

Loss of methyl bromide to the atmosphere during soil fumigation

Danny D. Reible

Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

(Received 5 February 1993; accepted in revised form 2 November 1993)

Abstract

Models of soil vapor transport were developed and applied to the prediction of atmospheric emissions of methyl bromide during soil fumigation. With effective cover placement and good injection depth control estimated cumulative methyl bromide losses to the atmosphere after 14 days ranged from 26% to 65% of that originally injected under a variety of injection conditions. The rate of emission after 14 days is small and was neglected. The best estimate of cumulative methyl bromide losses to the atmosphere under current emission practices is about half of that injected, in good agreement with estimates by Watson et al. [1] based on global concentrations of methyl bromide. The model suggests that deep injection with surface porosity control by moisture addition or use of low permeability covers could be an effective means of minimizing losses to the atmosphere during soil fumigation. Emissions would also be the smallest for high organic carbon content soils which tend to increase both reactivity and retardation due to sorption.

1. Introduction

Methyl bromide (CH_3Br) is a fumigant used to control nematodes, fungi and other pathogens in soils and for pest control in agricultural exports. It has been linked, however, with destruction of stratospheric ozone since bromine is far more efficient than chlorine in the destruction of ozone on a per molecule basis. In the Antarctic lower stratosphere, 20-30% of the observed ozone loss has been estimated to be the result of bromine [2]. Methyl bromide's atmospheric lifetime of 2 ± 0.5 yr [1] is, however, far shorter than the chlorofluorocarbons (CFCs) and bromine-containing halons that have been considered the major risk to stratospheric ozone. In addition, there exist significant natural sources of methyl bromide [3], indicating that elimination of anthropogenic emissions may not be effective in reducing stratospheric levels of the compound. Watson et al. [1] reviewed the available data and estimated that anthropogenic emissions represent $25 \pm 10\%$ of the total methyl bromide emissions and that elimination of anthropogenic emissions would be equivalent to accelerating

the phaseout of CFCs by 1.5–3 yr. On that basis, elimination of methyl bromide emissions is currently planned.

Watson et al. [1] estimated the proportion of total emissions from anthropogenic sources based primarily on the atmospheric lifetime of methyl bromide (2 ± 0.5 yr), the observed atmospheric abundance (9–13 pptv), and the observed interhemispheric ratio (1.3 ± 0.5), assuming that essentially all anthropogenic emissions are in the northern hemisphere. About 80% of the world-wide annual production of about 63000 metric tons (1990) is used for soil fumigation and thus losses to the atmosphere during these applications control the anthropogenic emissions. The purpose of the current work is development and application of a model capable of describing methyl bromide fate and transport during soil fumigation. The model will be used to predict the ultimate emissions to the atmosphere by current practices and to indicate opportunities for modifying current practices so that losses to the atmosphere can be minimized.

Processes influencing the fate and transport behavior of methyl bromide in soils include the method and depth of application, diffusion in the soil vapor space, sorption, hydrolysis, and demethylation reactions that occur in the soil matrix. A common method of injecting the soil fumigant is in a broadcast application through shanks 6–10" deep and spaced approximately 12" apart. Methyl bromide is injected as a liquid under pressure which immediately vaporizes upon exposure to the atmosphere. Typical application rates range from 240–350 lb/acre. A polyethylene cover is usually used for at least 2 days to control air concentrations during injection and maximize retention in the soil. Variations on this application include injection only to plant beds with the shank spacing equal to bed spacing (12–42"), injection at 18–24" with 2.5–5.5 ft between shanks, and spot fumigations after tree removal in orchards.

The rate of migration of methyl bromide through the soil is controlled by diffusion in the soil vapor space. The fraction of methyl bromide that is ultimately released to the atmosphere is a balance between the diffusion rate and the decomposition rate via hydrolysis and demethylation reactions. Factors that influence the diffusion rate include air-filled porosity and partitioning between the vapor and immobile water and soil phases. The soil cover above the injection point and the methyl bromide permeability of the polyethylene or other cover at the surface also influence the rate of movement of the fumigant to the atmosphere. The processes that influence the rate of decomposition of the methyl bromide in the soil are not as well understood. Hydrolysis of the methyl bromide occurs in the soil water and demethylation of the methyl bromide occurs through reaction with the organic matter in the soil.

Current information on the rates of these processes were used in a mathematical model of the transport and fate of methyl bromide in soil. The model allowed estimates of the ultimate loss of methyl bromide to the atmosphere as a result of soil fumigation and identifies practices which can reduce these losses. The model structure, assumptions, and parameter values are discussed below. In addition, the model is compared to a model of methyl isothiocyanate migration [4] to demonstrate the ability of the model to successfully predict soil vapor diffusion. Finally, estimates of methyl bromide losses to the atmosphere are presented. Simulations were conducted

of a base case which represents what are believed to be typical conditions. The sensitivity of the model predictions to commonly observed deviations from this base case was also determined.

2. Mathematical model

2.1. Model structure

The model assumes that methyl bromide moves only via vapor diffusion. Immediately after injection as a liquid, methyl bromide vaporizes. Since the molecular weight of methyl bromide is 94.9 compared to an average molecular weight of air of about 29, the vapors will tend to penetrate deeper into the soil as a result of their negative buoyancy. In silty-sandy soil with a porosity of 30% and a permeability of the order of 10^{-8} cm², this density difference would give rise to a downward velocity of about 42 cm/day (16 in/day) for pure methyl bromide. Rapid dilution of the methyl bromide with air, however, would decrease this downward movement significantly. 100000 ppm methyl bromide would move downward at a rate of only about 4 cm/day and 10000 ppm methyl bromide would move downward in this same permeability soil at only about 0.4 cm/day. Soil concentrations typically reach 10000–100000 ppm within a day after injection and buoyancy-driven flow can be neglected after this time. This effect is likely to be significant, however, in more permeable soils and would reduce the flux at the soil surface in a manner equivalent to that of increasing the effective depth of injection.

Potentially offsetting the buoyancy-driven downward movement of methyl bromide is the possibility of rapid upward movement through voids created by the shank movement through the soil. The presence of these voids should be minimized, however, by the working of the soil prior to soil fumigation. The placement of a soil cover immediately after injection also serves to minimize soil surface emissions due to rapid movement through voids. Finally, it should be recognized that the effective diffusivity of vapors through a soil matrix is generally within an order of magnitude of the diffusivity in an open air-filled channel. On the basis of these factors, any enhanced upward transport through soil voids was assumed negligible in the base case simulations. Simulations were also conducted with the methyl bromide injection assumed to be well-mixed between the desired injection depth and the ground surface to indicate the potential effect of these voids.

Much of the methyl bromide used for soil fumigation is injected such that the spacing between injection points is about the same as the depth of injection. Under such conditions, the methyl bromide would be expected to achieve lateral homogeneity relatively rapidly. Rolston and Glauz [5] showed that even if the spacing between injection points were more than double the depth of injection, methyl bromide concentrations 1 day after application varied by less than 50% everywhere at the injection depth. It thus appears appropriate to assume that methyl bromide is laterally homogeneous under conditions of most field applications, which means that only a one-dimensional model in the vertical direction is needed.

Considering only one-dimensional diffusion and first-order decomposition of methyl bromide in the soil, a mass balance suggests that the governing equation for methyl bromide migration is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[\frac{D_{\text{eff}}}{\varepsilon_a + \varepsilon_w K_{w/a} + \rho_b K_{s/w} K_{w/a}} \frac{\partial C}{\partial x} \right] - kC$$

where C is the vapor-phase concentration of methyl bromide, k is the effective decomposition rate constant (assumed first order), D_{eff} is the effective diffusion coefficient in vapor space of soil, ε_a is the air-filled porosity, ε_w is the water-filled porosity, ρ_b is the bulk density of soil, $K_{w/a}$ is the partition coefficient between the water and air phases and $K_{s/w}$ is the partition coefficient between the soil and water phases.

This model assumes that partitioning between the air, water and soil phases is linear, reversible and that a state of local equilibrium exists. Due to the high water solubility of methyl bromide (> 13000 mg/l at 25°C), this is likely to be appropriate under most conditions. Very dry soils, soils containing large amounts of organic matter or large fumigant application rates may result in nonlinear methyl bromide sorption phenomena (see [6]).

For simple fumigant application and soil conditions, this model can be solved analytically. Several analytical solutions were used to probe the rate of methyl bromide movement in the soil and to test more sophisticated models. To evaluate more general conditions, a numerical model was developed that solved the model equation via the numerical method of lines [7]. This method involves approximating the spatial derivatives of the differential equation at a number of grid points that represent different vertical depths in the soil. Preliminary experimentation suggested that grid points every 2 cm and a total depth of 2 m was sufficient to accurately predict methyl bromide diffusion. No barrier to downward vertical diffusion of the methyl bromide was incorporated in the model; the bottom boundary condition assumed flux continuity. Five-point centered difference formulas were used to discretize the equation at each grid point and a Runge–Kutta–Fehlberg algorithm [7] was used to solve the resulting 101 coupled ordinary differential equations in time.

The initial conditions provided to the model were methyl bromide concentrations in the vapor space at each grid point at the time of injection. For injections such that the methyl bromide was initially uniformly mixed over some depth, the initial condition was used directly and the problem solved entirely numerically. For point injections, an analytical solution assuming a locally constant diffusion coefficient was used to estimate migration for a short period, typically 0.2 days, and the numerical simulation was started from that time. This avoided oscillations and errors introduced by approximating the point source on the finite difference grid.

Application of the model requires specification of a number of model parameters such that they are representative of the observed soil and fumigation conditions. Although the model can be used to evaluate complicated injection conditions and stratified soils, the base case simulations assume an ideal impulse injection at the

desired depth and homogeneous soils. Generally the goal of the soil preparation prior to methyl bromide fumigation is homogeneity. It is likely, however, that the near surface environment may differ from the remainder of the soil zone and selected simulations investigated this effect.

2.2. Model verification

The ability of the model to predict vapor-phase diffusion in soils was tested by comparison to the experiments and predictions of methyl isothiocyanate migration of Leistra and Crum [4]. Fig. 1 shows the good agreement between the cumulative emission of methyl isothiocyanate from a greenhouse soil predicted by this model with the experimentally validated model of Leistra and Crum. The rate of emission is shown in Fig. 2 and again the agreement between this model and that of Leistra and Crum is very good, suggesting that the current model is consistent with other models of vapor diffusion in soils that have been experimentally validated. Small differences may be due to different assumptions about injection and soil conditions.

2.3. Model parameters

The application of the model to the prediction of methyl bromide fate and transport in the soil requires specification of a number of parameters including the effective diffusion and partitioning coefficients in the soil, the rate of hydrolysis and demethylation reactions, and injection conditions and depth.

The effective diffusion coefficient in porous soils (D_{eff}) has been correlated with the molecular diffusion coefficient in pure air (D_a) by Millington and Quirk [8]:

$$D_{\text{eff}} = D_a \frac{\varepsilon_a^{10/3}}{\varepsilon_t^2}$$

where ε_a is the air-filled porosity of the soil and ε_t is the total porosity. Typical near-surface soils might have a total porosity of 50%. A representative volumetric water content based on an average of 18 soil samples in California was 14.4% [9], giving an air-filled porosity of 35.6%. The estimated effective diffusion coefficient for methyl bromide in this soil is then about 0.1 m²/day. Alternative methods of estimating the effective diffusion coefficient (e.g. [10]) give results to within about a factor of two for this coefficient.

Partitioning of the methyl bromide to the immobile water and soil phases slows the rate of diffusion in the soil. The value of the water–air partition coefficient is 4.1 at 20 °C [11] and increases significantly at lower temperatures. The soil–water partition coefficient is typically estimated on the basis of an organic carbon based partition coefficient (K_{oc}) and the fraction organic carbon content of the soil (f_{oc}) [12]:

$$K_{\text{s/w}} = K_{\text{oc}} f_{\text{oc}}$$

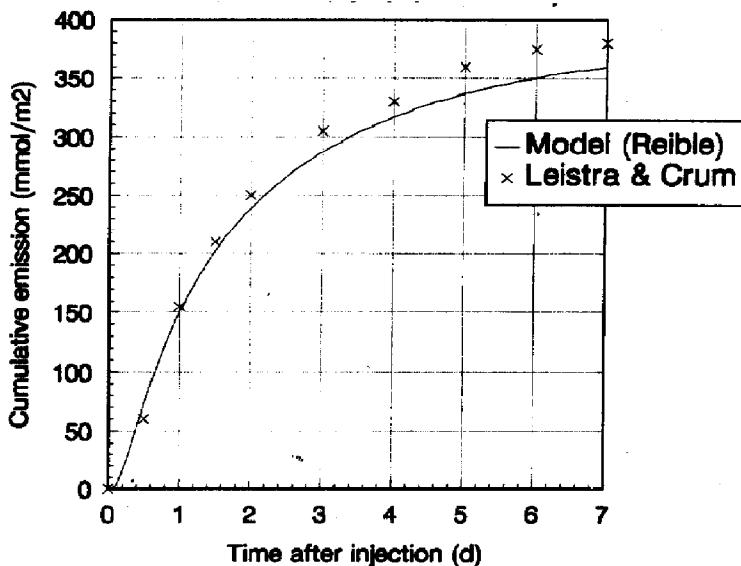


Fig. 1. Methyl isothiocyanate emission (using data of Leistra and Crum [4]).

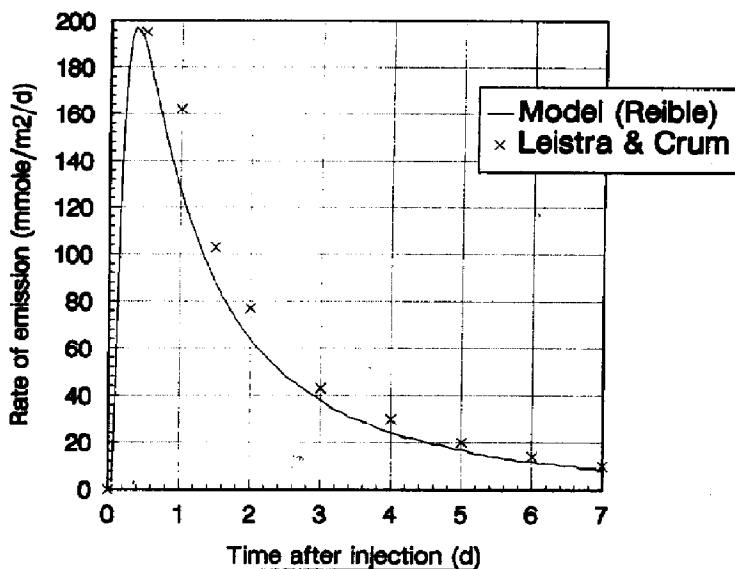


Fig. 2. Methyl isothiocyanate flux (using data of Leistra and Crum [4]).

The organic carbon based partition coefficient for methyl bromide is 83.1 [13]. The fraction organic carbon in fumigated soils can run from 0.5–1% to above 50% in peat soils. A typical range was assumed to be 2–4% organic carbon, giving a soil–water partition coefficient of 1.6–3.3. This partition coefficient is consistent with the data of Brown and Rolston [14] for a particular soil but significantly higher than the partition coefficients estimated by Arvieu [15].

The rate of decomposition of methyl bromide is not as well known as the other parameters in the model. The rate constant of hydrolysis in the water phase alone is 0.035/day (3.5%/day) at 20°C. Methylation of the methyl bromide with the soil organic matter also occurs. Siebering and Leistra [11] estimated an overall reaction rate constant (k) of 0.05/day (5%/day) on the basis of Br^- production in a soil. Brown and Rolston [14] estimated a reaction rate constant equivalent to a $k = 0.0187/\text{day}$ (1.9%/day) in the relatively low organic carbon content Yolo loam soil (1.3% organic carbon). Arvieu [15] measured reaction rate constants that varied between 0.014/day and 0.246/day in eight soils. Soils with organic carbon contents near 2-4% exhibited methyl bromide decomposition rate constants between 0.107 and 0.192/day. Herzel and Schmidt [17] estimated a half-life of 20 days ($k = 0.035/\text{day}$) in a soil with 2.64% organic matter and a very long half-life in a sand containing less than 0.1% organic matter. Gentile et al. [18] measured a rate constant of 0.055 to 0.1/day in slurries of three different soils. Based on the observed range of reaction rate constants, it is believed that a reasonable value of the overall rate constant, k , is 0.05/day except in low organic carbon soils. This corresponds to a soil half-life of about 14 days.

The base case fumigation conditions were selected to be injection at a depth of 25.4 cm (10 in) with a polyethylene film surface cover for the first 2 days after injection. Permeabilities of 14 different 1 mil fumigation films measured by TRICAL [9] varied from essentially 0 to 10 ml of methyl bromide $\text{h}^{-1} \text{m}^{-2} \text{ml}^{-1} \text{l}^{-1}$ (or $1 \text{h}^{-1} \text{m}^{-2}$). The most commonly used films had methyl bromide permeabilities of 8.2 and $8.41 \text{h}^{-1} \text{m}^{-2}$ and the average of these values was used in the model. Table 1 summarizes the base case fumigation and soil conditions.

3. Results

Forty-five percent of the methyl bromide applied under base case conditions was expected to be lost to the atmosphere within 14 days. Doubling the simulation period

Table 1
Base case fumigation and soil conditions

Injection amount	300lb/acre
Injection depth	10 in
Cover permeability	$8.31/\text{h}/\text{m}^2$
Cover period	2 days
Soil porosity	50%
Volumetric water content	14.4%
Air-filled porosity	35.6%
Soil bulk density	$1.3 \text{g}/\text{cm}^3$
Water-air partition coefficient	$K_{w/a} = 4.1$
Soil-water partition coefficient	$K_{s/w} = 1.66$ (2% org. carbon)
Reaction rate constant	$k = 0.05/\text{day}$
Effective diffusion coefficient	$D_{\text{eff}} = 0.1 \text{m}^2/\text{day}$

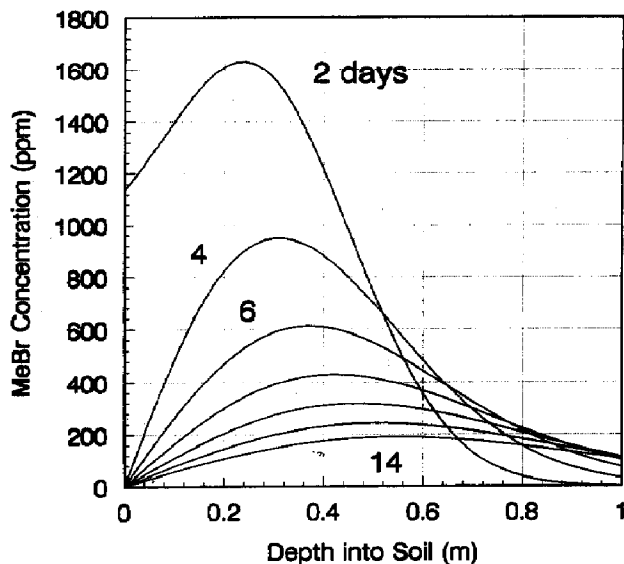


Fig. 3. Base case soil vapor concentrations (day 2 to day 14).

to 28 days typically only resulted in an additional 3–4% loss and therefore 14 days was used to indicate approximate total emissions of methyl bromide to the atmosphere. The rate of methyl bromide loss was greatest immediately after cover removal. Although the polyethylene film used for surface cover is permeable to methyl bromide, it poses a significant short-term barrier if it is not torn. The film increases the amount decomposed before emission at the soil surface. Fig. 3 illustrates the effect of the film cover on soil vapor space methyl bromide concentrations. A film cover or tarp was used for 2 days in the base case injection and, immediately prior to removal, methyl bromide concentrations near the soil surface exceeded 1000 ppm. Removal of the cover resulted in a rapid depletion of the methyl bromide concentration in the surface layer. In subsequent days, the soil vapor concentration of methyl bromide continued to decrease as a result of diffusion, decomposition and loss to the atmosphere. The depth of maximum concentration continued to move downward with time as a result of diffusion deeper into the soil. By the 14th day, the concentration profile was very flat (i.e. only a weak function of depth) but the maximum concentration occurred at double the depth of the original injection point. A barrier to downward vertical diffusion such as a shallow water table would eliminate this migration and increase the cumulative emissions from the soil.

The effects of varying application and soil parameters were also determined. The rate of methyl bromide emission to the atmosphere for three different cases is shown in Fig. 4. Compared to the base case emission rate is the emission rate due to base case conditions but with a 7 day cover (permeability $8.31 \text{ h}^{-1} \text{ m}^{-2}$) and the emission rate due to base conditions but with soil containing 4% organic carbon. The change in organic carbon content is assumed to affect only the sorption of methyl bromide and any effect on reaction rate is not considered due to the lack of consistent data to

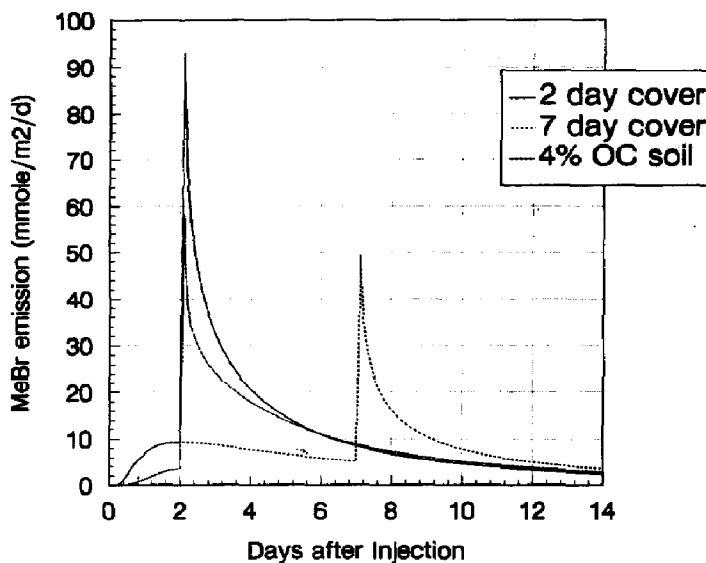


Fig. 4. Methyl bromide flux effect of cover/organic carbon.

quantify the effect. This figure shows the rapid increase in atmospheric emission rate immediately after cover removal. The use of a lower permeability cover could significantly reduce the emissions from the soil. Simulations were conducted with a cover permeability 10% of the base case permeability ($0.831\text{h}^{-1}\text{m}^{-2}$) and with a 7 day rather than a 2 day cover. The cumulative emissions of methyl bromide under these conditions were only 26% of that originally injected as shown in Table 2.

The total methyl bromide lost to the atmosphere under a variety of other conditions is also shown in Table 2. Shallow injections tended to increase the fraction of methyl bromide lost to the atmosphere. The surface cover was a significant influence in shallow injections or conditions which would otherwise lead to comparatively rapid transport to the atmosphere. Simulations for two effective diffusion coefficients are also shown in Table 2. The smaller effective diffusion coefficient case would be approximately equivalent to a reduction in effective porosity by a factor of about 1.2, e.g. by the presence of additional moisture to give a volumetric water content of about 20%. As expected, slower rates of diffusion would result in lower cumulative emissions of methyl bromide to the atmosphere.

The methyl bromide decomposition rate also has a significant influence on cumulative emissions. The best estimate available for moderate water and organic carbon content soils suggests that about 5% of the methyl bromide decomposes per day. The organic carbon content is likely to affect the reaction rate and it also affects the sorption of methyl bromide in the soil. Increases in the amount of methyl bromide that is sorbed to the soil or dissolved in the soil water slows the diffusion of the vapors in the soil air space allowing more time for methyl bromide decomposition before reaching the surface. As shown in Table 2, the total methyl bromide lost was reduced from 45% to 37% by doubling either the soil organic carbon content or the methyl

Table 2
Cumulative methyl bromide losses base case variations – homogeneous soil

Case Soil conditions as in Table 1 except as noted	Percentage of injected methyl bromide emitted to air over 14 days
Base, 10" injection, 2 day cover	45%
10" injection, no cover	52%
6" injection, 2 day cover	53%
18" injection, 2 day cover	28%
18" injection, no cover	29%
10" injection, 7 day cover	33%
10" injection, 7 day low permeability cover	26%
10" injection, 2 day cover, 10% decomposition/day	37%
10" injection, 2 day cover, 2.5% decomposition/day	51%
10" injection, 2 day cover, diffusivity 0.2 m ² /day	50%
10" injection, 2 day cover, diffusivity 0.05 m ² /day	36%
10" injection, 2 day cover, 4% organic carbon	37%

bromide decomposition rate. In contrast to these effects, conditions that result in an increased migration rate of methyl bromide in the soil, such as an increase in air-filled porosity, would increase the amount of methyl bromide ultimately lost to the atmosphere.

Note that the simulations suggest that 26–53% of the injected methyl bromide would ultimately return to the atmosphere except for very deep soil injections. A 36" injection, which is sometimes used for "spot" treatment of soils, would result in significantly less emissions but was not included in the table since that depth is not used for continuous injection. Calculations suggested, however, that only about 5% of the injected methyl bromide would be emitted to the atmosphere in the first 14 days after an injection at this depth in a uniform, compacted soil. Since injections 6–10" deep are the most common (45–53% released), the best estimate of the average methyl bromide emission for soil fumigation operations is approximately half of that injected. Combined with losses from the structural and commodity treatment applications of methyl bromide [9], this suggests that about 30,000 metric tons of methyl bromide per year is emitted from anthropogenic sources. This is in excellent agreement with the anthropogenic emissions estimated on the basis of the atmospheric methyl bromide budget presented by Watson et al. [1].

All of the above simulations assumed that the soil conditions were homogeneous and that methyl bromide was injected as an impulse source at the injection depth. The model is, however, capable of evaluating methyl bromide migration under nonuniform soil and non ideal injection conditions. The specific conditions evaluated include

(1) injection such that the methyl bromide is spread uniformly between the desired injection depth and the soil surface for effective diffusivities of 0.1 and 0.2 m²/day with soil cover in place for 2 days and for no cover, (2) 10" injection into a soil with a water table barrier to downward vertical diffusion at 15" below the surface, and (3) injection into a soil with an effective diffusivity in the top 2" of soil decreased by a factor of ten below that of the base case. The estimated loss percentages to the atmosphere for these conditions are shown in Table 3.

The uniform injection case represents the situation of rapid transport to the surface due to void creation by the injection shank. At the base case effective diffusion coefficient, the effect of the nonideal injection on 14 day cumulative emissions is small. The effect on the initial vertical concentration distribution and the initial surface fluxes would, however, be quite strong. A larger effect of nonideal injection would be expected if migration would otherwise be inhibited by a small effective diffusion coefficient. The effect of voids created by the injection shank would also be very significant for a deep injection, essentially eliminating the advantage of deeper injection on minimizing emissions.

The cumulative emissions for the nonuniform injection conditions were generally within the range of the standard cases presented in Table 2. Much more sensitive to the specific injection conditions, however, were the initial emission fluxes to the atmosphere. The first day emissions for the base case conditions averaged 4 $\mu\text{g m}^{-2} \text{s}^{-1}$. Shank-induced mixing to the surface from the desired injection point

Table 3
Cumulative methyl bromide losses injection and soil heterogeneities

Case Soil conditions as in Table 1 except as noted	Initial 24 h average flux ($\mu\text{g m}^{-2} \text{s}^{-1}$)	14 day cumulative CH ₃ Br emissions (%)
Base, 10" injection, 2 day cover Base case except initially uniform injection (surface to 10" depth)	4	45%
Base case except poor injection depth control (mixed surface to 10" depth), no effective cover	25	52%
Base case except poor injection depth control (mixed surface to 10" depth), no effective cover, diffusivity - 0.2 m ² /day	120	61%
Base case with 0.5 m water table (no flux barrier)	140	64%
Base case except near-surface heterogeneities, surface diffusivity - 0.01 m ² /day	4	63%
	1	32%

and lack of any cover, however, would result in average estimated first day emissions of $120 \mu\text{g m}^{-2} \text{s}^{-1}$. Fourteen day cumulative losses under these conditions would be about 61% of that initially injected. Use of an effective cover with the base case permeability, however, would reduce these emissions to about $25 \mu\text{g m}^{-2} \text{s}^{-1}$ over the first day and a cumulative 14 day loss of 52%. All of these estimates are based on a 300 lb/acre (350 mmol/m^2) injection rate. Thus, operational control over the injection, e.g. inadequate loosening or working of the soil prior to injection or delayed or poor cover placement, could result in high initial fluxes from the soil while having a comparatively small effect on the 14 day cumulative losses. First day fluxes are of interest in assessing worker and nearby receptor exposure but were not the primary focus of the current work.

The final case presented in Table 3 is the effect of an exponential change in effective diffusivity in the upper 5 cm of soil. The effective diffusivity at the surface was assumed to be a factor of ten smaller than that at a depth of 5 cm. The reduced diffusivity case represents the effect of drying at the surface or, alternatively, the effect of wetting the surface. At either extreme, the effective diffusion coefficient would be significantly reduced.

The effective diffusivity of vapors in very wet soils is reduced by elimination of available pore space as indicated by Eq. (2) and as a result of the additional accumulation of methyl bromide in the immobile water phase. A doubling of the soil water content to about 29% would change the effective diffusivity from the base case by about a factor of ten. Increases in soil water content would also increase the amount of methyl bromide in the aqueous and soil phases, further retarding the fumigant's movement. This suggests that a means of controlling methyl bromide emissions to the atmosphere is spraying the soil with water immediately after injection. Uniform saturation of the upper soil layers with water may be difficult in practice but would significantly reduce emissions if achievable. A similar effect could be accomplished by using a lower permeability surface cover.

Very dry soils also exhibit strong sorption of organic compounds (e.g. [6, 19]), thus increasing their sorption-related retardation. Ryan and Cohen [19], for example, reported a factor of ten decrease in the effective diffusion coefficient of lindane as the soil moisture content decreased to 1% from 3%. Such a change could occur as a result of surface heating of the upper soil layer during the day. Cooling to near the ambient dew point at night, however, could return the moisture to the soil and cause the effect of this phenomena on cumulative emissions to be negligible.

4. Summary and conclusions

Numerical models of soil vapor migration suggest that about half of the methyl bromide used in soil fumigations is ultimately released to the atmosphere. This estimate is in good agreement with the fraction of anthropogenic emissions lost to the atmosphere estimated by the global atmospheric budget of methyl bromide. The current estimate is based on representative soil and injection parameters. Only for shallow injections of 6" or less below the surface of the soil does the model predict

methyl bromide emissions that exceed 50% of that injected. Heterogeneous soils or poor injection depth control influence the fraction of methyl bromide lost to the atmosphere but the fraction lost still remains near 50% of that injected if an effective soil cover is placed immediately. Poor operational control of the injection, inadequate pre-injection soil loosening, placement of a permeable or holed cover, or delayed cover placement could, however, increase the cumulative emissions and would result in significantly higher initial fluxes. Research should be conducted to determine better estimates of methyl bromide decomposition rates in representative soils and to verify the effect of soil and injection heterogeneities on emissions to the atmosphere. Such studies should involve the direct determination of flux to the atmosphere under a variety of conditions and measurement of the Br^- ion in the soil to monitor methyl bromide degradation rate. Based on the available data, however, it is expected that current fumigation practices result in retention in the soil of a significant fraction of the injected methyl bromide. The fraction lost to the atmosphere could be further reduced by deep injections and by methods that minimize the effective diffusion coefficient in the near-surface soil layers.

Acknowledgements

This work was partially supported by the Methyl Bromide Global Coalition. The author also wishes to extend a special thanks to Greg Thoma, LSU, who assisted in the collection of some of the pertinent literature, and Tom Duafala, TriCal, who provided data and numerous suggestions.

References

- [1] R.T. Watson, D.L. Albritton, S.O. Andersen and S. Lee-Bapty (Eds.), *Methyl Bromide: Its Atmospheric Science, Technology, and Economics*, United Nations Environment Programme, United Nations Headquarters, Ozone Secretariat, P. O. Box 30552, Nairobi, Kenya, 1992.
- [2] WMO, *Scientific Assessment of Ozone Depletion*, World Meteorological Organization, Report No. 25, 1991.
- [3] H.B. Singh, L.J. Salas and R.E. Stiles, Methyl halides in and over the eastern Pacific (40 N-32S), *J. Geophys. Res.*, 88 (1983) 3684.
- [4] A. Cuany and J.C. Arvieu, Distribution patterns and nematocidal activity of methyl bromide in various soil conditions and methods of application, *Acta Horticulturae*, 152 (1983) 277–287.
- [5] D.E. Rolston and R.D. Glauz, Comparisons of simulated with measured transport and transformation of methyl bromide gas in soils, *Pest. Sci.*, 13 (1982) 653–664.
- [6] K.T. Valsaraj and L.J. Thibodeaux, Equilibrium adsorption of chemical vapors onto surface soils: Model predictions and experimental data, in: J.L. Schnoor (Ed.), *Fate of Pesticides and Chemicals in the Environment*, Wiley, New York, 1992, pp. 155–174.
- [7] W.E. Schiesser, DSS/2 (Differential Systems Simulator, Version 2), Lehigh University, Pennsylvania, 1987.
- [8] R.J. Millington and J.P. Quirk, Permeability of porous solids, *Trans. Faraday Soc.*, 57 (1961) 1200.
- [9] T. Duafala, TRICAL, Hollister, CA, personal communication, 1992.
- [10] D. Hillel, *Fundamentals of Soil Physics*, Academic Press, New York, 1980, p. 273.

- [11] H. Siebering and M. Leistra, Computer simulation of fumigant behavior in soil, in: D. Mulder (Ed.), *Soil Disinfestation*, Elsevier, Amsterdam, 1979, pp. 135–161.
- [12] W.J. Lyman, W.F. Reehl and D.H. Rosenblatt, *Handbook of Chemical Property Estimation Methods*, American Chemical Society, Washington, DC, 1990.
- [13] J.H. Montgomery and L.M. Welkom, *Groundwater Chemicals Desk Reference*, Lewis Publishers, Chelsea, MI, 1990.
- [14] B.D. Brown and D.E. Rolston, Transport and transformation of methyl bromide in soils, *Soil Sci.*, 30 (1980) 68–75.
- [15] J.C. Arvieu, Some physico-chemical aspects of methyl bromide behavior in soil, *Acta Horticulturae*, 152 (1983) 267–274.
- [16] J.C. Arvieu, Current problems arising from soil fumigation with methyl bromide, *Acta Horticulturae*, 152 (1983) 275–276.
- [17] F. Herzel and G. Schmidt, Zur Persistenz des Begasungsmittels Methylbromid im Boden und Wasser, *Wasser und Boden*, 12 (1984) 589–591 (cited by Willis Wheeler, USDA/CSRS, 202/401-6702).
- [18] I.A. Gentile, L. Ferraris and S. Crespi, The degradation of methyl bromide in some natural fresh waters, influence of temperature, pH and light, *Pest. Sci.*, 25 (1989) 261–272.
- [19] P.A. Ryan and Y. Cohen, Multiphase chemical transport in porous media, in: D.T. Allen, Y. Cohen and I.R. Kaplan (Eds.), *Intermedia Pollutant Transport: Modeling and Field Measurements*, Plenum Press, New York, 1989.
- [20] M.J. Kolbezen et al., Factors that affect deep penetration of field soils by methyl bromide, *Hilgardia*, 42(14) (1974) 466–492.
- [21] W. Mabey and T. Mill, *J. Phys. Chem. Ref. Data*, 7 (1978) 383–415.