

Environmental Hazards of Fumigants : The Need for Safer Alternatives

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Abstract

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Fumigants have been used effectively in agriculture and related areas for many years. A major use is as a soil application to reduce or eliminate soil borne diseases, insects, and weeds, which if not controlled would adversely affect the growth and production of agricultural crops. Fumigants have great advantages in that they effectively penetrate the materials being treated, are efficient in killing pests and usually dissipate leaving no hazardous residues. However, fumigants are toxic to humans and animals and are potentially hazardous during application and dissipation. Fumigants, of which methyl bromide is a prominent example, are usually allowed to evaporate into the atmosphere when used in soil or in fumigation chambers. Fumigants used in soil have been detected in ground water and certainly have the potential to enter drinking water and result in human exposure. A major concern today is the environmental impact of methyl bromide owing to its potential movement into the stratosphere and its contribution to the depletion of the stratospheric ozone layer. The search for safer alternatives to methyl bromide has been going on for several years. Potential replacements include the use of less hazardous chemicals, non-chemical soil disinfection using steam or soil solarization and applying other practices such as biological control and crop rotation to reduce pest infestation.

Introduction

Fumigants are small organic molecules that are volatile at temperatures above 5°C and are usually heavier than air. They commonly contain one or more of the halogens chlorine, bromine or fluorine. Most fumigants are highly penetrating, reaching large masses of material and are effective as insecticides, fungicides, nematocides and herbicides.

A number of fumigants are available at present. Methyl bromide has been the most widely used fumigant since the early 1900s. It is used for controlling pests in soil, stored commodities, structures and shipments that must meet agricultural quarantine regulations. With the cancellation of the fumigants ethylene dibromide (EDB) and dibromochloropropane (DBCP), methyl bromide use increased and became more critical in agricultural production and distribution. Other currently available fumigants are dazomet (Basamid[®], which releases methyl cyanate), metam sodium (Vapan[®], which releases methyl isothiocyanate), 1,3-dichloropropene (Telone II[®]), and mixture of 1,3-dichloropropene and methyl isothiocyanate (Vorlex[®]). These have various shortcomings such as registration status, economic considerations, comparative efficacy and toxicity. Currently Vorlex[®], which is considered the most reliable alternative, is scheduled for voluntary cancellation.

Methyl Bromide

Due to the importance of methyl bromide as a fumigant and the hazards associated with its use, this portion of the paper will review what is known about the uses of methyl bromide, its sources, its fate in soils, water and plants, its movement from soils into the atmosphere, its effect on stratospheric ozone and its health risks.

1. Uses of Methyl Bromide

The major use of methyl bromide in agriculture is soil fumigation. It is effective against all pests which can significantly reduce agricultural productivity. It is quite important to the production of strawberries, tree fruits and nuts, other small fruits, solanaceous crops, forestry, nursery and horticultural crops and vegetables.

Another important use of methyl bromide is in its quarantine work and in food preservation. In the U.S., it is the single most effective material in eliminating unwanted pests from food and other materials which the United States exports to other countries or which is imported to the United States. In some cases quarantine regulations specify the use of methyl bromide.

Methyl bromide is also used to eliminate unwanted pests in structures. The use ranges from the fumigation of houses to the fumigation of grain storage and milling facilities.

2. Sources of Methyl Bromide

a. Anthropogenic. Methyl bromide is manufactured for a number of agricultural uses and other applications. From 1984 to 1990 commercial production for these uses ranged from approximately 42,000 tons to approximately 63,000 tons. In 1990, 82% was used for soil fumigation, 13% for commodities, and 5% for structures. These figures are for production and agricultural use in North and South America, Europe, Africa, Asia and Australia (excluding China, India and countries formerly in the USSR) (2). Approximately 32,000 tons of methyl bromide were used in the United States (U.S.) in 1990; 22,000-24,500 tons were used for soil fumigation, 2,500 tons for post harvest and quarantine treatments, 2,000-4,500 for fumigating structures, and 3,000 tons as a chemical intermediate in manufacturing (4). Thus of the total used in the U.S., about 80% is for agriculturally related purposes.

b. Naturally Occurring. There is a number of naturally occurring sources of methyl bromide. The oceans represent an important source of organic halides. Methyl bromide was reported to be present in seawater off the coast of England (19). Subsequently it has been measured both in seawater and in the air above seawater. Concentrations in near surface water ranged from 0.5 to 3.7 ng/liter in the eastern Pacific Ocean (29), with a mean value of 1.2. Methyl bromide concentrations in air above the eastern Pacific Ocean averaged 23 parts per trillion (ppt). The authors suggested that northern hemisphere values (26 ppt) were much higher than the southern hemisphere values (19 ppt)(29). There have been additional reports of atmospheric levels of methyl bromide at or near ground level. These range from 10 to 15 ppt in the Northern Hemisphere and from eight to 11 ppt in the Southern Hemisphere (3, 10, 22). Reported levels of the presence of methyl bromide in the air of seven US cities ranged from 40 to 300 ppt with one value measured at 1000 ppt (28).

Just because methyl bromide is detected in the ocean or in the air above the oceans, it does not necessarily mean that it originates there. Although these levels could arise from man-made methyl bromide coming from land based sources, this does not seem likely. Singh (29) tested some hypotheses on the origin of methyl halides in seawater, and demonstrated a good correlation between the levels of methyl chloride and methyl bromide, suggesting a common organic source for these two materials. Singh (29) further suggested that the ocean to air flux could account for the then measured abundance of methyl bromide in the troposphere if the residence time was 1.2 years. The author indicated that this value was in reasonable agreement with an estimated mean tropospheric residence time of 1.7 years on the basis of the reaction with the hydroxyl radical ($\text{OH} = 7 \times 10^5 \text{ molec cm}^{-3}$).

Yvon-Lewis and Butler (36) recently reported on global, ocean-atmosphere box model to examine the potential effect that biological degradation can have on the lifetime of atmospheric methyl bromide. The impact of the oceans serving as a sink for methyl bromide had generally not been considered biological degradation processes in calculating the atmospheric lifetime. Table 1. shows estimates of sources and quantities of emissions of methyl bromide as well as revised estimates of various sinks for the compound.

3. Fate of Methyl Bromide in Soils, Water and Plants

Application of methyl bromide to soils results in movement of the chemical in soil, dissolution in water and movement from the soil into the atmosphere. Methyl bromide also undergoes chemically and biologically mediated degradation processes. A product of methyl bromide degradation is the bromide ion. In the mid-1970's, it was normal practice in some European countries to leach the soil after methyl bromide fumigation to reduce bromide concentrations in the soil and thus reduce uptake of bromide into edible crops grown on the soil (31). The leaching water contained significant bromide levels after it had percolated through the soils, but these levels diluted rapidly (32).

In the Netherlands, methyl bromide was used to fumigate glasshouse soils under tarp covers at a rate of approximately 100 grams/square meter (33). After two days, the tarps

covering the soils were partially lifted for aeration and were removed completely after seven days. Leaching of the soil was started immediately after the tarps were removed, and the leaching water passed into a drainage ditch. The level of methyl bromide in the leaching water increased sharply, reaching a maximum within 10 hours of the start of the leaching, and then decreased at a rate of 50% per day. The concentrations of bromide ion also increased sharply after the start of the leaching, but decreased more slowly than did methyl bromide. Fish mortality was observed in the drainage ditches around the glasshouse. Concentrations of methyl bromide in the drainage water exceeded the LD_{50} of one test fish species. The levels of methyl bromide in water declined by volatilization and degradation. The half-life of methyl bromide in these drainage waters was estimated at 6.6 hours at a water temperature of 11°C .

Table 1. Revised Budget for Atmospheric Methyl Bromide.

Source Type	Emissions (Gg/year)	Sink Type	Uptake (Gg/year)
Oceans	56	Oceans	77
Fumigation - Soils	32 ¹	OH and hv^2	86
Fumigation - Durables	6.6 ¹	Soils ³	43
Fumigation - Perishables	5.7 ¹	Plants ⁴	?
Fumigation - Structures	2 ¹	Total	206
Gasoline	15 ¹		
Biomass Burning	20 ¹		
Total	137		

¹ Source estimates from Butler and Rodriguez, 1996 (9) and references therein.

² Penkett *et al.*, 1995 (23) and Prinn *et al.*, 1996 (24).

³ Shorter *et al.*, 1995 (27).

⁴ Jeffers and Wolfe, 1977 (17).

This work was continued further as described in a later report (13). In these experiments, two kinds of tarp material were used to cover the soil. One was the typically used low density polyethylene (LDPE) and the other a gas tight material, Saranex 11. Methyl bromide was applied at a rate of 103 gms/square meter. The cover time was five days in both cases. In a second trial, a methyl bromide dose of 20 gms/square meter was used, Saranex 11 film was used and the cover time was 10 days. Soil temperatures were approximately 10°C for the first trial and 15°C for the second. Three weeks after the start of fumigation, leaching was started and water samples were collected. Leaching water from the gas tight film covered soil contained high concentrations of methyl bromide (maximum of 4.2 gms/m^3) during the first few days. When the LDPE cover was used, methyl bromide concentration in the drainage water was much lower (maximum of 0.22 gms/m^3). In the second trial using the lower application rate, methyl bromide in the leaching water ranged from zero to 0.014 gms/m^3 . In half the samples from the second trial, no methyl

bromide was detected (limit of detection was 0.0004 g/m³). Bromide ion was also measured in the leaching water. In the second trial, 101 gm/m³ was detected on the first day of leaching which dropped to 25g/m³ after four days. In terms of the relative quantities of methyl bromide degradation, only 12% of chemical applied at the high rate was transformed while 79% of the methyl bromide was degraded when applied at the lower rate. Use of a gas tight cover over soil fumigated at a low rate and held for three weeks, resulted in the loss of very little methyl bromide into the air and significant degradation of the material in the soil.

Soil fumigation with methyl bromide is not allowed in Switzerland for food crops due to concern of the build-up of high levels of bromine in these crops. It is allowed only in the production of flowers and in tree nurseries. In Germany, when methyl bromide is used to control potato nematodes, the production of vegetables on fumigated land is not permitted for the following three years.

The use of methyl bromide as a soil fumigant may lead to residues in food crops grown on treated soil. The authors of this review found no reports of residual methyl bromide in fresh agricultural products resulting from soil fumigation activities. There have been several reports on the analysis of fruits, nuts and grains that were fumigated post-harvest either for quarantine or preservation purposes. Ford *et al.* (14) analyzed 1132 nut samples for methyl bromide; the fumigant was detected in three of those samples at levels of 0.03 ppm (pistachios), 0.017 ppm and 0.014 ppm (processed walnuts). It was noted that most of the samples had been heat processed and that any residual methyl bromide would most likely have been driven off. Daft (12) reported analyzing approximately 50 samples of raw fruits and vegetables from the U. S. Food and Drug Administration's market basket studies for the presence of methyl bromide. No methyl bromide was detected in these samples. These reports suggest that residues of methyl bromide are not present to any appreciable extend in fruits, vegetables, nuts or other foods.

Methyl bromide undergoes transport and degradation in soils and the soil environment. Brown and Rolston (8) performed classic experiments to describe the transport and transformation of methyl bromide in soils. Experiments were conducted on dry sand, moist sand, a loam soil and a peaty muck soil to evaluate the influence of water, clay minerals and organic matter on the sorption/desorption of the chemical. Effects of methyl bromide flow rate in soil were also evaluated.

A first order kinetic model for the reversible sink term better described effluent curves than did a linear equilibrium model. Rates of bromide production were significant and influenced by soil type, with bromide production rates being greatest from muck, intermediate from loam and least with sand.

4. Movement of Methyl Bromide from Soils into the Atmosphere

There is very little quantitative data describing the loss of methyl bromide from agricultural fields after fumigation. Yagi *et al.*, 1993 (34) applied 75% methyl bromide/25% chloropicrin as a commercial operation to soil being prepared for strawberry production near Irvine, CA. The application rate was approximately 300 lbs/acre and during the application process a plastic film was placed over the soil. The film was removed 95 hours after application. Methyl bromide was measured in the air above the fields both before and after the film was removed. Based on directly observed fluxes from soil to the atmosphere, 87% of the total methyl bromide applied moved out of the soil. The authors noted a number of uncertainties over which they had no control. In a subsequent experiment, performed with better control of application technology, during the fall of 1993, the escape of methyl bromide into the atmosphere was approximately 35% of the material applied. To confirm this value, bromide ion concentration was measured in the soil before and after application. The added bromide levels present after application accounted for the 65% of methyl bromide not detected in the effluent material above the field.

Another field experiment was conducted by Seiber *et al.*, 1993 (26) near Davis, CA. Methyl bromide (67% plus 33% chloropicrin) was applied using commercial equipment at a depth of 10-12 inches and at a rate of 350 lbs per acre to 9.7 acres. A tarp was placed on the field as a part of the application process. After seven days, the tarp was removed. A second field, was treated with methyl bromide (99.5% plus 0.5% chloropicrin) at a depth of 10-12 inches and at a rate of 180 lbs per acre to 14.9 acres. No tarp was placed on this field. Twenty three percent of the methyl bromide was lost in a six days period following fumigation from the tarped field, and 98% was lost from the untarped field. Approximately 34% was lost from the tarped field by 10 days after application.

Yates *et al.*, 1996 (35) have performed significant research describing the environmental fate and transport of methyl bromide used as a soil fumigant. A summary of some of their work is presented in Table 2.

Table 2. Mass Emission of Methyl Bromide from Agricultural Fields – Experimental Results

Application Rate	Application Depth	Cover	Days	Emissions
843 kg/3.5 ha	0.25 m	1 mil polyethylene	3	61% based on 39% conversion to Br ⁻ 64% based on micrometeorological methods 59% based on flow-through chamber methods 62% based on aerodynamic methods
1143 kg/3.5 ha	0.68 m	None	22	21% based on appearance of Br ⁻ 1.9 - 4.9% based on chamber and micrometeorological methods

The 1143 kg/3.5 ha experiment resulted in some anomalies. The overall mass balance was 81 - 84%; the authors suggest that the 16 - 19% losses occurred during the application process.

During the work of Yates *et al.*, 1996 (35), a number of management techniques were found to have significant impact on methyl bromide emission reduction. In field experiments, it appears there are many factors that may influence methyl bromide transport, transformation in the soil-water-air system and then its ultimate volatilization from the soil surface. Among those factors are application method and depth, temperature, as well as soil and climatic conditions. In laboratory studies, injection depth, use of plastic films, soil-water content, and soil bulk density have profound effects on methyl bromide volatilization after soil injection.

Yates *et al.*, 1996 (35), using a model to describe transport and loss of methyl bromide in soil following application, studied the effects of depth of injection, soil-water content, presence or absence of a tarp, depth to a downward barrier, and irrigation after injection. To minimize volatilization, methyl bromide should be applied when temperatures are cool, relatively deep in moist soil, under tarped conditions, and the soil should be packed immediately after application.

Approaches to reducing volatilization loss of a fumigant will be of no value if the efficacy of the fumigant against weeds, insects, and diseases is reduced in the process. Current conventional fumigation guidelines are based on early studies and require keeping the subsurface soil "as dry as possible". It has been observed, however, that many soil pathogens and fungi are more susceptible to control by methyl bromide in wetter soils, because partitioning into the aqueous phase is required for methyl bromide to exert its biocidal action. Increasing the resistance to diffusion at the soil surface by using high barrier tarps and/or by irrigating the soil surface may permit use of reduced quantities of methyl bromide without loss of effectiveness. Table 3. shows the conditions that affect emissions of methyl bromide from the soil.

Table 3. High vs. Low Methyl Bromide Emissions from Soil

High Emissions	Conditions	Low Emissions
Shallow	Depth of Injection	Deep
High	Soil Temperature	Low
Low	Soil Moisture	High
No	Tarp	Yes
No	Pack Soil	Yes

5. The Ozone Depletion Potential of Methyl Bromide

The Clean Air Act, enforced by the U S Environmental Protection Agency, mandates that Class I ozone depleters be phased out of production and use by the year 2000. Further, the designation of a Class I material is based upon its "Ozone Depletion Potential" (ODP). This is a numerical value "which is a measure of the integrated ozone destroying capacity over a chosen time scale of a particular gas per kg emitted in the troposphere, relative to a reference gas (generally CFC₁₁, CFC-11)" (20). Numerical models and semi-empirical approaches (30) have been used to evaluate ODPs. The semi-empirical

methods use "measurements of tracers to determine the chlorine or bromine released into the stratosphere, estimated lifetimes, and information regarding the effectiveness of bromine in destroying ozone as compared to chlorine" (30). The ODP for methyl bromide has been estimated to be 0.65 (20). Since chemicals having ODP values greater than 0.2 are legally defined as Class I ozone depleters, then methyl bromide is considered to be a member of that category of ozone depleting substances. Questions have been raised concerning the values used in calculating the ODP, but until more data are available the ODP value of 0.65 will be used.

6. Health Risks of Methyl Bromide

Many incidents of human poisonings associated with methyl bromide have occurred since the compound became commercially useful at the beginning of the twentieth century. Exposures have resulted from chemical manufacturing processes, use of fire extinguishers containing methyl bromide and a variety of fumigation processes. The principal occupational hazard is associated with fumigation and re-entry into fumigated areas. Those directly involved are more likely to become intoxicated, but occasionally bystanders are affected. Because methyl bromide is colorless and has little odor at potentially dangerous concentrations, chloropicrin was added as a warning agent (16).

The absence of early warning symptoms and delays in the onset of toxicity with frequent failure to recognize less severe symptoms are cause for concern (16). Incorrect diagnosis and subsequent improper treatment of cases may also be a problem (5). There have been many clinical studies of poisoning incidents in addition to extensive research using animals in efforts to gain a better understanding of general effects, primary sites of action and risk detection methodology.

The general area of human exposure was thoroughly reviewed by Alexeeff and Kilgore in 1983 (1). They reported that the primary route of exposure is inhalation, but dermal contact is also a major route. Dermal exposure results in skin irritation and frequently systemic effects which are normally characteristic of inhalation, suggesting methyl bromide is absorbed through the skin. Acute, subchronic and chronic exposures have resulted in poisoning incidents. Deaths usually occur from acute exposures to high concentrations or from a higher than usual exposure following a history of chronic low level exposures. Chronic effects, which appear to decrease the threshold for a reaction to an acute exposure, are the result of an accumulation of the lesion since methyl bromide itself does not accumulate in the body.

Neurological and other physiological symptoms result from exposure. These other physiological symptoms are similar for acute, subchronic and chronic exposures. The most frequently reported effects involve the respiratory or gastrointestinal tracts. In acute cases some victims developed dry throat, eye irritation and kidney effects. The most commonly reported symptoms are associated with the nervous system (1). Neurological manifestations of acute exposure generally proceed through three stages (15). The first stage involves nausea, vomiting, vertigo and headaches. This is followed by tremors, convulsions, delirium or mania. When there is recovery, the final stage includes apathy, amnesia,

incoordination and often hallucinations or aphasia. There is considerable variation in the onset of symptoms and delays of 6-36 hours have occurred (1). There have been cases of a progression from mild to moderate to severe symptoms. In most of the severe non-fatal cases, a complete progression occurred in 14 hours. In acutely fatal cases, the time following exposure was 1-85 hours with most deaths occurring at 11-30 hours. Mild signs of neurological effects resulting from methyl bromide toxicity are headache, dizziness and fainting (1). More severe symptoms include visual disturbances, speech difficulties, chronic hallucinations and confusion (15). Progressive weakness, lack of coordination and paresthesias may occur; death, when it occurs, may be preceded by convulsions and coma (1, 15).

Methyl bromide can be used safely with proper precautions. However, operators must receive training and be highly qualified. Skin contact should be avoided; if such occurs, immediate washing is essential. Since methyl bromide may be trapped inside clothing and cause skin injury, jewelry, gloves or other gas confining apparel should not be worn. Loose, long sleeved shirts, long trousers and socks are appropriate and should be cleaned after each use. Under normal conditions, no respiratory protection is required. However, the applicator should have full-face respiratory protection available for use as needed. Complete health records should be available as well as any past history of known contact with methyl bromide and other chemicals.

Safer Alternatives to Methyl Bromide

Replacement chemical treatments probably will not be easily found. They must be efficacious, safe to humans, not

detrimental to the environment, and economically competitive. Some approaches to finding alternatives to methyl bromide have been discussed by many authors and have been reviewed by Braun and Supkoff (6).

I. Chemical soil disinfestation

A. Fumigants

Fumigants, other than methyl bromide, have been tested. Table 4. illustrates experimental trials in Florida which makes direct comparisons between two methyl bromide formulations as well as comparisons with vorlex and metam-sodium, two other readily available alternatives. Generally speaking, control with methyl bromide is superior to that of the other chemical substitutes used under these conditions.

Ohr *et al.*, 1996 (21) have reported that methyl iodide is an effective material for soil fumigation and is "ozone-safe". These scientists report that methyl iodide is an effective fumigant for the control of four species of pathogenic fungi, one species of nematode, and seven species of weeds. In seven experimental trials, it performed as well as, or better than, methyl bromide. Methyl iodide may be applied using the same equipment as is used for methyl bromide; it has chemical and physical properties that may make it less hazardous to applicators than is methyl bromide. Methyl iodide is reported to be destroyed rapidly by ultraviolet irradiation and thus should not pose any threat to stratospheric ozone. Issues regarding human toxicology and environmental impacts have not been resolved.

Table 4. Pest control ratings^a for methyl bromide, Vorlex and metam-sodium in Florida

Chemical	lb AI/A applied ^b	\$/A Treatment Cost	Ratings ^a			
			Weeds (9.3)	Insects (9)	Nematodes (9)	Pathogens (7.5)
Methyl Bromide 67/33 ^c	200	290	9	10	10	10
Methyl Bromide 98/2 ^d	200	184	10	10	10	7.5
Vorlex	87.7	381	7 ^e	10	9 ^f	7.5
Metam-sodium	190	250	5 ^e	5	7 ^f	3 ^g

^a Ratings: 10 = excellent; 1 = poor. Any rating less than the figure in parentheses for each pest group provides unacceptable control.

^b Pounds active ingredient per acre.

^c 67 percent methyl bromide and 33 percent chloropicrin.

^d 98 percent methyl bromide and 2 percent chloropicrin.

^e Nutsedge, a severe problem, is not controlled.

^f Control is dependent on method of application. Since Vorlex and metam-sodium are applied by chisel, control is limited to a narrow band. Metam-sodium requires water for activation.

^g Metam-sodium does not control *Fusarium* or *Verticillium* wilts.

B. Non-Fumigants

1. **Soil insecticides and nematicides.** A number of pesticides can be used as a pre- and post-planting treatments to control soil inhabiting insects and nematodes. They may be used for shallow rooted crops or to treat the upper soil fraction in combination with soil fumigants. Examples of these compounds are:

- a. Aldicarb. It is a systemic carbamate insecticide, nematicide and acaricide. It is applied as granules at planting time, and irrigating the soil after application will improve its effectiveness.
- b. Carbofuran. It is a carbamate systemic broad-spectrum insecticide and nematicide. It is applied in furrows as granules or flowable formulations.
- c. Ethoprop. It is an organophosphate soil insecticide and nematicide with contact action. It may be incorporated into the soil as granules or emulsifiable concentrate at planting and is also used as a post-planting treatment.
- d. Fenamiphos. It is an organophosphate systemic nematicide. It is applied as granules or emulsifiable concentrate before or after planting and also to established plants.
- e. Oxamyl. It is a carbamate insecticide, nematicide and acaricide with contact and systemic action. It is applied as granules or water-soluble liquid as a pre-planting treatment and should be incorporated into the soil.

However, none of these compounds is as effective as methyl bromide as a nematicide.

2. **Systemic fungicides.** Certain systemic fungicides can be used as a pre- and post-planting treatment to control specific plant pathogenic fungi. Examples of these compounds are:

- a. Benomyl. It is effective against a broad-range of plant pathogenic fungi such as *Verticillium*, *Fusarium*, *Rhizoctonia* and many other pathogens on a wide variety of crops. It may be applied through a sprinkler system or as a soil drench on some crops.
- b. Metalaxyl. It can be used during seedbed preparation to control specific soil-borne pathogenic fungi and is effective against species of *Pythium*, and *Peronospora*.

II. Non-chemical soil disinfestation

A number of techniques could be used either singly or in combination for controlling a variety of soil-borne pests.

A. Soil Solarization

This technique is considered an attractive and safe alternative to soil fumigation. Many pathogenic fungi, bacteria, weeds, and nematodes may be controlled by the use of soil solarization. It is compatible with chemical and biological methods and may be combined with soil fumigants, crop rotation and other methods to improve its efficacy and reduce the use of chemicals. For example, soil solarization is more effective in controlling soil-borne pests when combined with chloropicrin or a biological control agent. Species of *Fusarium*,

Phytophthora, *Pythium*, *Sclerotinia*, *Verticillium* and other genera have been successfully controlled by soil solarization. Soil solarization is also effective in controlling weeds. A number of annual winter and summer weeds, as well as, weed seeds may be effectively controlled by soil solarization. Examples of such weed genera are *Avena*, *Capsella*, *Lamium*, *Poa*, *Raphanus*, *Echinochloa*, *Malva*, and *Solanum* (18).

However, soil solarization has limitations, the most important of which is that farmers consider it too labor-intensive and not completely effective, and thus prefer to use soil fumigation for crop insurance. The soil has to be covered with plastic material leaving it unproductive for 6-8 weeks or delaying planting dates. Moreover, its efficacy depends on weather conditions, soil type, and pests to be controlled. However, the application of soil solarization in plastic houses is an effective method even in cool climates.

B. Steam

Steam effectively controls most soil-borne pathogens and weeds. Moreover, a mixture of steam and air selectively kills plant pathogens at 50 - 60°C in 30 minutes and could be used in nurseries as an alternative to soil fumigation. A negative pressure steaming method was developed and described by Runia (25) for greenhouse soil disinfestation, whereby steam is introduced under a sheet and forced into the deeper soil layers by negative pressure created in the soil by a fan which sucks air out of the soil through buried perforated polypropene pipes.

C. Biological Control Methods

The use of antagonistic microorganisms to become established in the infection site in advance of the pathogen to prevent infection of a crop is a fairly new and promising technique. These microorganisms have the potential of increasing crop yield without an adverse effect to the environment. The antagonistic microorganisms are released with the seeds at planting time. For example, the antagonistic *Trichoderma* and *Gliocladium* spp., when used as seed treatment, have shown potential to control soil-borne plant pathogens. These antagonistic agents are generally highly specific for the control of a certain disease, and thus could be an advantage in some instances but a disadvantage in others such as in a replant problem where many pathogenic organisms are involved. The development of biological disease control products on a commercial scale is still limited but is expected to develop in the near future to become an integral component of the disease management strategy for many crops (7, 11).

D. Crop Rotation

Traditionally crop rotation has been an effective method for suppressing damage to annual crops caused by pests with limited host range and thus minimize the use of pesticides. Moreover, crop rotation generally improves soil structure and maintains soil fertility. The disadvantage of crop rotation is that it needs time to be effective, and the crop is frequently rotated with non-cash crops which contribute little to farm income.

E. Resistant Varieties

Developing host plant resistance may contribute to the solution of many soil-borne pests, and resistant varieties may be incorporated into an effective crop rotation program.

However, a major drawback to breeding resistant varieties is that most genes are effective against a single pathogen and even only one race of a pathogen. Moreover, the availability of broad-spectrum and effective soil fumigants, such as methyl bromide, decreased the interest of plant breeders in developing resistant varieties. The increased concern over environmental pollution and the trend to minimize the use of chemicals, coupled with the advances in the field of biotechnology is already prompting scientists to develop resistant varieties.

Finally, Table 5. illustrates some of the approaches published in the United States EPA worldwide web page entitled "Methyl Bromide Alternatives, 10 Case Studies, Vol. II.

Conclusions

While methyl bromide is very important to agriculture, the risks associated with its use have lead to a great deal of

controversy about the continued availability of the compound. One risk in particular, that of ozone depletion has led to a scheduled phase-out and complete ban of its use in the near future.

The challenge is to find new pest control methods that have fewer risks to man and the environment. In the case of methyl bromide, replacement with a single method for control of pests currently controlled is extremely unlikely. The attention of the research community has been focused on this situation and hopefully some new and effective approaches will be developed. Developing IPM programs and evaluating different farming systems may provide a solution to the replacement of methyl bromide soil fumigation and the reduction of the use of and dependence on synthetic pesticides.

Table 5. Alternatives to Methyl Bromide

Approach	Usage	Target Organism	Economics	Effectiveness	Remarks
Resistant cultivars + Metam sodium	Soil	Nematodes	Comparable costs to non-resistant cultivars		Resistant cultivars need to be developed
Chloropicrin and chloropicrin plus telone	Soil Strawberries	fungal pathogens	Comparable to methyl bromide	Satisfactory	
IPM	Soil Strawberries		Lower yields but higher selling price	Yields up to 89% of MB treatment	
Solarization	Soil Field Crops	pests and pathogens	Lower cost than MB		
Solarization	Soil Orchards	Pathogens	Lower cost than MB		
IPM including other chemical pesticides	Grapes	All	Same as MB	Satisfactory	

المخلص

ويلر، ب. ويلز ونصري قعوار. 1997. المخاطر البيئية لاستخدام المدخنات: الحاجة إلى بدائل أكثر أماناً. مجلة وقاية النبات العربية. 15(2): 154-162. استخدمت المدخنات، على نحو فاعل، في الزراعة لعدة سنوات. وكان الاستعمال الرئيس هو استخدامها في التربة للتخلص من الأمراض والحشرات والأعشاب المنقولة معها والتي تؤثر، في حال عدم مكافحتها، سلباً في نمو المحاصيل الزراعية وإنتاجها. وتتسم المدخنات بمزايا عظيمة كونها تخترق المواد المعاملة، وكفاءتها في قتل الآفات، وعدم تركها لبقايا سامة. ومع ذلك، تبدي المدخنات أضراراً للبيئة والإنسان. فهي سامة للإنسان والحيوانات وضارة أثناء استخدامها وتطايرها. ويسمح للمدخنات، والتي يعتبر ميثيل البروميد مثالا بارزا عنها، بالتبخّر في الجو عند استخدامها في التربة أو غرف التدخين. وقد تم كشف المدخنات المستخدمة لتعقيم التربة في الماء الأرضي كما لها مقدرة على الدخول إلى ماء الشرب. والإهتمام الرئيس حالياً هو تأثير بروميد الميثيل في البيئة نظراً لما يتسم به من حركة في طبقات الجو وإسهامه في تخريب طبقة الأوزون في الجو. واستمر البحث عن بدائل أكثر أماناً لعدة سنوات. وتتضمن هذه البدائل استخدام كيمويات أقل سمية، تعقيم التربة بدون استخدام المبيدات وذلك باستعمال البخار أو تسميس التربة، واستخدام ممارسات أخرى كالمكافحة الأحيائية والدورة الزراعية لخفض التلوث بالآفات.

References

1. **Alexeff, G.V. and W. W. Kilgore.** 1983. Methyl bromide. *Residue Revues* 88:101-153.
2. **Anonymous.** 1992a. Synthesis report of the methyl bromide interim scientific assessment and methyl bromide interim technology and economic assessment. Montreal Protocol Assessment Supplement. 41 pp.
3. **Anonymous.** 1992b. Proceedings of the MBSW, Methyl Bromide Science Workshop, Washington, DC.
4. **Anonymous.** 1993. The biologic and economic assessment of methyl bromide. Report, United States Department of Agriculture, Washington, DC., 99 pp.
5. **Appel, G.G., R. Galen, J. O'Brien and R. Schoenfeldt.** 1975. Methyl iodide intoxication, a case report. *Ann. Intern. Med.* 82:534-536.
6. **Braun, A.L. and D.M. Supkoff.** 1994. Options to methyl bromide for the control of soil-borne diseases and pests in California with reference to Netherlands. Pest Management Analysis and Planing Program. 40 pp.
7. **Brill, W.J.** 1991. Use of microorganisms for crop agriculture. In: *Agricultural Biotechnology at the Crossroads.* Macdonald, J. F. (Ed.) NABC Report 3. National Agricultural Biotechnology Council, Ithaca, New York: 91-96.
8. **Brown, R.D. and D.E. Rolston.** 1980. Transport and transformation of methyl bromide in soils. *Soil Science* 130:68-75.
9. **Butler, J. H. and J.M. Rodriguez.** 1966. Methyl bromide in the atmosphere. In: *the methyl bromide issue,* C.Bell, N. Price and B. Chakrabarti (Eds). John Wiley and Sons. Ltd London.
10. **Cicerone, R.J., L.E. Heidt and W.H. Pollock.** 1988. Measurements of atmospheric methyl bromide and bromoform. *J. Geophys. Res.* 93:3745.
11. **Cook, R.J.** 1991. Biological Control Making It Work. Part 2: Technological Status. In: *Agricultural Biotechnology at the Crossroads.* Macdonald, June Fessenden (Ed.). NABC Report 3. National Agricultural Biotechnology Council, Ithaca, New York: 213-227.
12. **Daft, J.L.** 1992. Headspace method for rapid determination of methyl bromide in assorted nut samples. *J. Assoc. Off. Anal. Chem.* 75:701-706.
13. **de Heer, H. Ph. Hamaker, L.G.M. Th. Tuinstra and A.M.M. van der Burg.** 1986. Leaching of methyl bromide and bromide ions into surface water after fumigation of glasshouse soils. In: *Effects of Land Use on Fresh Waters: Agriculture, Forestry, Mineral Exploitation, Urbanization.* J. F. de L. G. Solbe (Ed.). Published for the Water Research Centre by E. Horwood, Chichester, England.
14. **Ford, J.H., M.G. Legendre, D.L. Ladner, J.A. Dawson and C. Raymond.** 1992. Automated closed-system headspace determination of methyl bromide in a variety of raw and processed nuts. *J. Assoc. Off. Anal. Chem.* 75:328-333.
15. **Goetz, C.G.** 1985. Pesticides and other environmental toxins. In: *Neurotoxins in Clinical Practice.* Spectrum Publications, New York.
16. **Guillemain, M.P., R.S. Hillier and C.A. Bernhard.** Occupational and environmental hygiene assessment of fumigations with methyl bromide. *Ann. Occup. Hyg.* 34:591-607.
17. **Jeffers, P.M. and N.L. Wolfe.** 1997. Degradation of methyl bromide by green plants. In: *Fumigants.* J.N. Seiber, J.A. Knuteson, J.E. Woodrow, N.L. Wolf, M.V. Yates and S.R. Yates (Eds.), pp. 53-59.
18. **Katan, J. and J.E. DeVay (Eds.).** 1991. *Soil Solarization.* CRC Press. Boca Raton, FL., USA.
19. **Lovelock, J. E.** 1975. Natural halocarbons in the air and in the sea. *Nature* 256:193-194.
20. **Mellouki, A., R.K. Talukdar, A.M. Schmoltnner, T. Gierczak, M.J. Mills, S. Solomon and A.R. Ravishankara.** 1992. Atmospheric lifetimes and ozone depletion potentials of methyl bromide (CH₃Br) and dibromomethane (CH₂Br₂). *Geophysical Research Letters* 19:2059-2062.
21. **Ohr, H.D., J.J. Sims, N.M. Grech, J.O. Becker and M.E. McGriffin, Jr.** 1996. Methyl iodide, an ozone-safe alternative to methyl bromide as a soil fumigant. *Plant Disease* 80: 731-735.
22. **Penkett, S.A., B.M.R. Jones, M.J. Rycroft and D.A. Simmons.** 1985. An interhemispheric comparison of the concentrations of bromine compounds in the atmosphere. *Nature* 318:550.
23. **Penkett, S.A., J.H. Butler, M.J. Kurylo, C.E. Reeves, J.M. Rodriguez, H. Singh, D. Toohy and R. Weiss.** 1995. Methyl bromide, in scientific assessment of ozone depletion: 1994, World Meteorological Organization Global Ozone and Monitoring Project Report No. 37.
24. **Prinn, R.G., R.F. Weiss, B.R., Miller, J.Huang, F.N. Aleya, D.M. Cunnold, P.B. Fraser, D.E. Hartley and P.G. Simmons.** 1995. Atmospheric trends and lifetime of trichloroethane and global average hydroxyl radical concentrations based on 1978-1994 ALE/GAGE measurements. *Science* 269:187-192.
25. **Runia, W. Th.** 1983. A recent development in steam sterilisation. *Acta Hort.* 152:195-199.
26. **Seiber, J.N., M.M. McChesney, M.S. Majewski and J.E. Woodrow.** 1993. Preliminary Report on the study of methyl bromide evaporative flux determination from tarped and untarped fields.
27. **Shorter, J.H., C.E. Kolb, P.M. Crill, R.A. Kerwin, R.W. Talbot, M.E. Hines and R.C. Harriss.** 1995. Rapid degradation of atmospheric methyl bromide in soils. *Nature* 377:717-719.
28. **Singh, H.B., L.J. Salas, and R. Stiles.** 1982. Distribution of selected gaseous organic mutagens and suspect carcinogens in ambient air. *Environ. Sci. Technol.* 16:872-880.
29. **Singh, H.B., L.J. Salas, and R.E. Stiles.** 1983. Methyl halides in and over the Eastern Pacific (40 N-32 S). *J. Geophysical Res.* 88:3684-3690.
30. **Solomon, S., M. Mills, L.E. Heidt, W. H. Pollock and A.F. Tuck.** 1992. On the evaluation of ozone depletion potentials. *J. Geophys. Res.* 97:825-842.
31. **VanAchter, A., G. Van Pee, E. Van Wambeke and C. Van Assche.** 1981. Bromide concentration in water after methyl bromide soil disinfestation I. Relation between soil type, efficiency of leaching and bromide

concentration in the leaching water. Med. Fac. Landbouww. Rijksuniv. Gent 46:343-349.

32. VanAchter, A., J. Feyaerts, E. Van Wambeke and C. Van Assche. 1981. Bromide concentrations in water after methyl bromide soil disinfection II. Relation between leaching of methyl bromide fumigated greenhouse soils and bromide concentrations in the surrounding surface waters. Med. Fac. Landbouww. Rijksuniv. Gent 46:351-357.
33. Wegman, R. C., P.A. Greve, H. De Heer and Ph. Hamaker. 1981. Methyl bromide and bromide-ion in drainage water after leaching of glasshouse soils. Water, Air, and Soil Pollution 16:3-11.
34. Yagi, K., J. Williams, N.Y. Yang, and R.J. Cicerone. 1993. Agricultural soil fumigation as a source of

atmospheric methyl bromide. Proc. Natl. Acad. Sci. USA. 90: 8420-8423.

35. Yates, S.R., J. Gan, W.A. Jury, Marylynn V. Yates, F. Gao, Y. Jin, D. Wang, F.F. Ernst, A. Mutziger, and W.F. Spencer. 1996. Determination of the environmental fate and transport of methyl bromide used as a soil fumigant. Final Project Report for USDA/CSRS/NAPIAD Agreement No. 92-34050-8152, 259 pp.
36. Yvon-Lewis, S.A. and J.H. Butler. The potential effect of oceanic biological degradation on the lifetime of atmospheric CH₃Br. Geophysical Research Letters 24 (10): 1227-1230.

Approaches for the Prediction of Environmental Fate of Pesticides

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Abstract

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The need for predictive approaches for the evaluation of environmental exposure to pesticides is envisaged not only by the scientific community but also by administrative authorities. Several international regulations require the use of predictive approaches for preventive risk assessment. Multimedia compartmental models are, at present, the most effective tool to predict the environmental distribution and fate of organic chemicals. An overview is given of the practical possibilities of applying these kinds of models, at different space scale, from micro ecosystems to global pollution. Examples of application and experimental validation are described. Value and limitations of the approach and research needs will also be discussed.

Introduction

There are several reasons for supporting the unreplaceable role of predictive approaches for the evaluation of environmental exposure to potentially dangerous chemicals. From a practical point of view, environmental monitoring can be performed only *a posteriori*, after the emission of contaminants and, in extreme cases, after the occurrence of an environmental damage. Therefore monitoring could allow to plan recovery rather than preventive measures.

From a scientific point of view, the measurement of a given environmental concentration gives a picture of a punctual situation, in time and space, but does not give information about the environmental processes producing it.

The knowledge of the main features of the biogeochemical cycle allows the development of conceptual instruments capable to describe and predict distribution and fate patterns. On this basis, the occurrence of a chemical in the ecosystems and its trend in time can be reconstructed. Moreover, it is evident that predictive approaches represent the only possibility to plan suitable preventive measures against the risk.

For these reasons, the need for predictive approaches for the evaluation of environmental exposure to pesticides is envisaged not only by the scientific community but also by administrative authorities. Several international regulations require the use of predictive approaches for preventive risk assessment. For example, in the Directive of the European

Union 91/414, concerning the placing of plant protection products on the market (8), predictive models are proposed as a tool for the quantitative assessment of predicted environmental concentrations (PEC).

In the last few years, several predictive approaches have been developed at different levels of complexity and descriptive/predictive precision.

The Role of Molecular Properties

A first, very simple approach, rough but practically useful at least for preliminary screening evaluations, can derive from the quantification of the main molecular properties regulating environmental partitioning of a chemical. The properties needed and their environmental meanings are the following:

- Water solubility (S). It quantifies the affinity of a substance for the water compartment.
- Vapour pressure (VP). It indicates volatility and, therefore, the affinity for the air compartment, even if the latter is better quantified by the Henry's law constant.
- Henry's Law Constant (H). It could be generally expressed as the ratio between vapor pressure and water solubility ($H = VP/S$). In practice, H represents, but for a constant, a partition coefficient between air and water. Therefore H can be assumed as an index of the affinity for the air compartment.
- Octanol/water partition coefficient (Kow). It quantifies the lipophilicity of a substance and is therefore assumed