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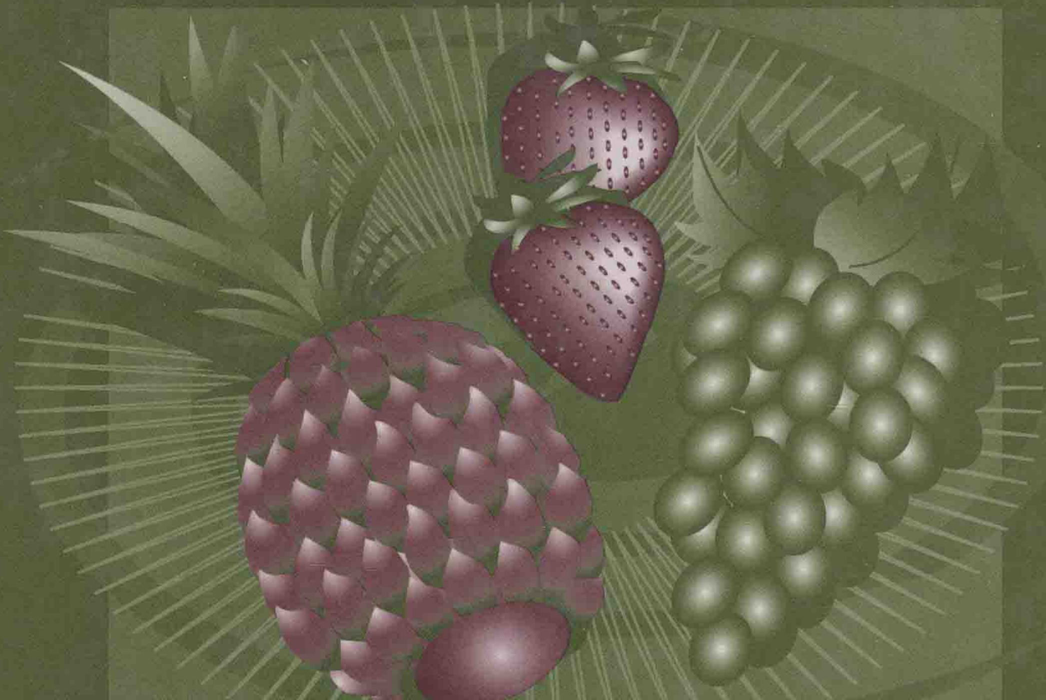
Fumigants

Environmental Fate, Exposure, and Analysis



EDITED BY

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ACS SYMPOSIUM SERIES **652**

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Fumigants: Environmental Fate, Exposure, and Analysis

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ACS Symposium Series

Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually "snapshots in time" of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

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Preface

FUMIGANTS ARE VITAL AGENTS in the production of many food crops, particularly the high-value crops such as strawberries and grapes, which are susceptible to nematodes and other soil-borne pests. They are also used, even required, for fumigating fruits, grains, and spices destined for export.

Fumigants are, however, mobile compounds in the environment and warrant exceptional safeguards in terms of application technology, minimizing worker exposure, and preventing movement to air and groundwater. This is a particular challenge because fumigants are volatile compounds and many are fairly soluble in water. They are also toxic chemicals and thus pose risks to applicators and field workers, and to a lesser extent, to those who live in the vicinity of fumigant operations.

In the past, society has banned agricultural chemicals that are too mobile and toxic to guarantee safety to people and the environment. The fumigant class has been hit hard in this regard. Dibromochloropropane (DBCP) and ethylene dibromide (EDB) have, for example, been banned because of a combination of mobility (groundwater contamination) and toxicity (potential carcinogenicity).

Of the remaining fumigants, virtually all (methyl bromide, 1,3-dichloropropene (Telone), and ethylene oxide) have been threatened with severe limitations, including outright bans. Fortunately, there may be time to learn more about them so that a ban is not necessary. To avoid a ban, we must be able to control exposures as well as air and groundwater contamination.

The focus of the symposium on which this volume is based was to share information on what is known about fumigants and how we can use this information to prevent exposure and adverse effects, while still enjoying the benefits fumigants afford in food production and pest control. The Symposium was presented at the 210th National Meeting of the American Chemical Society and was sponsored by the Division of Agrochemicals, in Chicago, Illinois, from August 20–25, 1996. The chapters in this book cover several fumigants and include information on their environmental fate, properties, emissions, downwind behavior and exposure, and analytical methods.

The Symposium organizers wish to thank the authors and the American Chemical Society for their time and dedication to this publication.

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Chapter 1

Health and Environmental Concerns Over the Use of Fumigants in Agriculture: The Case of Methyl Bromide

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With the discovery of oceans and soils as net sinks for methyl bromide (MeBr), a decrease in ozone depletion potential from 0.7 to about 0.45 and overall lifetime from 2.0 to between 0.8 and 1.0 yrs. have been estimated. Further, MeBr has tested negative as a carcinogen. Stringent fumigation rules, at least in the United States, have been effective in reducing exposure. This new information on MeBr weakens the argument for an outright ban of MeBr and suggests that, with better management practices, the chemical could continue to be used beneficially. MeBr is predominantly a naturally occurring compound and anthropogenic sources represent about 25% (+/-10%) of the total emissions.

Methyl bromide (MeBr) has been used as a fumigant since the 1940s with production peaking at 71,500 metric tons in 1992 *(1)*. After the loss of the effective fumigant ethylene dibromide in the early 1980's, MeBr began to be used more widely and became the fumigant of choice because of its effectiveness against a wide spectrum of pests including arthropods, nematodes, fungi, bacteria and weeds (see Chapter 2). Agriculture is the major consumer of synthetic MeBr, followed by structural use and the chemical industries. It is used in strawberry cultivation, and for vegetables such as tomatoes, peppers, and eggplants. Vineyards are fumigated with MeBr before replanting of new vines. It is used to fumigate the soil in fruit and nut orchards. Other important uses of MeBr include the production of tree seedlings for reforestation, and in the strawberry nursery industry to keep the young plants free from soil borne diseases.

Post harvest fumigation now depends mostly on MeBr. It is the primary fumigant recommended for use in the movement of susceptible commodities from a quarantined area containing an introduced pest. Recognizing this fact, the signatories to the Montreal Protocol exempted quarantine uses from regulation. MeBr production has been frozen at

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the 1991 levels and it is scheduled to be banned from usage on January 1, 2001, in the USA.

As the understanding of the role of chlorine and bromine in the destruction of ozone in the midlatitude lower stratosphere is improving, the anthropogenic sources of chlorine and bromine compounds are under scrutiny as contributors to the global ozone depletion problem. Chlorofluorocarbons (CFCs), for example, are now being replaced with hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) which are more reactive in the atmosphere and thus do not survive to the stratosphere for release of Cl atoms. Halons, a class of brominated organic compounds formerly used as fire retardant, are no longer produced. There are no other large uses of brominated organic compounds other than MeBr, so that MeBr is being specially scrutinized for its role in ozone loss in the midlatitude lower stratosphere. Because it has a fairly long atmospheric lifetime it is considered to be capable of diffusing into the stratosphere where it could undergo photodissociation to release bromine atoms which can then react with ozone. Thus MeBr has been identified as an ozone depleting substance *(2)*.

According to the U.S. Clean Air Act any compound having an ozone depleting potential (ODP) ≥ 0.2 is classified as an ozone depleting substance (ODS). The ODP of a compound is dependent on the amount emitted and its ability to release ozone depleting breakdown products following diffusion to the stratosphere and on the lifetime of the compound in the atmosphere. Based on somewhat incomplete scientific information, the ODP of MeBr was first estimated as 0.7 *(2)* placing it clearly in the ODS group. The Montreal Protocol and the subsequent Copenhagen Amendments and Adjustments relating to the phaseout of MeBr production and consumption were based on this incomplete knowledge. The Protocol recommends phaseout of MeBr by 2010 in industrialized countries, and a freeze in consumption by 2002 in developing countries. In the U.S., the Clean Air Act Amendment requires a phaseout of MeBr by 2001 because of the ODP. The estimation of the annual MeBr addition to the atmosphere, the overall lifetime of the molecule, the amount of ozone depletion caused exclusively by MeBr, and the general sense of environmental conservatism prevailing at the time were some of the other important factors that were responsible for this extreme measure. It was estimated that over 50% of MeBr produced for fumigation is emitted into the atmosphere which amounts to an annual addition of 3pptv or 51Gg of MeBr. This is based on broad estimates of emission factors for different areas of the world, with their diverse soil types and application practices. Hence these estimates of losses must be viewed with caution.

The overall lifetime of MeBr was estimated as 2.0 yrs. *(2)* based only on its reaction with OH radicals in the atmosphere. Oceanic, soil, and plant foliage sinks were not known and not addressed. The estimation that at current levels of MeBr emissions bromine would account for 5-10% of the total global ozone loss is, once again, a rough estimate since it is dependent on the rate of formation of HBr in the stratosphere about which there is a major uncertainty *(2)*. Although the science of MeBr in the environment was in a nascent state and unable to provide definitive answers to many questions, a sense of conservatism guided the recommendations for elimination of MeBr.

Since the Montreal Protocol first addressed these issues in 1992 and in its subsequent meetings (Copenhagen, 1994 and Vienna, 1995), significant new information has been uncovered which might support a re-evaluation of the phaseout of MeBr. This is especially important considering the huge economic losses that the phaseout could bring to a country's agricultural sector and economy at large *(3)*. New information regarding the sources, emissions, fate and transport, and sinks have lowered the estimated lifetime of MeBr in the atmosphere to between 0.8 yr. *(4)* and 1.0 yr. *(5)* and the ODP to 0.45. The focus of this chapter is therefore to provide an update on the issue of MeBr and its effect on ozone depletion, and to relate some of the experiences with MeBr to other fumigants.

Sources

MeBr has both natural and anthropogenic sources which complicates the estimation of global burden, lifetime and ODP. Adding to the complication is the presence of such sources as biomass burning which has both natural and anthropogenic origins.

Natural Sources

Biomass Burning: The WMO 1995 *(6)* report suggests a range of 10-50 Ggy^{-1} and recent work puts the best estimate at 20 Ggy^{-1}*(7)*. There is a large amount of uncertainty in this term because the proportion of MeBr emitted depends on the temperature of the flame and, to some degree, upon the composition and location of the vegetation. Global extrapolation of limited measurements increases the uncertainty of this estimate *(4)* even further. Estimating the definite amounts caused by each source and then quantifying the MeBr released from these separate sources have proven difficult.

Oceanic Source: Another source with much uncertainty is the ocean. Complication arises from the fact that the ocean is both a source and a sink. The WMO 1995 *(6)* report puts the source at 90 Ggy^{-1} with a possible range of 60-160 Ggy^{-1} based mainly upon the data of Khalil et al. *(8)* and the review of Singh and Kanakidou *(9)*. NOAA *(10)* places the oceanic source at 45 Ggy^{-1}. This subject is receiving much research interest and hence the source and sink parameters and resulting lifetime estimates are undergoing frequent revision. The current best estimate is 60 Ggy^{-1} with a probable range of 30-100 Ggy^{-1} *(5)*.

Anthropogenic Sources

Anthropogenic sources are primarily emissions from pre-plant soil, post-harvest quarantine and structural fumigations, and automobile emissions. Industrial production peaked in 1992 at 71,500 metric tons (71.5 Gg). Of this production 77% was used for pre-plant soil fumigation, 12% for post-harvest commodity fumigation and structural fumigation while 6% was used in chemical intermediates *(11)*.

Automobile Sources: Automobiles using leaded gasoline, mostly in developing countries, with ethylene dibromide as an additive emit small but measurable amounts of MeBr. The WMO 1995 *(6)* report cites two studies. One places the emissions between 0.5-1.5 Ggy^{-1} while the other places the emissions between 9-22 Ggy^{-1}, an order of magnitude higher than the first. Thus there is a large disagreement in extrapolations of these data and the emissions range from 0.5-22 Ggy^{-1}.

Post-harvest And Structural Fumigation: Emissions from post-harvest (See Chapter 14) and structural fumigations are well quantified. These emissions are placed at 20 Ggy^{-1} *(6)* which is approximately 25-30 % of the total MeBr production and constitutes 10-20% of the total anthropogenic emissions of MeBr to the atmosphere.

Pre-plant Soil Fumigations: The emission figures from pre-plant soil fumigations have been better defined in recent years although there are still uncertainties with respect to soil properties and application procedures in extrapolating the figures to the global scale (See Chapters 11-13). Emission estimates range widely depending mainly on the application procedure. For a tarped field the emission varies from 25 to 35% of the amount applied depending on the period of coverage *(12, 13)*, while for an untarped field the emission is as much as 90% of amount applied *(14)*. This source contributes between, 20-60 Ggy^{-1} of MeBr *(6)*. Chapter 10 describes some strategies for significantly reducing the emission source for MeBr, while Chapter 9 describes this as well for 1,3-dichloropropene.

Inter And Intra Phase Transport

Transport in Air: The major natural inputs of MeBr into the atmospheric compartment are oceanic and biomass burning while the major anthropogenic input is the emission from pre-plant soil fumigation. The major removal mechanisms are i) reaction with OH radicals and other chemical species, ii) photodissociation in the stratosphere, iii) flux into the oceans and, iv) uptake by soils and/or plants.

Transport In Water: The solubility of MeBr in water is between 16 and 18 g/L at 20°C. In soil water it is partially hydrolyzed to bromide ion. After fumigation the soil may be leached with water to prevent uptake of bromide ions by plants that may be planted after fumigation. It has been found that methyl bromide is able to diffuse through and be adsorbed by certain plastics (e.g., polyethylene). Thus drinking water pipes in the vicinity of fumigated fields could become contaminated within a few days of the use of MeBr *(11)*.

Transport In Soil: MeBr vapor has a density of 3.974 g/L at 20°C and thus is heavier than air. When injected into soil MeBr diffuses through the soil either by mass flow or molecular diffusion to depths of 60-240 cm *(15)*. Some MeBr hydrolyzes and some gets decomposed by microorganisms, but a major portion eventually dissipates into the atmosphere. The rate of MeBr degradation in soil is about 6-14% d^{-1} at 20°C *(16)*, and MeBr can be detected up to three weeks after fumigation, with the highest content being found in the upper 40 cm of soil layers and traces detectable to a depth of 80 cm *(17)*. Reversible sink processes such as sorption and dissolution, and irreversible sink processes such as reaction with the soil organic matter and hydrolysis that occur simultaneously during transport also affect the transport properties of the compound *(15)*. MeBr, in addition to being physically bound to the organic matter, is believed to methylate the carboxylic groups and the N- and S- containing groups of aminoacids and proteins in soil organic matter *(18)*. The sink (reversible and irreversible) capacity of a soil depends on its moisture and organic matter content. Chisholm and Koblitsky *(19)* found the sink capacities decreasing in the sequence peat, clay, and sand. In soils with high humic content the halflife of MeBr was 10 days, while in a less humic soil, it was 30 days, and in sand, about 100 days *(11)*. Reible *(20)* predicted that when soil organic carbon content was increased from 2 to 4% the MeBr emission rate would decrease from 45 to 37% following a tarped - 2 day, 25 cm deep - application. Gan et. al.*(21)* reaffirm the fact that soil organic mater content and moisture increase the sink capacities and decrease volatilization/emissions (See Chapters 10 and 11). In shallow top soils the major portion of MeBr dissipates into the atmosphere while simultaneously undergoing degradation as mentioned above. It is relatively persistent in the underlying strata where diffusion into the atmosphere is less likely. In such a situation, if low temperatures prevail, the water table is high, and the matrix is composed of a low density matter, then the potential for ground water contamination by MeBr is fairly high.

The irreversible sink processes produce significant amounts of bromide ion, which decreases to pre-fumigation levels in about one year. The highly mobile bromide ion is available for uptake by plants or can be leached by water *(22)* and contaminate groundwater.

Transformation / Sinks

MeBr undergoes transformations in various compartments of the environment (See Chapters 4-6). Most transformations result in the release of water soluble bromide anion while photolytic dissociation and reaction with hydroxyl radicals in the atmosphere yield bromine species, some of which later react with ozone and cause ozone depletion.

Geosphere

Hydrolysis: Methyl bromide hydrolyzes at neutral pH to methanol, bromide and hydrogen ion:

$$CH_3Br + H_2O \rightarrow CH_3OH + H^+ + Br^-$$

Hydrolysis rates under environmental conditions depend mainly on temperature and thus the half-lives vary from several hours to several days. The hydrolysis rates and half lives of MeBr at different temperatures are tabulated in Table 1. Recently Gan et al *(21)* have observed a similar dependence of the rate of hydrolysis on temperature. Moisture, as described earlier, enhances the sink/hydrolysis capacities of the soil.

Table 1. Hydrolysis rate constant (k) and half life of methyl bromide in water at different temperatures *(23)*

Temperature (°C)	Observed Rate Constant (s^{-1})	Half Life
17	1.07×10^{-7}	75.0 days
25	4.09×10^{-7} *(24)*	20.0 days
25	3.57×10^{-7}	21.3 days
35.7	1.65×10^{-6}	4.9 days
46.3	6.71×10^{-6}	1.2 days
100	1.28×10^{-3}	0.6 h