

Volatility, Adsorption, and Degradation of Propargyl Bromide as a Soil Fumigant

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During the 1960s, propargyl bromide (3-bromopropyne, C_3H_3Br , or 3BP) was used in a soil fumigant Trizone, a combination of chloropicrin, methyl bromide, and propargyl bromide. Since a great deal of attention is being placed on finding replacements for methyl bromide (CH_3Br , MeBr) in soil fumigation, there is a revived interest in developing propargyl bromide as an alternative fumigant. However, at present, no information exists for assessing its behavior and safety in the environment. In this study, several important parameters needed to determine its environmental fate are obtained. These include basic parameters such as solubility, saturated vapor density, the Henry's law constant, adsorption, and degradation. These parameters are compared to MeBr and 1,3-dichloropropene (1,3-D), a methyl bromide alternative. At 25 °C, the Henry's law constant, K_H , for 3-bromopropyne is 0.046, which is smaller than that for MeBr and similar in magnitude to that for 1,3-D. In water at 25 °C, the solubility is $\approx 1.5\%$ and 3BP slowly degrades with a hydrolysis half-life of 47 days. In soil, the degradation half-life ranged from 1.2 to 5 days, depending on the soil type. Under typical agricultural conditions, 3BP will move readily in soils, a desirable characteristic for fumigants, but, due to its short soil degradation time, should not pose a serious environmental risk.

Keywords: *Propargyl bromide; methyl bromide alternative; Henry's law constant; degradation; solubility; hydrolysis; adsorption, vapor density*

INTRODUCTION

Beginning in 2001, methyl bromide (MeBr) will no longer be available for use in soil fumigation in the United States unless Congress acts to exempt MeBr from certain provisions of the Clean-Air Act. Unless effective alternatives can be found, farmers and agricultural producers will experience a severe adverse economic impact (NAPIAP, 1992; Ferguson and Padula, 1994). Intensive research is currently being conducted to identify replacements for MeBr. For example, methyl iodide has been proposed as a replacement for MeBr in soil fumigation (Sims et al., 1995), and it has been shown to be equivalent to MeBr, on a molar basis, for controlling a wide variety of soil-borne pests such as weeds, nematodes, and fungi (Ohr et al., 1996; Zhang et al., 1997; Becker et al., 1997). However, the cost of producing methyl iodide and safety issues are still of concern. Other alternatives include 1,3-dichloropropene (1,3-D), chloropicrin, and methyl isothiocyanate. Because these alternatives have narrower spectra of activity than MeBr (Noling and Becker, 1994), it is likely that combinations of two or more of these chemicals in large quantities will have to be used.

Another potential alternative fumigant is propargyl bromide (3-bromopropyne, 3BP). Developed by Dow Chemical Co. (FCH, 1997) during the 1960s, 3BP was abandoned due to its sensitivity to shocks. Since 3BP has never been a registered pesticide, many aspects of its environmental behavior are unknown. In fact, no reported information on critical environmental parameters could be found in the literature. Therefore, information on 3BP's transformation and partitioning behavior in the soil–air–water system would be very valuable. Knowledge of these processes is critical before

a decision can be made whether 3BP should be used as a soil fumigant. It is also important for designing application methodology that minimizes the application rate and optimizes the control of target organisms.

The objective of this paper is to determine several basic physical properties of 3BP that are needed to assess its environmental behavior. The saturated vapor density and Henry's law constant at various temperatures are obtained to characterize volatility. This information is important in determining volatilization and vapor diffusion in soils and plays an important role in both chemical distribution in soils and losses to the atmosphere. The solubility and hydrolysis in water are obtained. This information is important for determining whether 3BP might leach to groundwater. In addition, the adsorption and degradation in three soils are also determined. Using these chemical parameters, several mobility indices are calculated to elucidate how 3BP will move in the environment. From this information, a preliminary assessment of the environmental consequence of the use of 3BP as a MeBr replacement can be made.

MATERIALS AND METHODS

Chemicals and Soils. Propargyl bromide (C_3H_3Br , 3BP) with a purity of 97% was purchased from Fluka Chemie AG (Buchs, Switzerland). The Arlington sandy loam (Field 2B, University of California Experimental Station, Riverside) was used in previous field studies on methods for reducing MeBr emissions (Wang et al., 1997a,b) and has 0.92% organic matter content. The Carsitas loamy sand (Coachella Valley Field Station, University of California, Coachella) and Linne clay loam (Santa Barbara, CA) were used in determining the degradation and adsorption of MeBr and 1,3-D (Gan et al., 1994, 1997). Carsitas loamy sand was also used in experi-

ments for testing the efficacy of methyl iodide (Ohr et al., 1996; Becker et al., 1997). The organic matter contents for the Carsitas and Linne soils are 2.51 and 2.99%, respectively. The pH for the three soils ranged from 7.2 to 7.5. The clay contents for Arlington, Carsitas, and Linne soils, respectively, are 7, 11, and 25%.

Before use, the water content of the original soil was determined and the soils were air-dried and passed through a 2-mm sieve. The water content for Arlington and Carsitas soils was readjusted to 12%, and the water content of the Linne clay loam soil was adjusted to 20% due to its higher clay content.

Solubility and Saturated Vapor Density. The solubility and saturated vapor density for 3BP were obtained for the temperature range 2–40 °C. An excess quantity of 3BP was transferred to triplicated headspace vials (8.7 mL for solubility and 121.2 ± 0.6 mL for vapor density), and 5 mL of water was added to the vials used for determining the solubility. Next, the vials were capped with Teflon-faced butyl rubber septa and aluminum seals and placed in a constant-temperature incubator or water bath and allowed to equilibrate at a selected temperature. At equilibrium, the solubility was determined by taking a 50- μ L aliquot of the water phase and transferring it to a solvent trap. The saturated vapor density was determined by taking a 0.25-mL (30 and 40 °C) or 0.5-mL (2–25 °C) aliquot of the headspace using a gastight syringe and transferring it to a solvent trap. The solvent trap consisted of an 8.7-mL GC vial containing 5 mL of ethyl acetate and 3 g of anhydrous sodium sulfate to remove any residual water, when present (Spencer and Cliath, 1970; Gan and Yates, 1996). The gas- or liquid-phase concentration was determined using an HP5890 GC equipped with an electron capture detector. The GC parameters were RTX-624 capillary column (Restek Co., Bellefonte, PA), 70 °C oven temperature, 240 °C injection port temperature, 270 °C detector temperature, and 1.1 mL min⁻¹ column flow rate (helium).

Degradation in Water and Soil. Degradation in water was determined at 25 °C. Stock solution containing \approx 400 mg/L of 3BP in water was prepared and transferred into 36 8.7-mL headspace vials (Supelco, Co., Bellefonte, PA). The vials were completely filled with solution, capped with Teflon-faced butyl rubber septa and aluminum seals, placed in a constant-temperature incubator, and allowed to equilibrate. At selected times, 3–4 vials were randomly sampled by transferring 100 μ L of the solution to a solvent trap for GC analysis. Once sampled, the vials were discarded.

For the "live" soil incubation experiment, no further modifications to the soil were made. For the "sterilized" soil incubation experiments, \approx 650 g of each soil type was autoclaved twice for 30 min. Since autoclaving changes the soil moisture content, sterile water was added to bring the moisture content back to prescribed levels. A total of 11.2 g of moist soil was placed into 21-mL headspace vials, and 5 μ L of acetone containing 40 μ g/ μ L of 3BP was added to each soil vial. The vial was immediately sealed and placed in a constant-temperature room at 25 °C. The initial concentration of 3BP was 20 μ g/g of soil. At predetermined times, three replicate samples from each treatment were removed from the incubator and kept in a freezer at -15 °C until they were analyzed for 3BP. Before analysis, the soil vials were de-capped, 10 mL of ethyl acetate was added, and the vials were recapped. Extraction was accomplished by shaking the solvent-soil mixture at high speed on a mechanical shaker for 60 min. An aliquot of the supernatant was transferred into GC vials containing a small amount of anhydrous sodium sulfate to remove any residual water. The water-dried extract of ethyl acetate was then transferred into a GC vial and analyzed on the GC. The degradation coefficient was obtained by determining the slope of the natural logarithm time vs concentration, using linear regression.

Air–Water Partition Coefficient, K_H . The linearity of the equilibrium air–water partition coefficient, K_H , was determined over a concentration range from 150 to 4600 mg/L at 25 °C. Stock solutions containing approximately 150, 600, 1200, 2300, 3500, 3800, and 4600 mg/L of 3BP in ultrapure

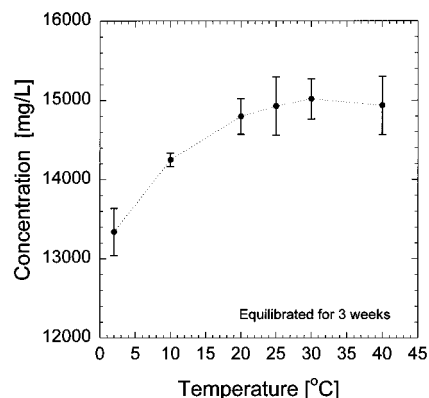


Figure 1. Solubility of 3-bromopropyne (C_3H_3Br) at various temperatures after a 3 week equilibrium period.

water were prepared in volumetric flasks. Five milliliters of the stock solutions was transferred into triplicated headspace vials (21.6 mL; Supelco, Co., Bellefonte, PA), sealed with Teflon-faced butyl rubber septa/aluminum seals (Supelco), placed in a constant-temperature room (25 ± 0.2 °C), and allowed to equilibrate for at least 24 h. Preliminary experiments showed that the 24-h equilibration under the above conditions was adequate for achieving equilibrium. During sampling, 0.5 mL of the headspace and 100 μ L of the liquid phase were withdrawn with a 1-mL gastight syringe and transferred into separate solvent traps for GC analysis.

The temperature dependence of K_H was obtained for the temperature range 2–40 °C. Approximately 30 mL of stock solution at a concentration of 150 or 1200 mg/L was transferred to a blank headspace vial (121.2 ± 0.6 mL, Supelco). The vials were immediately capped with Teflon-faced butyl rubber septa and aluminum seals, placed in a constant-temperature incubator, and allowed to equilibrate at a selected temperature for at least 24 h. During the equilibration, all of the vials were occasionally shaken by hand. After equilibrium, the vapor density of the headspace (C_a) and the concentration in the water phase (C_w) were determined and the dimensionless $K_H = C_a/C_w$ was obtained.

Adsorption in Soil, K_d . The interior volumes of 40 121.2 ± 0.6 mL headspace vials were measured, and 20 g (dry weight) of each soil was added to 8 replicated vials (24 vials total). Next, 20 mL of deionized water was placed into 8 replicated headspace vials. The remaining 8 vials were left empty. To each vial was added 10.0 μ L of 97% 3BP, and the vial was immediately capped with Teflon-faced butyl rubber septa and aluminum seals and placed in a constant-temperature room at 25 ± 0.2 °C for 24 h. The sample vials were shaken occasionally during the equilibration period. After the 24-h equilibration period, 0.5 mL of each vial's headspace was transferred to a solvent trap and analyzed on the GC. The concentrations in the eight blank vials were used to estimate the average mass added to each vial. The vials containing deionized water were used to estimate the liquid–vapor partitioning or K_H . The K_d can be obtained by relating the total concentration, C_T , to the concentration in the headspace using $C_T = \{[(\theta + K_d\rho_b)/K_H] + a\}C_a$ and solving for K_d , where θ , a , and ρ_b are water content ($cm^3\ cm^{-3}$), air content ($cm^3\ cm^{-3}$), and bulk density ($g\ cm^{-3}$), respectively.

RESULTS AND DISCUSSION

Solubility. A chemical's solubility in water is an important parameter affecting how rapidly a chemical will move through porous media. Shown in Figure 1 is the 3BP solubility in water for the temperature range 2–40 °C. At low temperatures, the solubility increases rapidly as temperature rises and levels off at \approx 25–30 °C. This behavior was also observed from two other sets of measurements but is not reported since they had shorter equilibrium periods. At 25 °C, the 3BP solubil-

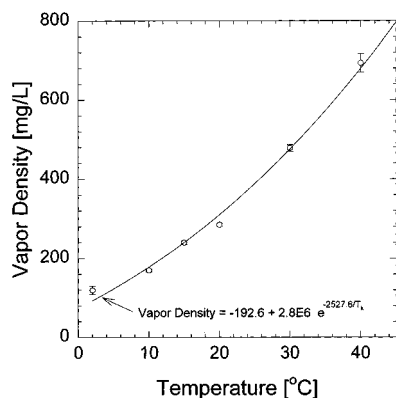
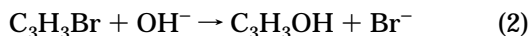
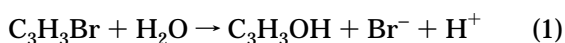


Figure 2. Saturated vapor density for 3-bromopropyne (C_3H_3Br) in the temperature range 2–40 °C. The solid line is a fitted Arrhenius equation with an enthalpy of vaporization of 21.0 kJ/mol and T_k is temperature in kelvin.

ity is 14 900 mg/L or $\approx 1.5\%$ and is comparable to that of MeBr (13 400 mg/L; Wauchope et al., 1992). The solubility of 1,3-D in water is much less than that of 3BP with values at 25 °C (Wauchope et al., 1992; J. Knuteson, Dow-Elanco, Indianapolis, IN, personal communication, 1996) of 2320 mg/L (*trans*-1,3-D) and 2180 mg/L (*cis*-1,3-D). Therefore, under conditions of high leaching, a larger fraction of 3BP will move with the water.

Saturated Vapor Density. The vapor density gives an indication of the volatility of a chemical and is important in the loss of agricultural chemicals from soil (Spencer and Cliath, 1970). Generally, all of the agricultural fumigants have high vapor density since it is desirable to rapidly move the chemical throughout the soil. Shown as open circles in Figure 2 is the saturated vapor density for 3BP over the temperature range 2–40 °C. The error bars indicate the standard deviation of the three replicates. Except at high temperatures, low variability between replicates was observed. The solid line in Figure 2 is a fitted Arrhenius equation relating the vapor density to temperature (kelvin). From this relationship, the enthalpy of vaporization ($\Delta_{vap}H = 21.0$ kJ/mol) can be obtained. At 25 °C the saturated vapor density, $\rho_{v,sat}$, is ≈ 388 mg/L and is greater than the estimated $\rho_{v,sat}$ for 1,3-D [i.e., 205 mg/L (*cis*) and 137 mg/L (*trans*)] at 25 °C (J. Knuteson, personal communication, 1996). Both 3BP and 1,3-D have lower saturated vapor densities compared to MeBr ($\rho_{v,sat} \approx 3878$ mg/L), which was calculated for a vapor pressure of 1 atm, the largest value that can be maintained in an open system. For both 1,3-D and MeBr, the vapor density was estimated using the ideal gas law.

Hydrolysis in Water and Degradation in Soil. It is likely that 3BP undergoes nucleophilic substitution (S_N2) with H_2O as follows



producing propargyl alcohol, bromide ion, and hydrogen ion. Shown in Figure 3 is the persistence (or dissipation) of 3BP in water as a function of time, which follows a pseudo-first-order relationship. Fitting a linearized first-order model gives a half-life, $t_{1/2}$, of 47 days. This value is similar to the 50-day $t_{1/2}$ reported for propargyl

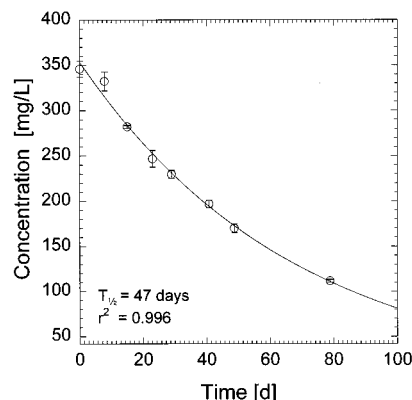


Figure 3. Hydrolysis of 3-bromopropyne (C_3H_3Br) in water at 25 °C. Open circles are measured values and solid line is a first-order degradation model. The estimated half-life is 47 days.

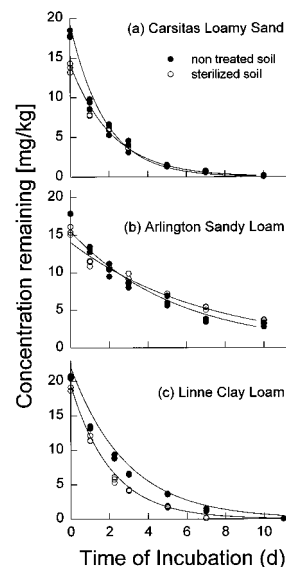


Figure 4. Degradation of 3-bromopropyne (C_3H_3Br) at 25 °C in three California soils. Circles indicate the measured soil concentration, and the lines are fitted first-order degradation models. The degradation coefficients are reported in Table 2.

bromide by Moje (1960) and the 20–50-day values for MeBr hydrolysis in water (Mabey and Mill, 1978; Gentile et al., 1992; Arvieu, 1983) and is longer than the hydrolysis $t_{1/2}$ reported by McCall et al. (1987) for 1,3-D, i.e. 3–51 days, for temperatures ranging from 30 to 10 °C, respectively.

The degradation of 3BP in three soils was determined by measuring changes in the residual concentration with time (Figure 4). The degradation kinetics were well described using a first-order model (Table 2). Also, the first-order degradation coefficient, k , was nearly the same regardless of whether the soil was natural or sterilized. This implies that biodegradation was not significant and chemical degradation was predominant during the short equilibrium time. Under field conditions where microorganisms may acclimate to the presence of 3BP, however, biodegradation may become more significant and further research is warranted.

The reaction pathways for 3BP are slightly more complicated compared to those for MeBr or methyl iodide since the molecule can be attacked at the acetylenic hydrogen, the triple bond, or the bromide atom (GAFC, 1953). Since 3BP degradation in the three soils was considerably faster than hydrolysis, other reactions

Table 1. Physical–Chemical Properties of Propargyl Bromide, Methyl Bromide, and 1,3-D

property	C ₃ H ₃ Br	CH ₃ Br	1,3-D (<i>cis</i>)	1,3-D (<i>trans</i>)
density (g cm ⁻³)	1.585 (20 °C)	1.73 (0 °C)	1.224 (20 °C)	1.217 (20 °C)
MW	119	95	111	111
vapor pressure (mmHg)	na ^a	1824 (25 °C)	34.3 (25 °C)	23.0 (25 °C)
Henry's constant, <i>K</i> _H	na	0.24 (20 °C)	0.074 (25 °C)	0.043 (25 °C)
bp (°C)	89	3.6	104	113
solubility in water (%)	na	1.34	0.22	0.23

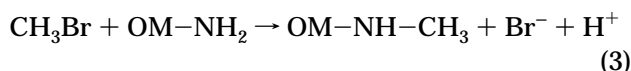
^a na, not found in the literature.

Table 2. First-Order Degradation Rate Constants (Day⁻¹) for 3-Bromopropyne (C₃H₃Br), Methyl Bromide (CH₃Br), and 1,3-D in California Soils

soil	nonsterilized	sterilized
3-Bromopropyne		
decay rate, <i>k</i> (day ⁻¹)		
Arlington sandy loam	0.18 ± 0.01 (<i>r</i> ² = 0.95)	0.14 ± 0.01 (<i>r</i> ² = 0.97)
Carsitas loamy sand	0.57 ± 0.02 (<i>r</i> ² = 0.98)	0.46 ± 0.01 (<i>r</i> ² = 0.99)
Linne clay loam	0.39 ± 0.01 (<i>r</i> ² = 0.99)	0.48 ± 0.01 (<i>r</i> ² = 0.99)
Methyl Bromide ^a		
decay rate, <i>k</i> (day ⁻¹)		
Greenfield sandy loam	0.03 (<i>r</i> ² = 0.97)	0.03 (<i>r</i> ² = 0.97)
Carsitas loamy sand	0.12 (<i>r</i> ² = 1.00)	0.13 (<i>r</i> ² = 1.00)
Linne clay loam	0.12 (<i>r</i> ² = 0.099)	0.16 (<i>r</i> ² = 1.00)
1,3-D (<i>Z</i>) ^b		
decay rate, <i>k</i> (day ⁻¹)		
Arlington sandy loam	0.15 (<i>r</i> ² = 0.96)	0.13 (<i>r</i> ² = 0.99)
1,3-D (<i>E</i>) ^b		
decay rate, <i>k</i> (day ⁻¹)		
Arlington sandy loam	0.19 (<i>r</i> ² = 0.97)	0.15 (<i>r</i> ² = 1.00)

^a Data from Gan and Yates (1996). ^b Data from Gan et al. (1997).

were apparently involved. In a few studies, it has been established that halogenated hydrocarbons react with nucleophilic functional groups (e.g., -NH₂, -NH, -SH, -OH) of soil organic matter, releasing halogen and alkylating the functional groups (Arvieu, 1983; Gan et al., 1994). In the case of MeBr, the reaction can be described as



Similar mechanisms may also be involved in the degradation of 3BP in soil.

In the same soil, 3BP degrades at a similar rate as 1,3-D but much more rapidly than MeBr (Table 2). The calculated *t*_{1/2} for MeBr would be 3–6 times that for 3BP in the same soil (Table 2). In the Greenfield sandy loam, a *t*_{1/2} as long as 22 days was obtained for MeBr in the nonsterilized soil, whereas in Arlington sandy loam (very similar to Greenfield sandy loam), the *t*_{1/2} for 3BP was ≈3 days. Since degradation is an irreversible process, it is an important factor affecting the fraction of chemical available for volatilization to the air and/or diffusion to the groundwater (Wagenet et al., 1989). In theory, without degradation all of the chemical will eventually volatilize or enter groundwater (Yates et al., 1996d). The effect of degradation on MeBr volatilization has been investigated by Gan et al. (1996), who found reduced volatilization in soil columns containing soils rich in organic matter. Since 3BP degrades rapidly in soil, it will likely result in lower volatilization and more limited downward movement compared to MeBr.

Henry's Law Constant. The partition of a chemical between air and water phases, represented by its Henry's law constant *K*_H, is extremely important in determining how easily a chemical moves in soils and the fraction of chemical that enters the atmosphere

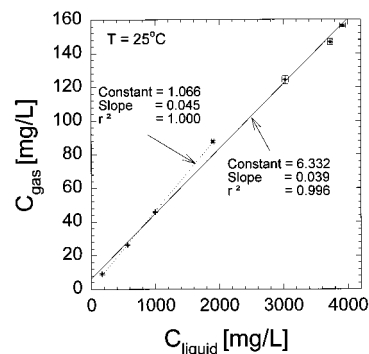


Figure 5. Test of the linearity of liquid–gas-phase partition coefficient at 25 °C. Measurement standard deviations are provided for both *C*_{liquid} and *C*_{gas}. Solid and dashed lines were obtained using linear regression.

through volatilization. To check whether the partitioning of 3BP follows the Henry's law relationship, the linearity of the *K*_H was determined in the range 150–4600 mg/L for 25 °C. This is shown in Figure 5 where the solid line was obtained using all of the measured values and the dotted line using the four lowest concentrations. The small deviation between the fitted (solid line) and measured values throughout this range indicates that the assumptions for the Henry's law constant are largely met. At lower concentrations, i.e., 0–2000 mg/L, the fit to the measured values is improved. From the slopes of these lines, the estimated dimensionless Henry's law constant at 25 °C is from 0.039 to 0.045.

The temperature dependence of the *K*_H was determined for the range 2–40 °C. This is shown in Figure 6, where *K*_H is plotted with respect to temperature. At 25 °C, the *K*_H was found to be 0.046 and nearly doubled to 0.080 at 40 °C. The dashed line in Figure 6 is the Arrhenius equation fitted to the temperature–*K*_H data.

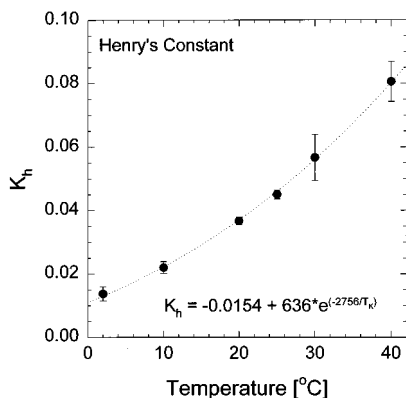


Figure 6. Henry's law coefficient as a function of temperature in the range 2–40 °C. The dashed line is a fitted Arrhenius equation with an activation energy of 22.9 kJ/mol and T_K is temperature in kelvin.

Table 3. Measured K_H and K_d for C_3H_3Br and CH_3Br on Three Soils

soil type	organic matter (%)	C_3H_3Br	CH_3Br^a
K_H ($n = 8$)		0.051 ± 0.002	0.30 ± 0.02
K_d (measured) ($n = 6$) ($cm^3 g^{-1}$)			
Arlington sandy loam	0.93	0.084 ± 0.004	
Greenfield sandy loam	0.92		0.07
Carsitas loamy sand	2.51	0.056 ± 0.005	0.09
Linne clay loam	2.99	0.148 ± 0.014	0.10
K_d^b (corrected) ($n = 6$) ($cm^3 g^{-1}$)			
Arlington sandy loam	0.93	0.049 ± 0.003	
Greenfield sandy loam	0.92		0
Carsitas loamy sand	2.51	0	0
Linne clay loam	2.99	0.033 ± 0.010	0

^a Data from Gan and Yates (1996). ^b Corrected for degradation.

From this relationship, the enthalpy of solution was calculated to be 22.9 kJ/mol.

This K_H value for 3BP is approximately the same as that for 1,3-D (Table 1) and is ~ 5 times smaller than the value for MeBr at 20 °C as reported by Goring (1962; $K_H = 0.244$) and measured by Gan and Yates (1996; $K_H = 0.3$ at 21 °C). With a K_H of 0.244 at 20 °C, MeBr transport in soil is rapid and results in deep penetration into soil and rapid volatilization from the soil surface. Measurements of MeBr volatilization after field application at 25-cm depth and covering of the soil surface with high-density polyethylene plastic film have shown that from 32 to 87% of the applied material will volatilize into the air (Yagi et al., 1993, 1995; Majewski et al., 1996; Yates et al., 1996a–c, 1997; Gan et al., 1996; Wang et al., 1997a,b). With a K_H of 0.046 at 25 °C, the movement of C_3H_3Br in soil can also be expected to be dominated by gas-phase diffusion (Jury et al., 1984) but should be at a rate slower than MeBr.

Adsorption. The measured K_d values for 3BP on these soils ranged from 0.07 to 0.39 cm^3/g and were not strongly correlated with soil organic matter content (Table 3). After correction for degradation during the equilibrium period, the amount adsorbed on the Carsitas soil was within the range of experimental errors, and K_d becomes negligible (Table 3). For Arlington and Linne soils, small adsorption parameters remain. After correction for degradation, K_d for 3BP on the tested soils ranged from 0 to 0.049 cm^3/g . This compares to reported K_d of ≈ 0 cm^3/g for MeBr (Gan and Yates, 1996) and vapor sorption coefficients of 0.026–0.071 for *cis*-1,3-D and 0.015–0.042 cm^3/g for *trans*-1,3-D in a humous sand

Table 4. Mobility Indices for Selected Pesticides

pesticide	RF ^a	AF ^a $l = 25$ cm	t_c^a $l = 10$ cm	t_D^a $l = 10$ cm	class ^b
3-bromopropyne	1.25	0.18	3.75	11.54	3
methyl bromide	2.37	0.59	7.12	4.03	3
1,3-D (<i>Z</i>)	2.81	0.042	8.44	16.19	3
1,3-D (<i>E</i>)	2.79	0.019	8.38	27.60	2
methyl isothiocyanate	1.34	0.37	4.01	55.18	2
2,4-D (acid)	2.10	0.33	6.31	<i>c</i>	1
atrazine	6.52	0.56	19.62	<i>c</i>	1
carbaryl	17.6	0.0001	52.69	<i>c</i>	1
lindane	61.7	0.45	185.19	<i>c</i>	1

^a RF, AF, t_c , and t_D indicate, respectively, retardation factor, attenuation factor, convective mobility time, and diffusive mobility time. ^b Classification scheme of Jury et al. (1984) with larger numbers indicating high mobility. ^c $> 10^5$.

for the temperature range 2–20 °C (Leistra, 1970). Using the reported K_{oc} ($32 cm^3 g^{-1} \text{foc}^{-1}$; Wauchope et al., 1992) and the organic matter content of Leistra (1970; 5.5%), the estimated K_d for a mixture of *cis*- and *trans*-1,3-D is 1.76 cm^3/g . Converting the vapor sorption values from Leistra (1970) to K_d gives the range 1.3–1.5 cm^3/g .

Behavior in Soil. Several mobility indices were computed to determine how 3BP will behave in soil, including the retardation and attenuation factors (Rao et al., 1985; NRC, 1993) and the convective and diffusive mobility times (Jury et al., 1984). The retardation factor [$RF = 1 + (K_d \rho_b / \theta) + aK_H / \theta$] is an index of the relative time needed for a pesticide to move past some specified depth, compared to a nonadsorbing tracer, where ρ_b , θ , and a are, respectively, the bulk density, water content, and air content. The attenuation factor [$AF = \exp(-k\theta(RF)/q)$] is the fraction of pesticide mass that is likely to move past some specified depth, l , given some specified water flow rate, q . This index includes the effects from adsorption, RF, and degradation, k . The convective and diffusive mobility times give a measure of the time needed for a pesticide to travel a distance, l , by convection, $t_c = (\theta + K_d \rho_b + aK_H)l/q$, or diffusion, $t_D = l^2 \phi^2 (\theta + K_d \rho_b + aK_H) / (D_g^a a^3 1/3 K_H)$, where ϕ is the soil porosity and D_g^a is the gas diffusion coefficient (cm^2/day) in air. A summary of these indices is given in Table 4 for 3BP, MeBr, 1,3-D and a few other common pesticides.

The RF is a measure of the effect of adsorption (e.g., atrazine, carbaryl, and lindane) and vapor partitioning (e.g., fumigants) on a pesticide's mobility. The RF values for all of the fumigants range from 1.2 to 2.8 and are less than the other commonly used pesticides listed in Table 4. On the basis of this index, all of the fumigants should be transported at a slower rate compared to a conservative tracer, even though their adsorption coefficients are nearly zero. Also, since 3BP has the lowest RF, it should behave most nearly like a conservative tracer. The AF, which includes the effects of degradation, indicates that $\approx 18\%$ of the 3BP will travel 25 cm compared to 59% of the MeBr, an amount that is 3 times less. If the travel distance is extended to 50 cm, only 3% of the 3BP remains compared to 34% for MeBr. The attenuation of 3BP is somewhat less than that of 1,3-D, which ranges from 2 to 4% after traveling 25 cm.

The effect of convection and diffusion on the movement of 3BP and the other fumigants in soil may be seen from the behavior of the convective and diffusive mobility times, t_c and t_D . In this example, the transport distance, l , and the flux density, q , are 10 cm and 1 cm^3/day .

day, respectively. These are the same values used by Jury et al. (1984, Table 1), which allows comparison to additional pesticides. Using their classification schemes, it is found that (1) all of the fumigants have high convective mobility, (2) 3BP and MeBr have high diffusive mobility, (3) 1,3-D ranges from high to moderate diffusive mobility, and (4) MITC has moderate diffusive mobility. Since diffusive mobility is the principal reason fumigants are rapidly transported in soil, pesticides with low diffusive mobility may suffer from difficulties achieving a uniform soil concentration throughout the treatment zone. This has been observed in field studies using MITC to control root gall in tomatoes and strawberries (Olson and Noling, 1994) and has caused others to develop better methods for distributing MITC (Juzwik, 1994; McHenry, 1994). Due to its relatively high diffusive mobility and low retention on soils, 3BP should readily move through the soil and provide a reasonably uniform concentration distribution.

It should be noted that for all of the agricultural fumigants, the high convective and diffusive mobility and low retention factors promote significant volatilization losses following application to soils, unless the soil surface is covered with a diffusion barrier (i.e., impermeable plastic). Very high emission rates have been reported for MeBr and 1,3-D under both field and laboratory conditions (Yagi et al., 1993, 1995; Majewski et al., 1995; Jin and Jury et al., 1995; Yates et al., 1996a,b; Gan et al., 1996). From one perspective, rapid fumigant movement into the air may be desirable since it would reduce phytotoxicity and the potential for causing groundwater contamination. On the other hand, rapid movement into the atmosphere may be an increased nuisance and may cause undesirable health effects on persons living or working near treated fields. As indicated by its AF, 3BP possesses the desirable trait of high degradation. This will help limit the amount of applied chemical that reaches the atmosphere or groundwater after application, compared to MeBr. From this preliminary study it appears that 3BP shows promise as a replacement for MeBr. Additional research is needed to determine if 3BP is effective in controlling pests, to characterize the volatilization rate and movement in soils after soil fumigation, and to develop methods for reducing chemical movement away from the treatment zone.

ACKNOWLEDGMENT

We thank C. Taylor and Q. Zhang for obtaining some of the reported data.

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Received for review September 12, 1997. Revised manuscript received November 18, 1997. Accepted December 4, 1997.

JF9707849