STATUS OF ALTERNATIVES FOR METHYL BROMIDE IN THE UNITED STATES

Judy A. Johnson, Spencer S. Walse and James S. Gerik, San Joaquin Valley Agricultural Sciences Center, Parlier, CA, USA outline the current situation regarding possible replacements for methyl bromide in US agriculture.
Send correspondence to: Judy Johnson, USDA-ARS, 9611 S. Riverbend Ave., Parlier, CA, 93648, USA;
Tel: +1 (559) 596-2768; Fax: +1 (559) 596-2726; E-mail: judy.johnson@ars.usda.gov

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Methyl bromide (MeBr, CH_3Br) is used in the agricultural sector as a broad-spectrum biocidal fumigant for soils, commodities, wood packing materials or structures, targeting pest insects, nematodes, weeds, pathogens and rodents. MeBr was identified as a chemical that contributes to the depletion of stratospheric ozone, and its production and use are subject to regulation under the US Clean Air Act. As one of the original signatories of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer, the United States ratified the Protocol in 1988. Amendments to the Clean Air Act were enacted in 1990 to include Title VI on Stratospheric Ozone Protection to ensure that the United States would satisfy its obligations under the Protocol. The United States committed to a gradual reduction of MeBr use, leading to a near complete ban on January 1, 2005. The Montreal Protocol and the US Clean Air Act allow yearly requests for Critical Use Exemptions (CUEs); Quarantine and Preshipment (QPS) applications as well as emergency uses are also exempt from the ban.

Use of MeBr in the United States

Prior to the phase-out of MeBr, the United States used roughly 27,000 metric tons (MT) annually (Ragsdale & Vick 2001). Of this about 75% was used for soil fumigation, 11% for commodity treatments, and 6% for structural fumigation, with the remainder used as feedstock in industrial chemical production. The Montreal Protocol set 1991 consumption levels as a baseline for subsequent phase-out schedules. For developed countries, consumption was frozen at 1991 levels until 1998, and then reduced incrementally until 100% reduction, with some exceptions, was reached by a target date of 2005. Within the United States, the baseline level was about 25,500 MT, not including QPS applications. In keeping with the schedule set by the Montreal Protocol, MeBr usage in the US has declined significantly (Fig. 1).

Since 2005, only those non-QPS applications approved as CUEs are allowed (Table 1, USEPA 2011a), with other applications being made from stocks of MeBr existing before the phase-out. More than 90% of the allowance goes to pre-plant soil fumigations, with strawberries alone taking up 30–66%. Postharvest uses take less than 10% of the total allowance, with mills and processors receiving 71–92% of this. The

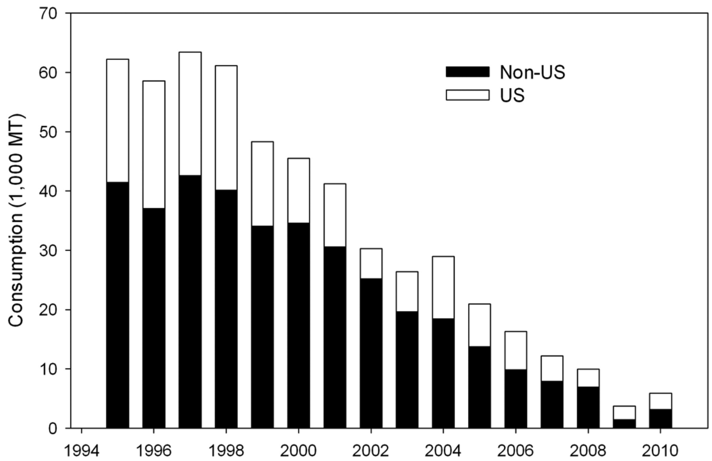

Figure 1. World and United States consumption of methyl bromide 1995–2010. QPS applications are not included.

Table 1. United States Critical Use Exemptions for Methyl Bromide (MT)*

Year	**2009**	**2010**	**2011**	**2012**
Postharvest				
Mills and processors	291.4	173.0	135.3	74.5
NPMA food processing structures	54.6	37.8	17.4	0.2
Commodities	45.6	19.2	5.0	2.4
Dried cured pork	19.0	4.5	3.7	3.7
Total	410.6	234.5	161.4	80.9
Preplant				
Strawberries – field	1,269.3	1,007.5	812.7	678.0
Tomatoes – field	1,003.9	737.6	292.8	54.4
Peppers – field	549.0	463.3	206.2	28.4
Cucurbits	407.1	303.0	195.7	59.5
Orchard replant	292.8	215.8	183.2	18.3
Forest nursery seedlings	122.1	117.8	93.5	34.2
Ornamentals	107.1	84.6	64.3	48.2
Eggplant – field	48.7	32.8	19.7	6.9
Nursery stock – fruit, nut, rose	25.3	17.4	8.0	1.6
Sweet potato slips	18.1	14.5	11.6	8.7
Strawberry runners	7.9	4.7	6.0	3.8
Total	3,851.3	2,998.9	1,893.8	942.0
Grand Total	4,262.0	3,233.5	2,055.2	1,022.8

*Values are those exemptions granted by the Parties to the Montreal Protocol

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Table 2. Quarantine Use of Methyl Bromide in the United States.

Total MB Usage (MT)	2005	2006	2007	2008	2009	2010
Export*	101.3	113.8	113.8	87.1	71.5	56.5
Import	213.5	245.1	233.7	248.9	251.1	252.4
Total	314.8	358.9	347.5	336.0	322.6	309.0
Commodity Type						
Fresh Fruits and Vegetables	190.8	216.7	210.1	215.8	224.7	210.3
Propagative Plant Material	1.0	0.9	0.5	0.8	0.8	0.6
Cut Flowers and Greenery	2.2	4.7	4.9	5.3	5.5	5.0
Other**	120.8	136.5	132.0	114.2	91.5	93.1
Total	314.8	358.9	347.5	336.0	322.6	309.0
Country of Origin (Import only)						
Chile	148.7	166.1	154.5	149.4	164.9	150.6
Peru	20.9	25.8	32.3	37.6	36.6	34.3
Costa Rica	9.4	11.0	12.6	16.3	9.6	10.9
Italy	9.1	7.1	6.8	10.1	8.5	11.2
China	4.5	9.3	9.7	9.8	7.7	7.8
All Others	20.9	25.8	17.8	25.8	23.8	25.8
Total	213.5	245.1	233.7	248.9	251.1	240.6

* Data from APHIS methyl bromide use database, includes only APHIS supervised treatments; amounts supervised at the state and county level are not included in the table
** Includes tile, steel, and logs

amount of MeBr used for quarantine is difficult to track, as there is no single source for these data (Schneider & Vick 2002). Amounts used under USDA Animal and Plant Health Inspection Service (APHIS) supervision are given in Table 2, but additional MeBr is used by industry and supervised by state and local regulators with few records taken. Imports require roughly twice that for exports, and produce from Chile receives the bulk used for imports. Among the commodities treated, grapes receive the most MeBr used for quarantine treatments, followed by logs. Additional MeBr is used for preshipment treatments, also exempt under the Protocol.

MeBr Alternatives for Preplant Applications

Mixtures of MeBr and chloropicrin have traditionally been used before planting to control soil-borne pathogens, weeds and nematodes in several high value crops (Martin 2003). Although MeBr was scheduled to be phased out by 2005, it continues to be used before the planting of several crops. CUEs for US pre-plant applications have been granted by the Parties to the Montreal Protocol every year since 2005 and the US Environmental Protection Agency (EPA) continues to nominate CUEs on behalf of growers in the U. S. For the year 2011, the proposed amount of MeBr allocated for pre-plant use was 1,382,206 kg, which is 8.1% of the US 1991 MeBr consumption baseline (USEPA 2011c). CUEs were granted for 11 categories of crops listed in Table 1. In addition to the CUEs, MeBr is also being used on these and other crops from stocks of MeBr existing before the phase out. Estimates of the amounts used are available for some of the commodities listed from the National Agricultural Statistics Service (NASS) (USDA 2011), and better data are available for use in California from the Department of Pesticide Regulation (CDPR 2011). For 2010, 343,868 kg was used on California nursery crops, 87,815 kg was used nation-wide on ornamentals, 109,633 kg was used on peppers in the southern US, 452,957 kg was used nation-wide on strawberry, 22,277 kg was used on strawberry nurseries, and 266,848 kg was use for tomato production in the southern US The NASS survey data described above are not consistent with CDPR records, which lists use in California on strawberry alone as 1,140,367 kg. Other pre-plant uses reported by the CDPR include apple, asparagus, blackberry, blueberry, celery, chestnut, grain, grass seed, lemon, lettuce, pecan, raspberry, rice, rye, turf, and wheat. It is likely that many of the uses reported for some of the above low value crops were for seed production and not crop production. The total amount of MeBr used for preplant applications in California in 2009 was 2,523,139 kg. US EPA is still making CUEs nominations and is currently seeking applications of CUEs for the 2014 calendar year.

Several alternative fumigants to MeBr had been registered in the US before the phase-out. These include chloropicrin (Pic), 1,3-dichloropropene (1,3-D), and methyl isothiocyanate generators which include metam sodium, metam potassium and dazomet (Martin 2003). Two new fumigants have been registered recently, iodomethane and dimethyl disulfide (DMDS) (USEPA 2011b), though these have not been registered in all states. These alternative fumigants are generally used in various combinations with one another (Martin 2003).

An economic analysis of alternative treatments for tomato production was conducted over a six year period in North Carolina (Sydorovych *et al.* 2008). The authors concluded that Pic, 1,3-D plus Pic and metam sodium provided a better economical return than the MeBr standard. Other combinations including iodomethane resulted in economic losses when compared to the standard.

Researchers in Florida studied the efficacy of various alternative combinations for the control of nematodes and nutsedge (*Cyperus* spp.) in bell pepper production (Gilreath *et al.* 2005). They reported that metam sodium plus Pic, and

Figure 2. Yellow calla lilies being grown in soil fumigated with a mixture of 1, 3-dichloropropene and chloropicrin prior to planting near Moss Landing California.

two formulations of 1,3-dichloropropene plus Pic provided equal or better control of *Meloidogyne* spp. compared with the MeBr standard, but control of nutsedge was not as good as the standard. Also in Florida, researchers studied alternative treatments for strawberry production (Gilreath *et al.* 2008). 1,3-D plus chloropicrin and dazomet, 1,3-D plus Pic, Pic and metam sodium, and fosthiazate (an OP nematicide) and Pic proved to be as valuable as the grower-standard MeBr plus Pic on strawberry plant vigor, sting nematode control, and early and total marketable yields. In California, researchers found that an emulsifiable formulation of 1,3-D and Pic applied through irrigation water consistently resulted in yields of 95% to 110% relative to standard MeBr plus Pic treatment (Ajwa & Trout 2004).

The above reports and others show that these MeBr alternatives can be efficacious in the production of many crops, and the acceptance of them by growers is increasing. Perhaps the segment which has most embraced the use of alternative fumigants is the California strawberry producers. In 2009, there were 1,140,367 kg of 1,3-D applied for strawberry production in 325 applications to 4183 hectares (CDPR 2011); this represents approximately 43% of the fumigated strawberry ground. Almost all of the 1,3-D applied to strawberry is InLine® , which is formulated as 60.8% 1,3-D and 33.3% Pic that is emulsified and injected through drip irrigation tapes on raised beds under plastic film. During the same year, California flower growers used 25,216 kg of MeBr on area covering 104 hectares (both inside and outdoors), while they used 6,546 kg of the alternative, metam sodium, on 59 hectares; this represents 36% of the fumigated area. California walnut growers planted 6139 hectares in 2009 of which 20% was fumigated with 1,3-D and the rest with MeBr, while only 18% of 4270 hectares of almond ground was fumigated with the alternative. It is likely that growers of perennial crops prefer the consistency of MeBr and are unwilling to risk such a large investment on an unfamiliar alternative.

Other non-fumigant alternatives to MeBr are being tested and used in some cases. Non-chemical methods include host resistance, organic amendments, crop rotation, soil solarization, and cultural practices (Chellemi 2002). These methods are suitable for an integrated pest management approach where the grower relies on multiple methods of pest control to achieve the desired pest control result, as opposed to the broad spectrum of activity and consistency of MeBr fumigation. These approaches may also be compatible with organic production where synthetic chemicals are not allowed to be used.

MeBr alternatives for postharvest, structural and QPS applications

Non-pre-plant uses of MeBr are for the purpose of controlling pest populations in commodities, processing facilities, and marketing channels and are categorized based largely on regulatory distinction. MeBr predominates in gaseous form at normal atmospheric temperatures and pressures and is able to diffuse homogeneously within the headspace of enclosures, penetrating into the pore spaces of treated commodities. These features enable a toxicant to be delivered to pests with uniform exposure, and as such, are highly coveted characteristics for any chemical alternative to methyl bromide, particularly those intended for postharvest, structural, and QPS applications.

Postharvest MeBr uses involve the direct treatment of commodities in marketing channels that are not subject to domestic and international quarantine requirements. An estimated 9–20% of the world's food supply each year is destroyed or contaminated by pests after harvest (Pimentel 1991), which requires food handlers and processors to implement pest management programs tailored to commodity-specific scenarios. Fumigation plays a critical role when pest control is required within hours or days after harvest and/or when processed products are amenable to infestation by storage pests. At the present time, phosphine and sulfuryl fluoride are registered fumigants being considered as alternatives to MeBr for postharvest treatment of insect pests as related to CUE requests from US industries. Other alternative fumigants, such as ammonia, ozone, methyl iodide, ethane dinitrile, and carbonyl sulfide have proven effective in certain situations and work continues to develop efficacy data, industry acceptance, and registrations for their use on foodstuffs.

Postharvest use of sulfuryl fluoride (SF), which has nearly the same infrastructural requirements as MeBr, has increased consistently since its registration in 2004. Numerous studies report that for post embryonic life stages of postharvest insect pests, SF is generally more toxic than MeBr for a given species (Kenaga 1957, Thoms & Scheffrahn 1994). However, insect eggs are relatively more tolerant to SF than to MeBr, often requiring many times the dosage required to control adults of the same species (UNEP 2011, Walse *et al.* 2009). Practical strategies for overcoming the tolerance of eggs to sulfuryl fluoride include multiple fumigations to allow for egg hatch or extending SF exposures beyond the duration of the egg stage. However, SF fumigations in the US are restricted both by label requirements that specify a maximum dose (128 mg/L) and exposures (1500 mgh/L) as well as the resultant maximum residue levels (MRLs) on treated commodities. CUE requests from the dried fruit and nut sector continue because

SF exposures required to control eggs of target pest species exceed regulatory allowances, particularly when fumigations must be conducted <20°C. The technical and regulatory limitations of SF are exacerbated when processors need to treat large amounts of product rapidly to meet specific market demands, such as California walnuts and dates intended for holiday markets. Ongoing research at ARS addresses these challenges by pairing SF with a potent ovicide. Unfortunately, due to concerns over fluoride residues in treated foods, the EPA has proposed withdrawing SF tolerances and gradually phasing out commodity treatments. Obviously, this regulatory action, should it occur, would make SF unavailable as a MeBr alternative for US commodity treatments.

Phosphine, in its various commercial forms (pellets, generators, cylinders), has been used in a postharvest capacity for decades with new application technologies that serve to reduce fire hazard (a spontaneous ignition with atmospheric oxygen occurs at phosphine levels >18,000 ppm) and decrease the exposure time required for insecticidal efficacy. When applied at recommended doses (500–2000 ppm), complete mortality of all insect life-stages is species specific and typically requires exposures of 2–7 days, as compared to 2–3 hours needed for MeBr. From both a technical and economic perspective, phosphine use is not without limitations, due to logistically challenging time and volume requirements as well as corrosion issues that are prohibitive to many US industries. Phosphine-resistance in target insects has been well documented (Pimentel *et al.* 2008), occurring when the correct doses or other treatment parameters are sub-optimal. The recently developed Horn-Diluphos System (HDS) safely and rapidly delivers 100% phosphine, achieving levels ~ 10,000 ppm within hours. With the HDS, the utilization of phosphine as a MeBr alternative is expected to increase, particularly for fresh fruits and vegetables that can be successfully treated under commercial cold-storage conditions (Horn *et al.* 2005). Research is currently underway at ARS to engineer efficacious and rapid phosphine fumigations through the integration of physical and chemical approaches, such as the use of vacuum or combining phosphine with other physiologically active gases. The goal of this research is to provide a phosphine alternative to those industries that require hydrocooling and cold-storage of fruit to combat spoilage, but must market fruit within hours or a day after harvest.

Recent advances in the formulation and delivery of pesticides as aerosols, which are actually fine mists of liquid material, have expanded the scope of chemicals being considered as alternatives to MeBr in many postharvest scenarios where surface pests are targeted. For example, new delivery technologies allow for a more efficacious use at normal atmospheric temperatures and pressures of propylene oxide and ethyl formate, insecticides that have shown potential against some pests of tree nuts, grains, fresh fruit, and dried fruit (Navarro *et al*. 2004, Ryan & Bishop 2003). Further regulatory acceptance and guidelines for use of pesticides as aerosols on foodstuffs in the US are likely in the near future, given the continued interest by industry and the history of chemical registration by EPA and the US Food and Drug Administration (FDA).

Non-chemical alternatives suggested for those products listed under the postharvest commodity CUE (walnuts, dried fruit and fresh dates) include various heat treatments, controlled atmosphere, cold treatments, and irradiation. Since these applications are often for time-sensitive markets, alternatives that require longer treatment times, such as controlled atmospheres or cold, are not feasible. Research using commercial radio frequency heating units for walnuts shows promise (Wang *et al.* 2007a, b), but industry is concerned that the treatment would reduce shelf-life.

Structural MeBr use, categorized as the treatment of buildings and various non-edible materials, includes the disinfestation of mills and food processing facilities and is the largest requested postharvest CUE (Table 1). SF appeared to be the best candidate to replace MeBr for this application, but the ongoing re-evaluation of SF by the US EPA may severely restrict its use in food plants. Phosphine use as a structural fumigant continues and is expected to expand in scenarios where protections against corrosion are implemented. Taking precaution against corrosion is often expensive and technically difficult, particularly when facilities contain considerable amounts of metal with a potential for damage (Bond et al. 1984). In addition to alternative fumigants, heat is often suggested for disinfestation of mills, processing plants and empty storage silos. Some facilities have had good results with regular heat disinfestation treatments, either using built-in steam systems or portable heaters brought in by contracted heat treatment companies. The success of these treatments is dependent upon obtaining temperatures of about 50°C throughout the facilities. As product residues have been shown to insulate pest insects from the heat, sanitation of the facilities before treatment is very important (Brijwani *et al.* 2010, Opit *et al.* 2011).

QPS uses of MeBr refer to those required by regulatory entities to ensure pest-free commodities. In the US, these applications enhance distribution and safety of commodities, promote and retain access of US commodities to domestic and foreign markets, and protect the US and its trading partners from the threat posed by pests. As the use of MeBr declines, QPS applications constitute a growing percentage of the total, and there is pressure to end the exemption under the Montreal Protocol. MeBr alternatives for QPS use must be consistent with international phytosanitary standards (IPPC 2009), generally requiring dose response data and confirmatory treatments that kill sufficient numbers of insects to provide the required quarantine security (usually probit 9 or 99.9968% mortality) for each pest of quarantine concern (Couey & Chew 1986). The elimination of MeBr for QPS applications would require specific analyses of the technical efficacy and economic feasibility for each applied scenario and alternative. Alternatives acceptable for one particular quarantine pest and commodity may not necessarily be applied to other applications without sufficient data to support the regulatory allowance.

Although SF shows great promise as a QPS alternative, the possible withdrawal of tolerance allowances may make SF unavailable for commodity treatments. The HDS method of phosphine application for fresh commodities may eventually replace many QPS MeBr uses, but data for many specific pests are still lacking. A variety of non-chemical alternatives have been approved as commodity quarantine treatments (APHIS 2011). These include hot water immersion, steam vapor heat, forced hot air, cold, irradiation, systems approaches and Controlled Atmosphere Temperature Treatment System (CATTS). Gradual adoption of these alternatives has helped reduce the use of MeBr for quarantine treatments, but issues of cost, product quality, and the acceptance by importing countries must be overcome. Of particular concern is the treatment of domestic products or imports requiring treatment upon arrival at port and inspection facilities. Because these QPS fumigations are generally time-sensitive and involve large amounts of product, most MeBr alternatives are not acceptable. Preventing the release of MeBr into the atmosphere following chamber fumigations may extend QPS use. Currently, there are several commercially available recapture systems, and research continues to develop commercially viable processes to contain, destroy or reuse MeBr and alternative fumigants after use to lessen agricultural impacts on air-quality.

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Judy Johnson is a research entomologist with the Crop Protection and Quality Research Unit, San Joaquin Valley Agricultural Sciences Center, Agricultural Research Service, USDA. She received her Baccalaureate and Ph.D. from the University of California. Her research concentrates on non-chemical controls for postharvest insects of fresh and dried fruits, tree nuts and beans. Of particular interest is the development of non-chemical alternatives to methyl bromide, including radio frequency treatments, low pressure treatments, and cold storage.

Spencer Walse is a Postharvest Specialist in the Crop Protection and Quality Research Unit, San Joaquin Valley Agricultural Sciences Center, Agricultural Research Service, USDA. Baccalaureate and Ph.D. degrees were obtained in chemistry at Univ. of Illinois at Urbana-Champaign and Univ. of South Carolina, respectively. His research is linked to the development of efficient postharvest technologies to sustain and enhance production and distribution of US – grown crops, promote and retain access to domestic and foreign markets, and protect the US and trading partners from the agricultural, ecological and economic threat posed by quarantine pests. The expected results of this research are chemical and non-chemical alternatives to methyl bromide, more efficient and environmentally benign use of fumigants to solve postharvest infestation and residue-related problems, more efficacious and safe techniques for fumigation, and production strategies integrated to reduce demands on postharvest treatment.

James Gerik is a research plant pathologist with the USDA – ARS in the Water Management Research Unit at the San Joaquin Valley Agricultural Sciences Center in Parlier, CA. He received his B.S and M.S. degrees from Texas A&M University, and his Ph.D. degree in Plant Pathology from the University of California – Berkeley. For the past ten years he has been a member of a team of scientist with the Water Management Unit conducting research on alternatives to methyl bromide for pre-plant soil fumigation. His work focuses on control of soil-borne fungal plant pathogens. Formerly he was a Plant Pathologist with Holly Sugar Corporation, and also with the USDA-ARS Sugarbeet Production Unit in Salinas, CA.

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- The benefits of plant breeding
- IP and saved seed in Europe
- Why are there not more GM crops?
- The Waste Directive
- Non-target or secondary effects of fungicides
- Fungicide resistance in Brazil
- Insecticide discovery in the post-genomic era
- The SCARDA programme and its impact on African agriculture
- Opportunities for non-food crops in today's farming systems
- Controlling potato cyst nematode in potato crops with a fungus
- Pesticide container disposal from US and International perspectives
- Counterfeiting and other illegal PPPs
- The abuse of the parallel trade rules for the supply and distribution of illegal/unregistered PPPs across Europe
- Insecticide Toxicology with particular reference to cotton ecosystems
- The changing face of farm economics in Europe
- Opportunities and Initiatives to minimise children's exposures to pesticides
- Economics of insect pathogens used for insect management