites on soil organic matter (for example, —SH, —NH, $—NH_2$ and —OH groups) with different affinities for propargyl bromide as an electrophile, a number of transformation reactions (including hydrolysis) may occur simultaneously in these soil samples. The observed transformation rate in soil therefore represents the overall rate of many simultaneous reactions. Although depletion of propargyl bromide at each initial concentration in each soil could be described using a first-order model in these experiments, the overall reaction did not follow first-order kinetics. The rate of propargyl bromide transformation was dependent on the soil organic matter content and initial propargyl bromide concentration. It is likely that other factors, including temperature and soil moisture, are also important in determining the rate of propargyl bromide transformation in soil. This information is important in determining the potential effectiveness of propargyl bromide as a soil fumigant. Sufficient concentrations are required for adequate pest control, but prolonged persistence may result in off-site movement and environmental contamination. These factors must be balanced when determining management practices for propargyl bromide use.

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