Gas-Phase Sorption–Desorption of Propargyl Bromide and 1,3-Dichloropropene on Plastic Materials

S. E. Allaire,* S. R. Yates, F. Ernst, and S. K. Papiernik

Abstract

The goal of this research was to provide information for choosing appropriate materials for studying gas-phase concentrations of propargyl bromide (3BP) and 1,3-dichloropropene (1,3-D) in laboratory experiments. Several materials were tested and found to sorb both gas-phase chemicals in the following order: stainless steel (SS) < Teflon polytetrafluoroethylene (PTFE-FEP) ≈ flexible polyvinyl chloride (PVC) ≈ acrylic < low-density polyethylene (PE) < vinyl ≈ silicone < polyurethane foam (PUF). Sorption of SS was insignificant and PUF sorbed all the fumigant that was applied. For the other materials, linear sorption coefficients (K_d) for 3BP ranged from 3.0 $cm^3\ g^{-1}$ for PVC to 215 $cm^3\ g^{-1}$ for silicone. Freundlich sorption coefficients for 1,3-D ranged from 11.5 to 371 $cm^3\ g^{-1}$. First-order desorption rate constants in an open system ranged from 0.05 to 1.38 h^{-1} for 3BP and from 0.07 to 1.73 h^{-1} for 1,3-D. In a closed system, less than 2% of sorbed fumigant desorbed from vinyl while up to 99% desorbed from PVC within 24 h when equilibrated at the highest headspace concentration. Sorption of both fumigants was linearly related to the square root of time except for vinyl and silicone. This may indicate non-fickian diffusion of fumigant into the polymer matrix. Vinyl, silicone, PE, and PUF should be avoided for quantitative study of organic gases, except possibly as a trapping medium. Use of PTFE, PVC, and acrylic may require correction for sorption–desorption and diffusion.

Emissions of volatile organic compounds are often measured with flux chambers. Different materials have been used to build flux chambers such as galvanized metal (Gao et al., 1997; Matthias et al., 1980; Thomson et al., 1997), acrylic (Rochette et al., 1997; Russell et al., 1998), clear polycarbonate (McGinn et al., 1998), Perspex (Fang and Moncrieff, 1996), Teflon (Carpi and Lindberg, 1998), and copper (van Bochove et al., 1998). To prevent leakage from a chamber, sealants are often used between movable joints and parts. Foam (Carpi and Lindberg, 1998; Nay et al., 1994; Rochette et al., 1997), neoprene (McGinn et al., 1998), and rubber (Thomson et al., 1997) have been reportedly used along with frequent use of silicone. Tubing is often used to connect chambers to a vacuum or pressure source or to direct air to a sampling point. A description of the type of tubing used in experiments is often neglected (e.g., Fang and Moncrieff, 1996; Gan et al., 1998) although use of Tygon (Matthias et al., 1980; van Bochove et al., 1998), Teflon (Carpi and Lindberg, 1998), polyvinyl chloride (Gao et al., 1997), and aluminum (Carpi and Lindberg, 1998) have been reported.

The effect of sorbing materials on the performance of experimental equipment, such as chambers, has not been studied in detail. As a first step, a sorption–desorption experiment was conducted to obtain information to assist in developing laboratory equipment to study the transport and fate of 3BP and 1,3-D. The fumigant 1,3-D is a chemical replacement for methyl bromide and 3BP is considered for use in soil fumigation. Fumigants are highly volatile pesticides used to control pests in soils, greenhouses, and timber. While information exists on fumigant sorption to agricultural plastic films (Papiernik et al., 1999) and methyl bromide sorption to Teflon (Ren et al., 1997), to our knowledge, there is limited information on vapor sorption–desorption of fumigants to materials commonly used in laboratory equipment. There is also little information on the diffusion of gaseous compounds into polymers. Vonk and Veenendaal (1983) suggested that the diffusion of toluene onto PVC may be non-fickian due to the swelling process occurring during sorption while the sorption appeared fickian for low-density PE. The non-fickian behavior is more difficult to predict. Berens (1989) also indicated that diffusion of gases through polymers could be two to four orders of magnitude faster than liquid solvents. In the case of organic chemicals in aqueous solution, it is known that sorption to low- and high-density polyethylene, polypropylene, rubber, flexible and rigid PVC, polyamide (nylon), polyurethane, silicone-modified elastomer, rubber, Nalgene 180 (Nalge Nunc Int., Rochester, NY), Tygon, and Teflon is significant (Curran and Tomson, 1983; Devlin, 1987; Gillham and O'Hannesin, 1990; Kovacs and Campbell, 1999; Parker and Ranney, 1997; Topp and Smith, 1992).

The objective of this study was to provide information on vapor sorption–desorption of two fumigants (3BP and 1,3-D) on several different materials that are commonly used to carry, sample, store, or build experimental equipment for the study of gases. It should be noted that the term "sorption" used herein describes the combined effects of adsorption and diffusion into the polymer matrix.

Materials and Methods

Materials

A series of sorption–desorption tests were conducted with 3BP (Fluka, Buchs, Switzerland) and 1,3-D (47% *cis* and 51%

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Abbreviations: 3BP, propargyl bromide; 1,3-D, 1,3-dichloropropene; GC, gas chromatography; K_d, linear sorption coefficient; K_f, Freundlich sorption coefficient; PE, polyethylene; PTFE, polytetrafluoroethylene; PUF, polyurethane foam; PVC, polyvinyl chloride; SS, stainless steel.

trans; Chem Service, West Chester, PA). Eight materials were selected: (i) 0.5 g of a 20-mm-thick PUF (weather strip self-stick high density; Frost King Thermal Products Co., Paterson, NJ); (ii) 2.5 g of flexible vinyl tubing (6.4-mm i.d., 1.5-mm wall thickness, Tygon formula R-3606, 55 d hardness; United States Plastic Corp., Lima, OH); (iii) 2.5 g of Teflon PTFE-FEP tubing (2.08-mm-i.d. wall thickness; DuPont, Wilmington, DE); (iv) 2.5 g of 12-mm flat acrylic (S&W Plastics, Eden Prairie, MN); (v) 2.5 g of flexible, 4.0-mm-thick PVC pipe (Schedule 40, 50.8-mm diameter); (vi) 1.0 g of hardened silicone (Dow Corning Corp., Midland, MI) with an average diameter from 4.8 to 6.4 mm; (vii) 2.5 g of 1.6-mm-thick stainless steel rod; and (viii) 1.0 g of low-density PE tubing with a 6.4-mm i.d. and 1.5-mm wall thickness (50 d hardness; Dig Corp., Vista, CA).

Sorption Coefficients and Desorption in a Closed System

Samples of each material were placed into 21.6 ± 0.2 $\mathrm{cm^3}$ glass headspace vials (Supelco, Bellefonte, PA). Six replicate vials were spiked with 10 μL of either 3BP or 1,3-D solution at one of five concentrations. During spiking, the solution was placed on the vial walls so that complete vaporization occurred before reaching the material. The concentration of fumigant in the hexane solution ranged from 1.59×10^4 (0.01 L $\mathrm{L^{-1}}$) to 7.93×10^5 μg $\mathrm{mL^{-1}}$ (0.5 L $\mathrm{L^{-1}}$) of 3BP and from 1.22×10^4 (0.01 L $\mathrm{L^{-1}}$) to 6.1×10^5 (0.5 L $\mathrm{L^{-1}}$) μg $\mathrm{mL^{-1}}$ of 1,3-D. The vials were immediately capped with PTFE-faced butyl rubber septa and aluminum seals. The samples were put in a controlled chamber at 20 ± 0.1°C. After 24 h, 100 μL of headspace was sampled from each vial using gas-tight syringes (pressure lock series; Alltech Associates, Deerfield, IL) and transferred into 8.8 ± 0.1 $\mathrm{cm^3}$ vials that were immediately capped with PTFE-faced butyl rubber septa and aluminum seals. The samples were stored at −71°C until gas chromatography (GC) analysis.

Linear sorption coefficients (K_{d}, $\mathrm{cm^3\ g^{-1}}$) were calculated using:

$$C_{\mathrm{s}} = K_{\mathrm{d}} C_{\mathrm{h}} \qquad [1]$$

where C_{s} is the sorbed mass (μg $\mathrm{g^{-1}}$) and C_{h} is the headspace concentration (μg $\mathrm{cm^{-3}}$) at equilibrium. Regressions were not forced through the origin. Logarithmic transforms of C_{s} and C_{h} were used to determine nonlinear Freundlich coefficients (K_{f}, $\mathrm{cm^3\ g^{-1}}$) and $1/n$:

$$C_{\mathrm{s}} = K_{\mathrm{f}} C_{\mathrm{h}}^{(1/n)} \qquad [2]$$

After sampling the headspace, the vials were decapped and the materials transferred to clean 21.6-$\mathrm{cm^3}$ headspace vials, which were immediately recapped. After a 24-h desorption equilibrium time at 20°C, a 100-μL sample of the headspace from each vial was transferred to a clean, 8.8-$\mathrm{cm^3}$ vial for headspace GC analysis.

Sorption Kinetics in a Closed System

Six materials were used for these tests: vinyl, PTFE, acrylic, PVC, silicone, and PE. Either 1 or 2.5 g of material was placed into each 21.6-$\mathrm{cm^3}$ vial and spiked with 10 μL of solution containing 3.96×10^5 and 3.05×10^5 μg $\mathrm{mL^{-1}}$ of 3BP and 1,3-D, respectively. A set of vials was prepared for each sampling time so that each vial was sampled only once. The sampling method is the same as the sorption coefficient test described above. Sampling was completed at 1, 2, 5, 10, and 20 min. A sample was also collected after a longer time period (up to 72 h) to ensure an equilibrium measurement.

Desorption in an Open System

Information on the desorption from the six materials was obtained by spiking eight sets of vials, each set containing six replicates, with 10 μL of 3.96×10^5 of 3BP solution in hexane and 3.05×10^5 μg $\mathrm{mL^{-1}}$ of 1,3-D solution. The vials were capped and stored at 20 ± 0.1°C for 24 h. After 24 h, 100 μL from the headspace of each vial was sampled to determine how much chemical was sorbed. Then, the content of one set of vials was immediately transferred to a set of clean vials containing 10 mL of hexane to extract the fumigant sorbed to the material. This provides the initial mass sorbed to each material. The remaining sets of vials were decapped and their contents placed on aluminum sampling cups in a fume hood so that fresh air continuously swept over the material. The materials were kept in the fume hood for 0.030, 0.083, 0.25, 1.0, 6.0, 24, and 48 h. At each of these times, a set of materials were placed into clean 21.6-$\mathrm{cm^3}$ vials containing 10 mL of hexane and agitated for 5 min. A 1-mL aliquot of the hexane extract was sampled and analyzed with GC.

Recovery–Mass Balance

Blanks were prepared (i.e., vials without materials) for each test to estimate losses due to sorption onto the vials and septa, sampling, transfer, storage, and degradation. This also provides a measure of the precision of the technique. Losses from the vials were measured over a period of two weeks. One set of vials was used for each sampling event to estimate the stability of the aliquot at 20°C. Degradation in this case refers to photolysis or chemical interactions with the material releasing $\mathrm{Br^-}$ or $\mathrm{Cl^-}$.

A test was needed to show that the sorbed mass estimated using the headspace concentration ($M_{\mathrm{sorbed}} = M_{\mathrm{tot}} - M_{\mathrm{headspace}}$) corresponded to the sorbed mass obtained by hexane extraction. To do this, two sets of vials were prepared as described earlier. After 1 and 24 h (one set of vials for each sampling event), 100 μL of the headspace was sampled. Then, the contents of each vial was transferred into clean vials containing 10 mL of hexane, shaken for 5 min, and the extract analyzed with GC.

At the same time, blank vials and vials containing the materials were prepared. A series was used to measure $\mathrm{Br^-}$ and $\mathrm{Cl^-}$ before desorption and another series after desorption. Five milliliters of water was added to extract $\mathrm{Br^-}$ and $\mathrm{Cl^-}$, degradation products of 3BP and 1,3-D. The samples were agitated for 1 h. The $\mathrm{Br^-}$ and $\mathrm{Cl^-}$ contents in water extracts (50 μL) were measured with ion chromatography (DX-100 ion chromatograph equipped with a 4-mm AS-14 column with 7.5 m*M* $\mathrm{Na_2CO_3}$ + 2.5 m*M* $\mathrm{NaHCO_3}$ as eluant; Dionex, Sunnyvale, CA).

Samples of 3BP and 1,3-D concentration in the headspace were measured with the method of Gan et al. (1998) with GC (Model 5890; Hewlett-Packard, Palo Alto, CA) equipped with an electron capture detector and connected to an autosampler (Model 7000; Tekmar-Dohrmann, Mason, OH). Liquid samples in hexane were measured with a Hewlett-Packard 6890 GC with a DB624 column and He was the carrier gas with flow rates of 0.46 and 1.05 mL $\mathrm{min^{-1}}$ for 3BP and 1,3-D, respectively. The oven temperature was programmed to ramp from 70 to 140°C in 3 min for 3BP and in 2 min for 1,3-D.

For every test, six replicates were completed. All values were corrected for recovery. Mean separations were made with an LSD test. Linear and nonlinear regressions were performed with the least squares and Marquardt methods, respectively.

Results and Discussion

Recovery–Mass Balance

In the closed system, the recovery (% of applied mass that was measured) followed an inverse power function with time. The mass balance was nearly 100 ± 2% during the first 10 min of storage, then decreased and leveled off to about 70 ± 5% for 1,3-D and 60 ± 8% for 3BP after about 6 h. The decrease in recovery was probably due to fumigant sorption or entrainment into the septa, since leakage from incompletely sealed vials would cause a continued decrease in concentration with time. Kovacs and Campbell (1999) tested the sorption of volatile organic compounds by septa similar to the type used to cap the glass vials. They found that loss of chemical due to sorption on septa followed the same trend observed here. In their case, hexane loss reached about 50% in two weeks, which is about 10% lower than observed for 3BP (Fig. 1). Other possible sources of variation include leakage from vials, leakage from syringes, and losses during transfer of material between vials. To allow correction for recovery, a series of blanks was included in every experiment.

The loss of mass from the headspace and the mass extracted from the material with hexane after a 1-h incubation period agreed to within 1% for all materials. After a 24-h incubation, the difference between headspace mass and the mass in the hexane extract for both chemicals was within approximately 20% for all the materials except PTFE and acrylic in combination with 1,3-D (Table 1). Given that acrylic in combination with 3BP had a ratio of 104%, it is likely that the high value for 1,3-D is a result of experimental error. Therefore, it was assumed that 100% efficiency would be appropriate for acrylic and both fumigants. The systematically low values for PTFE could be due to the fumigants diffusing into the PTFE polymers. This mass would not be recovered during a relatively short 5-min solvent extraction. The extraction efficiency due to irreversible sorption would depend on the material properties and its interaction with hexane. Also, the accuracy was consistent for the different polymers; for example, vinyl and silicone had low coefficients of variation (<5%) while PVC had high variation (>6%) throughout the experiments. Therefore, correction values for extraction efficiency were used to correct further extractions values.

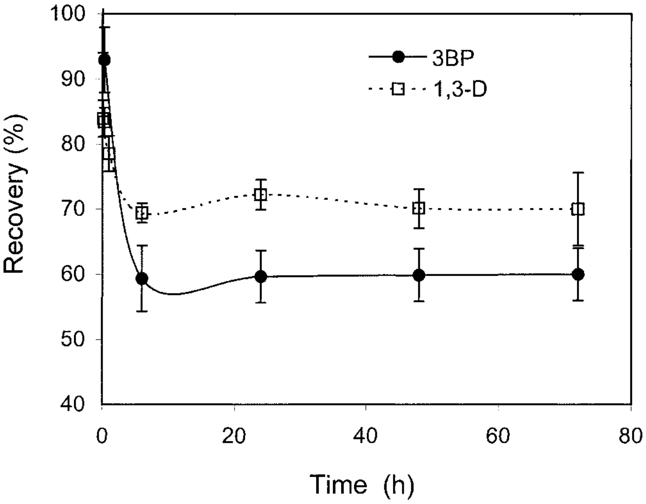

Fig. 1. Recovery (% of applied mass that is measured) as a function of time for propargyl bromide (3BP) and 1,3-dichloropropene (1,3-D) in blank vials. Vertical error bars represent confidence interval.

An example of mass balance for desorption in a closed system is given in Table 2. The mass balance ranges from 49 to 107% for 3BP and 39 to 94% for 1,3-D. The highest recoveries were for PTFE and PVC (89–100%) followed by PE (72–85%), acrylic (60–73%), silicone (54–60%), and vinyl (39–49%). The lowest mass balance corresponded to the least desorbing material and degradation was found to have little effect on mass balances. In the case of silicone, some mass may be lost during transfer of material between vials since it desorbs very quickly. For vinyl, the fumigants may have penetrated the material during the 48 h since spiking. Then the hexane extraction would not lead to complete recovery. Comparing these results to Table 1 suggests that increasing the incubation time from 24 to 48 h increases the amount of fumigant that is irreversibly bound or entrained in the material.

The Br^- and Cl^- concentrations represented less than 0.1% of the applied mass in the blank vials. Also, Br^- (on a 3BP basis) concentrations represented less than

Table 1. Efficiency of hexane extraction from six plastic materials as compared with the use of headspace concentration to estimate the sorbed mass 24 h after spiking.†

Sorption	Vinyl	PTFE	Acrylic	PVC	Silicone	PE‡	PUF	SS
				3BP				
Headspace, μg g^{-1}	3098 ± 9.7	1238 ± 115	2194 ± 101	1702 ± 311	7137 ± 55	5758 ± 313	7400 ± 502§	ND¶
Extract, μg g^{-1}	2682 ± 68	533 ± 54	2423 ± 166	1327 ± 98	7229 ± 287	6086 ± 696	–	–
Ratio, %#	86 ± 2.2	44 ± 7.5	104 ± 6.7	79 ± 12	100 ± 4.3	101 ± 13	–	–
				1,3-D				
Headspace, μg g^{-1}	2335 ± 24	745 ± 243	1517 ± 149	1143 ± 129	5476 ± 100	4807 ± 242	5805 ± 121§	ND
Extract, μg g^{-1}	2085 ± 76	552 ± 129	2306 ± 101	1979 ± 179	5464 ± 134	5482 ± 437	–	–
Ratio, %	90 ± 4.1	74 ± 27	157 ± 11	106 ± 34	99 ± 2.3	110 ± 6.3	–	–

† 3BP, propargyl bromide; 1,3-D, 1,3-dichloropropene; PE, polyethylene; PTFE, polytetrafluoroethylene; PUF, polyurethane foam; PVC, polyvinyl chloride; SS, stainless steel.

‡ Not at equilibrium.

§ Sorbed almost all that was applied.

¶ Not detected.

Ratio = (sorbed estimated from extract/sorbed estimated from headspace) × 100. Applied headspace concentration of 367 μg cm^{-3} of 3BP and 282 μg cm^{-3} of 1,3-D.

Table 2. Percent of the sorbed mass that desorbed in a closed system and was extracted for both fumigants and six materials.†

	Vinyl	PTFE	Acrylic	PVC	Silicone	PE
	%					
			3BP			
Desorption‡	2.0 ± 0.09	84 ± 19	44 ± 3.5	89 ± 4.9	13 ± 0.54	43 ± 2.5
Hexane extractable§	47 ± 1.1	9.46 ± 2.4	15.6 ± 0.37	11.6 ± 1.0	47.1 ± 0.51	42.6 ± 2.9
Br^-¶	0.02 ± 0.004	0.14 ± 0.06	0.08 ± 0.02	0.35 ± 0.11	0.10 ± 0.024	0.10 ± 0.022
Total recovery#	49 ± 1.2	94 ± 21	60 ± 3.3	101 ± 6.1	60 ± 0.68	86 ± 2.0
			1,3-D			
Desorption‡	2.0 ± 0.33	89 ± 8.5	53 ± 7.7	74 ± 6.0	11 ± 0.59	33 ± 2.5
Hexane extractable§	37 ± 1.3	6.1 ± 0.8	18.6 ± 1.0	16.4 ± 0.84	42.6 ± 1.6	37.6 ± 0.84
Cl^-¶	0.13 ± 0.02	0.55 ± 0.19	1.3 ± 0.66	2.1 ± 0.20	0.26 ± 0.13	0.89 ± 0.25
Total recovery#	39 ± 1.4	96 ± 8.9	73 ± 8.8	93 ± 6.5	54 ± 1.8	71 ± 3.3

† 3BP, propargyl bromide; 1,3-D, 1,3-dichloropropene; PE, polyethylene; PTFE, polytetrafluoroethylene; PVC, polyvinyl chloride.
‡ Desorption occurred 24 h after sorption equilibrium (i.e., 48 h after spiking).
§ Hexane extractable = % of the mass that was extracted from each material with hexane.
¶ Br^- or Cl^- = % of the mass that degraded into Br^- (given in equivalent 3BP) or into Cl^- (given in equivalent 1,3-D) 48 h after spiking.
# Total recovery = summation of desorption, hexane extractable, and Br (i.e., percent of the mass that "disappeared" from the headspace during sorption).

0.1% of sorbed mass to all but PVC and PTFE (Table 2). The Cl^- (on a 1,3-D basis) concentrations represented about 1% of the sorbed mass, except for acrylic and PVC, for which it was less than 2% (Table 2). Since the presence of Br^- and Cl^- is due to fumigant degradation, fumigant lost over time was not significantly due to degradation.

Sorption

Both fumigants sorbed onto the different materials in the following order: PUF > silicone ≈ vinyl > PE > acrylic ≈ PVC ≈ PTFE > SS (Table 3). Polyurethane foam sorbed nearly all the applied fumigant and SS had no significant sorption. Therefore, SS and PUF materials were not considered further.

Sorption isotherms for 3BP were linear except for vinyl (Table 3). Values for K_d ranged from 3.0 for PVC to 215 $cm^3\ g^{-1}$ for silicone. The K_d value of PE was probably higher than that of silicone because it was still sorbing for at least 48 h. Sorption of 1,3-D to the plastic materials was best described by nonlinear Freundlich coefficients (K_f). Values for K_f ranged from 11 for PVC to 371 $cm^3\ g^{-1}$ for silicone (Table 3).

The presence of solvent gas may have affected fumigant sorption and diffusion into the polymers. At a low concentration of fumigant (0.01 mL, i.e., 7.3 $\mu g\ cm^{-3}$ headspace concentration), there was 0.99 mL of gaseous hexane in the vials. Laboratory observations indicated that silicone swells to about double its size in the presence of liquid hexane, suggesting that swelling may occur in the presence of the gaseous hexane. Vonk and Veenendaal (1983) affirmed that PVC swells in the presence of liquid solvent and suggest that swelling increases chemical sorption by polymers. Shlyapnikov and Giedraityte (1997) indicated that high-density polyethylene sorbed more additives in the presence of liquid hexane and a similar behavior was observed for low-density polyethylene in solutions. The authors state that the sorption process of two components is complex as it affects the sorption centers around knots and entanglements of the polymer chains. These studies provide evidence that the presence of hexane in our closed system may have increased fumigant sorption. This effect would then be more important at low (high in hexane) than high fumigant concentrations (low in hexane) and would result in an overestimate of the C_s vs. C_h slope (i.e., K_d).

Table 3. Linear sorption coefficients (K_d) of propargyl bromide (3BP) and nonlinear Freundlich coefficients (K_f) of 1,3-dichloropropene (1,3-D) for six plastic materials 24 h after spiking.

	3BP		1,3-D		
Material†	K_d	r^2‡	K_f§	$1/n$§	r^2¶
	$cm^3\ g^{-1}$		$cm^3\ g^{-1}$		
Vinyl	171.1b#	0.510	221.2b	0.744	0.610
PTFE	3.14a	0.979	15.07a	0.597	0.923
Acrylic	5.82a	0.997	14.25a	0.867	0.968
PVC	3.02a	0.992	11.48a	0.790	0.931
Silicone	214.6b	0.992	370.7b	0.678	0.950
PE	65.67††	0.997	158.9¶	0.647	0.879

† PE, polyethylene; PTFE, polytetrafluoroethylene; PVC, polyvinyl chloride.
‡ All regressions were significant at $P < 0.01$, except for PE ($P < 0.05$) and vinyl ($P < 0.5$).
§ $C_s = K_f C_h^{(1/n)}$.
¶ Correlation coefficients for the linearized Freundlich regression.
# Values associated with different letters are significantly different at $P = 0.05$ using the LSD tests.
†† Did not reach equilibrium, K_d and K_f are expected to be much higher.

Desorption

For 3BP, the percent of mass that desorbed after a 24-h incubation period in a closed system appears linearly related to the initial sorbed mass (Fig. 2). For an initial sorbed mass of about 1000 $g\ g^{-1}$, PVC and PTFE released about 85%, acrylic about 42%, PE about 7%, and silicone and vinyl less than 2%.

For 1,3-D, percent desorption with respect to sorbed mass behaved differently compared with 3BP (Fig. 2). The release was linearly related to the logarithm of the sorbed mass. Also, at the same initial sorbed mass, desorption of 1,3-D was greater than that of 3BP, with desorbed masses from 2 to 50% more than 3BP. Materials released both chemicals following the same sequence.

Kinetics

Sorption kinetics for most materials followed a negative exponential function of the form:

$$C_s(t) = a[1 - \exp(-bt)] \qquad [3]$$

where $C_s(t)$ is the sorbed mass as a function of time (t),

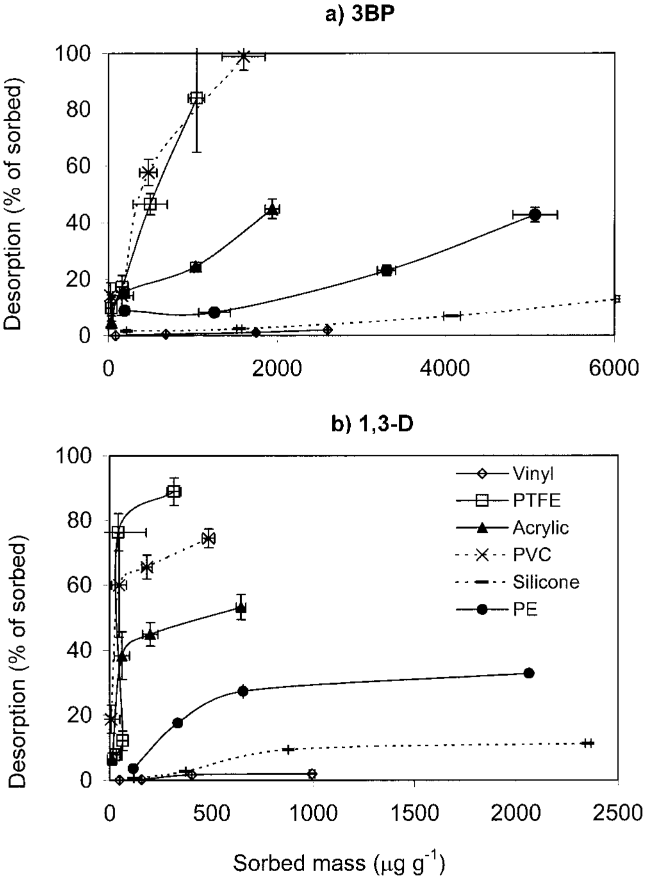

Fig. 2. Desorption of propargyl bromide (3BP) and 1,3-dichloropropene (1,3-D) (percent of sorbed that desorbed) from different polymers as a function of sorbed mass. Vertical and horizontal error bars represent confidence interval.

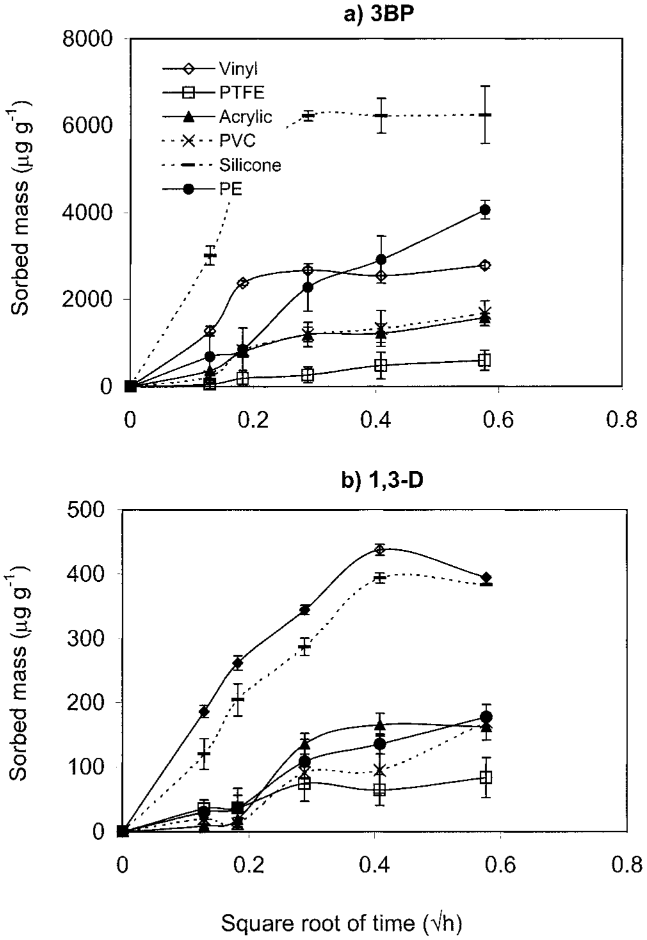

Fig. 3. Sorption kinetics of propargyl bromide (3BP) and 1,3-dichloropropene (1,3-D) on six plastic materials during the first 20-min period. Vertical error bars represent confidence interval.

and *a* and *b* are parameters obtained from nonlinear regressions. In general, the kinetics for 3BP (Fig. 3a) and 1,3-D (Fig. 3b) were the same. For 3BP, apparent sorption equilibrium occurred within 10 min for vinyl, acrylic, and PVC, in 0.5 h for silicone, within 5 h for PTFE (data not shown), and more than 48 h (data not shown) for PE, while 1,3-D sorption occurred within 20 min for all materials except PE.

We use the term "apparent" equilibrium because our apparatus could not detect any changes in headspace concentration after a certain time although equilibrium may not have been reached. Considering that the fastest diffusion of gases through PVC would be in the range of 10^{-6} cm^2 s^{-1} (Berens, 1989), that the thickness of our materials ranged from 1.5 to 6 mm, and that both sides of the polymers are in contact with the fumigants, it would take about 24 h to reach the middle of the polymers if diffusion alone would have occurred. Therefore, equilibrium was probably not reached in 20 min but changes could not be detected at later times except for PE and PTFE, for which changes in the headspace concentration were detected for at least 72 h.

If we assume that the loss of mass in the headspace was due to diffusion, then the diffusion appeared fickian for PTFE, acrylic, PVC, and PE since the sorbed mass was linear as a function of the square root of time (Fig. 3) for both fumigants. Diffusion for vinyl and silicone may not be fickian as the initial sorption rate was fast and leveled off thereafter (Fig. 3). The non-fickian behavior of silicone may be due to its swelling property and to the lack of fumigant left in the headspace, as silicone sorbed almost all the applied mass.

The first-order kinetic rate constant (μ) for desorption was calculated with:

$$C_s(t) = C_{so} \exp(-\mu t) \qquad [4]$$

and linearized into:

$$\ln C_s = -\mu t + \ln C_{so} \qquad [5]$$

where C_{so} is the initial sorbed mass (μg g^{-1}) and $C_s(t)$ is the sorbed mass (μg g^{-1}) at any given time (t, h). First-order rate constants range from 0.051 to 1.38 for 3BP and 0.05 to 1.73 h^{-1} for 1,3-D (Table 4). The ratio of $\mu_{1,3\text{-D}}$ to μ_{3BP} ranged from 1.25 to 1.80 (Table 4), indicating that 1,3-D desorption was faster than 3BP for all materials except for PE. Nearly 100% desorption of both fumigants occurred within 48 h except from vinyl, which took more than 100 h.

There was an important difference in desorption between the closed and the open systems, although each material had the same initial sorbed mass. For 3BP in

Table 4. First-order rate constant of two fumigants kinetically desorbing from six plastic materials, propargyl bromide (3BP) and 1,3-dichloropropene (1,3-D). All regressions were significant at $P < 0.0001$.

	3BP		1,3-D	
Material†	μ‡	r^2	μ	r^2
	h^{-1}		h^{-1}	
Vinyl	0.051 ± 0.006a§	0.994	0.075 ± 0.002a	0.901
PTFE	0.101 ± 0.006b	0.968	0.16 ± 0.011de	0.987
Acrylic	0.092 ± 0.005b	0.922	0.17 ± 0.006d	0.968
PVC	0.093 ± 0.001b	0.947	0.14 ± 0.008c	0.979
Silicone	1.38 ± 0.049c	0.804	1.73 ± 0.51e	0.784
PE	0.15 ± 0.002d	0.990	0.11 ± 0.002b	0.961

† PE, polyethylene; PTFE, polytetrafluoroethylene; PVC, polyvinyl chloride.

‡ $C_s(t) = C_{so} \exp(-\mu t)$.

§ Values associated with different letters are significantly different at $P = 0.05$ using the LSD tests.

the open system, all materials except vinyl desorbed more than 96% of the sorbed mass during 24 h. In a closed system, desorption percentages after 24 h were 2, 13, 43, 44, 84, and 99% for vinyl, silicone, PE, acrylic, PTFE, and PVC, respectively (Fig. 2). From Table 4, it can be inferred that 3BP desorption from silicone was the most rapid. It was expected to have the highest desorption ratio in the closed system (Table 2), although this was not the case. Silicone had the second-lowest desorption ratio at any concentration in the closed system. Moreover, sorption of 1,3-D followed the same trend. One reason may be the presence of gaseous hexane in the closed system and its absence in the open system during desorption. Another reason may be the fumigant concentration built up in the closed system that decreased the rate of desorption.

Note that the variation between replicates was consistently low (<5%) for PUF, vinyl, and silicone while it was higher (>10%) for acrylic, PVC, and PE. This indicates that some materials are more heterogeneous than others.

Material Comparison

Polyurethane foam sorbed almost all the 3BP and 1,3-D that was applied at low (data not shown) and high concentrations (Table 1). This is the reason that PUF is commonly used to extract moderately volatile organic compounds from air samples. After PUF sorption under 73.4 $\mu g\ cm^{-3}$ applied headspace concentration, the corresponding desorption was 59% of the sorbed 3BP mass and less than 13% of the 1,3-D sorbed mass. Although useful for extracting moderately volatile organic chemicals from air, its use should be avoided for extracting highly volatile fumigants and in the development of laboratory equipment for quantitative study of fumigants.

Silicone is an alternative sealant. It sorbed large quantities of fumigant at all concentrations. Even at the highest concentration, it sorbed about 90% of the applied 3BP and 80% of the 1,3-D within 15 min. Its sorption increases by more than 200 times with the headspace concentration (Table 3). Within 48 h, about 95% of 3BP and 1,3-D desorbed in an open system. Therefore, silicone should be used with caution, and its contact with fumigants should be minimized.

Stainless steel is a good choice of material for apparatus since sorption of fumigants is insignificant. However, due to its high cost, researchers often choose alternatives such as vinyl, PE, and PTFE. Vinyl sorbed both fumigants very rapidly during the first 10 min (Fig. 3). At the highest concentration used in this study, about 90% of 3BP and 78% of 1,3-D present in the headspace was sorbed. Vinyl's K_d for 3BP was the highest (except for PE) with 171 $\mu g\ cm^{-3}$ (Table 3). After 24 h of desorption in a closed system, only 2% of the sorbed mass was released in the headspace (Fig. 2). Similarly, desorption in an open system was slow and occurred over more than two days (Table 3). Therefore, the use of vinyl in quantitative studies should be minimized. Vinyl tubing may also have to be replaced between experiments since it desorbs for a long period of time.

In a closed system, vinyl sorbed more than PE for the first few minutes (Fig. 3) but the sorption rate for PE decreased less than for vinyl even at the lowest concentration. After 24 h of sorption, PE had sorbed about twice as much as vinyl. In addition, PE continued to sorb a significant amount of fumigant mass for more than three days. In both open and closed systems, PE desorbed more and faster than vinyl. Also, the sorption–desorption property of vinyl in this experiment was more homogeneous than PE. Therefore, vinyl would be preferable for both fumigants over PE.

Polytetrafluoroethylene sorbed a significant mass of fumigants in the gas phase (Tables 1 and 3). At the highest concentration studied, PTFE sorbed about 1040 $\mu g\ g^{-1}$ of 3BP, which is an average of 80 μg per linear cm (in all inner surface area). Its K_d value was not significantly different from acrylic and PVC but was lower than PE and vinyl (Table 3). In a closed system, PTFE released about 80% of 3BP and about 90% of sorbed 1,3-D within 24 h (Fig. 2). Also, sorption and desorption of both fumigants from PTFE continued for about 2 d. For short experiments, since its sorption was lower than that of other polymers, PTFE tubing may be a best option among the plastic materials used in this study. Its sorption–desorption properties may, however, be of concern for studies in which low concentrations have to be measured during a long period of time.

For the construction of a large apparatus, SS, acrylic, or PVC are frequently used. Acrylic is often chosen for its transparency and PVC for its price. Acrylic and PVC sorbed (Table 3) in the same order of magnitude. In a closed system, most of the sorption of both fumigants to PVC and acrylic occurred during the first 10 min (Fig. 3). In an open system, desorption rates of 3BP were similar while the 1,3-D desorption rate was slightly faster for the acrylic than for PVC (Table 4). In a closed system at any concentration, PVC desorbed one to three times more than acrylic (Fig. 2). Therefore, if desorption is of concern, acrylic is preferable over PVC.

Conclusions

The polymers tested in this paper affect the measured fumigant concentrations in the gas phase. Sorption–

desorption characteristics of different instrumentation parts should be carefully considered before choosing instrumentation for quantitative analysis of organic gases.

Vinyl, silicone, PE, and PUF should be avoided for quantitative study of organic gases while values for PTFE, PVC, and acrylic have to be corrected for sorption and desorption. Additional experiments are needed for low concentrations and for long-term studies.

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