Methyl Bromide Alternatives – Meeting the Deadlines

Status of Chemical Alternatives to Methyl Bromide
for Pre-Plant Fumigation of Soil

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ABSTRACT

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None of the chemical alternatives currently registered and available has the full spectrum of activity and versatility of methyl bromide as a pre-plant soil fumigant. Chloropicrin and 1,3-dichloropropene (Telone) can provide significant control of many plant pathogens in soil and growth stimulation in annual crops. These compounds, however, provide limited control of weeds or other residual plant materials in soil of concern in nursery production systems, and some perennial replant diseases. Methyl isothiocyanate generators such as metam sodium have broad biocidal activity in soil, but are more difficult to apply effectively. In

most soil applications, the available alternatives are likely to be used in combinations, either as mixtures (e.g., 1,3-dichloropropene and chloropicrin) or sequentially (e.g., chloropicrin followed by metam sodium). They may also be supplemented with other more specific pesticides and cultural controls. Among the alternatives currently under active development but not yet available, methyl iodide and propargyl bromide probably have activity that most closely parallels that of methyl bromide in soil. However, all of the chemical alternatives to methyl bromide will be subject to continuing review and more regulation. Furthermore, we do not know the actual prospects for registration of the new fumigants currently under development and there is a risk that registered fumigants will not be available for large-scale use in soil indefinitely.

Methyl bromide has been used as a pre-plant soil fumigant for over 40 years. It has activity in soil against a wide spectrum of plant pathogens and pests, including fungi, nematodes, insects, mites, rodents, weeds, and some bacteria. In addition, methyl bromide is sufficiently volatile to penetrate soils for some distance from the points of application. Although methyl bromide is acutely toxic, methods of soil fumigation with methyl bromide have evolved to meet current registration and safety requirements. In agricultural practice, it is versatile, highly effective, and relatively easy to use. Approximately 20,000 metric tons are applied annually to soils in the United States, making it one of the most used pesticides in the country (23).

The states with the highest use of methyl bromide in soil are California and Florida, and the crops with the largest use in soil include tomatoes, strawberries, peppers, ornamentals, nurseries, tobacco, grapes, and melons (23). Most of the methyl bromide use is in high-input, high-value horticultural production systems in which the expense of fumigation is a small part of the whole and returns are potentially large. Because of the input costs, however, the risks of large monetary losses in these systems without fumigation are high. Furthermore, much of the land involved is of relatively high value and requires continuous production of high-value crops to make farming profitable. Where certain high-value crops such as strawberries and tomatoes are replanted on the same ground, pre-plant fumigation of soil with methyl bromide gives the largest benefits (19,30). While certain annual cropping systems are the largest users on an annual basis, pre-plant fumigation of soil with methyl bromide is also important to the control of replant diseases in perennial crops and for nursery propagation of

pathogen-free, quality planting materials of many kinds. The extent to which methyl bromide has been used in soil and the predicted losses following its pending phase-out show the importance of this pesticide to U.S. agriculture (3).

The process leading to the phase-out of methyl bromide in the United States was initiated in 1993 when the U.S. Environmental Protection Agency (EPA) officially determined that methyl bromide is a Class I Stratospheric Ozone Depleting Substance. Effective 1 January 1994, domestic production was capped at 1991 levels and methyl bromide use was scheduled to be eliminated by 2001 under provisions of the U.S. Clean Air Act (23). Regulations in the United States have since been changed to conform with the current provisions of the Montreal Protocol for the international reductions and phase-out of methyl bromide in developed countries, i.e., 25, 50, 70, and 100% reductions (relative to 1991) in 1999, 2001, 2003, and 2005, respectively (2). For developing countries, the reductions are more gradual and the phase-out is delayed until 2015. While the Montreal Protocol allows for some critical and quarantine use exemptions after 2005, the circumstances under which methyl bromide use in soil would be allowed are likely to be highly restricted (2). With a continued demand for methyl bromide and reduced supply, growers will soon not be able to obtain sufficient amounts of methyl bromide to meet previous needs. Therefore, there is a pressing need for effective alternatives to methyl bromide fumigation of soil. Unfortunately, nonchemical alternatives are not sufficiently developed or effective to meet current needs and growers will be turning to one or more of the known chemical alternatives to methyl bromide for fumigation of soil for the near future. This has already begun, for example, in Australia where chloropicrin use has increased as methyl bromide use declined in recent years (22). This review will emphasize those chemical alternatives for which there is sufficient information to suggest that they will be effective in soil and possibly available for agricultural use in the foreseeable future. Further-

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more, the focus here is on chemical alternatives to methyl bromide under investigation for strawberry production in California. Brief reviews of alternatives in other regions or other crops can be found elsewhere (16,22).

Strawberry cultivation in California has evolved over the last 40 years into a highly productive system that relies heavily on soil fumigation with methyl bromide (30). Although a variety of crop production systems have relied on methyl bromide for soil fumigation (23), in recent years, there has been more research on the alternatives to methyl bromide for strawberry than for any other crop production system. Although specific pests and pathogens targeted by soil fumigation vary between cropping systems and locations, the alternative fumigants that are found to work for strawberry production are also likely to have activity and applications in other production systems. Since about 1965, well over 90% of the land used for strawberry production in California has been fumigated with mixtures of methyl bromide and chloropicrin before each crop is planted, both for fruit production and for runner plant production in nurseries (30). The resulting high level of control of soilborne pathogens has allowed breeders to concentrate on developing cultivars with very high yield potential and berry quality, and has allowed horticulturists to further optimize California's annual production system (30,37). As a result, average berry yields have increased from 11 to 13 tons/ha in the era before fumigation to over 45 tons/ha in more recent years (30). California now produces roughly 80% of the U.S. fresh market strawberries and about 20% of the total worldwide. In 1999, strawberries were produced on over 9,700 ha and had a farm gate value over \$800 million. In addition, there is a large nursery industry producing several hundred million runner plants each year, many of which are exported. Soil fumigation remains central to this production system. A recent summary analysis of 45 studies, in which strawberry yields in California were compared with and without standard methyl bromide-chloropicrin fumigation of soil, showed that on average fumigation increased yield 94% (25).

Benefits of soil fumigation. Soil fumigation was first developed for strawberries in California because of a pressing need to control *Verticillium* wilt and weeds (30,31). Similar to other cropping systems, the advantages of soil fumigation with methyl bromide and chloropicrin mixtures for control of other soilborne pathogens of strawberry, including important *Phytophthora* spp. and nematodes, soon became apparent (23,29,30). In addition, soil fumigation generally increases root health, growth, and fruit yields in strawberry even when major pathogens are not present in soil (30,37). Although the microbiology underlying this general

growth response has been researched extensively (29), it has remained a fertile area of investigation. The growth response has been attributed in part to a temporary inhibition of nitrification and increased ammonia-N in soil (22,29,30), but other shifts in microbiology are surely important. Soil fumigation with mixtures of methyl bromide and chloropicrin reduces the incidence of *Pythium*, *Cylindrocarpon*, and binucleate *Rhizoctonia* spp. damaging to strawberry roots (17,18,30,32,34). Endomycorrhizae are reported to benefit strawberry (6), but they are also reduced following fumigation (J. Hao and J. M. Duniway, unpublished data). Although a reduction of pathogens in soil is a major benefit of fumigation, it is important to note that fumigation with methyl bromide and chloropicrin does not sterilize soil (29). For example, significant populations of bacteria survive fumigation and *Pseudomonas* spp. rapidly recolonize fumigated soils; some of these colonize strawberry roots in high numbers (33). Individual isolates of *Pseudomonas fluorescens*, *Pseudomonas putida*, and *Pseudomonas chlororaphis* from strawberry roots growing in fumigated soils increase the growth of strawberry significantly in natural soils in greenhouse experiments (33). Therefore, beneficial root colonizing bacteria may contribute to the favorable response of strawberry to soil fumigation. Whatever the underlying mechanisms turn out to be, the lack of economic yields in strawberry without fumigation is in part a replant problem. A survey of fumigation trials in California suggests that the benefits of soil fumigation on strawberry increased over the first 3 years of consecutive strawberry culture on the same ground (25). More specifically, when ground with no history of strawberry culture was first planted with strawberry for several consecutive years with and without annual fumigation of the same plots, the beneficial effects of fumigation on yield increased with years of repeated strawberry (Fig. 1) (J. M. Duniway, unpublished data). Unfortunately, because of high land costs and the need for high potential returns each year, many strawberry growers in California are forced to replant strawberries in the same fields yearly without rotation.

Chemical alternatives to methyl bromide. Table 1 lists most of the chemicals that have been discussed recently as possible alternatives to methyl bromide for soil fumigation (2). A majority of these chemicals were considered to be potential fumigants as soil fumigation technology evolved about 40 years ago, but methyl bromide rapidly became the preferred fumigant (29). While the list of possible alternatives seems long, sufficient information on activity in soil is available only for a minority of the chemicals listed, and still fewer are registered pesticides and available for agricultural use in the United States. Chemical alternatives that are available and that have known broad-spectrum activities in soil are chloropicrin, 1,3-dichloropropene (1,3-D), and the methyl isothiocyanate (MITC) generators, metam sodium and dazomet. Each may be used individually, but they are more likely to be used as mixtures (e.g., 1,3-D and chloropicrin) or in

Fig. 1. Yield of fresh market strawberries in nonfumigated soil as a percentage of the yield obtained in fumigated soil, plotted as a function of years of consecutive strawberry cultivation on the same soil. Three replicate beds were either fumigated with 364 kg/ha of 67% methyl bromide and 33% chloropicrin or not fumigated each year and planted with cv. Selva strawberry. The plots were located in a field near Watsonville, CA, with no history of strawberry cultivation for the previous 12 years.

TABLE 1. Chemical alternatives to methyl bromide for soil treatment

Currently available	Requiring further development	
	MBTOC ^a	Additions ^b
Chloropicrin	Methyl iodide	Other halogenated hydrocarbons
1,3-Dichloropropene	Propargyl bromide	Propylene oxide
Methyl isothiocyanate	Ozone	Sulfur dioxide
Generators	Formaldehyde	Peroxyacetic acid
Metam sodium	Sodium tetrathiocarbonate	Acrolein (2-propenal)
Dazomet	Carbon disulfide	Others to be developed
	Anhydrous ammonia	
	Inorganic azides	
	Natural compounds	

^a Alternatives considered by the 1998 report of the Methyl Bromide Technical Options Committee, United Nations Environmental Programme (2).

^b Alternatives added by J. M. Duniway.

sequential applications (e.g., chloropicrin followed by metam sodium). Fortunately, improved methods of application for these chemicals to soil are evolving at this time (1,36). While the available alternatives do not cause depletion of stratospheric ozone, relative to methyl bromide, they all have limitations in activity or versatility as soil fumigants. Among the chemical alternatives that are not registered, methyl iodide and propargyl bromide stand out for having good information on their level and broad spectrum of activity in soil. They are also not sufficiently stable in the atmosphere to cause significant stratospheric ozone depletion. The other chemical alternatives listed as requiring further development have either insufficient activity or feasibility for soil fumigation, or too little is known about them to suggest they might actually become a useful and registered replacements for methyl bromide. These, and other chemicals that may yet surface as prospective alternative fumigants in soil, are not likely to become available for general use for several years and, therefore, are not reviewed further here. In addition, a variety of more specific pesticides that target certain fungi, bacteria, nematodes, insects, or weeds might be used to supplement soil treatments with one or more of the chemical alternatives listed. These more specific pesticides are also not reviewed here, the concentration being on chemical fumigants with broad-spectrum activity in soil that might be available in the next few years.

Chloropicrin (trichloronitromethane). The early use and development of chloropicrin as a soil fumigant is reviewed elsewhere (19,29,30). Chloropicrin was first used for strawberry culture in California to control *Verticillium* wilt and it has strong fungicidal activities in soil (29–31). Chloropicrin also has beneficial nematocidal activity, but is much less nematocidal than methyl bromide or 1,3-D (13); it also has somewhat less activity on dormant weeds and seeds in soil. In the 1960s, the use of chloropicrin alone as a soil fumigant in strawberry production was rapidly replaced by mixtures of chloropicrin with methyl bromide. This occurred because the mixture has a broader spectrum of activity (e.g., including weeds) and because of the synergistic activity of methyl bromide and chloropicrin on control of *Verticillium dahliae* in soil (29–31). Various mixtures of methyl bromide with chloropicrin (e.g., 67/33 and 57/43%) have become the standard for strawberry production in California and elsewhere, although chloropicrin has been used less in Europe because of its stigma from use as tear gas in World War I (30). The odor and eye irritation caused by chloropicrin are perceptible at very low levels, and as a result, it is used as a warning agent in methyl bromide when the latter is used as a stand-alone fumigant.

More recent trials of chloropicrin as a stand-alone soil fumigant for strawberry production in California show that it is still effective. For example, in large replicated field experiments done near Watsonville, CA, broadcast fumigation with chloropicrin at 336 kg/ha gave 94 to 96% of the strawberry yields obtained with a standard mixture of methyl bromide and chloropicrin (Fig. 2) (9). Similar results were obtained in southern California near Oxnard (5; M. D. Coffey and A. O. Paulus, *unpublished data*). These experiments were done in commercial strawberry fields with histories of methyl bromide fumigation, but fumigation with the methyl bromide/chloropicrin standard each year increased yields 44 to 85% over those obtained in nonfumigated soil, even though *V. dahliae* and *Phytophthora* spp. were not present at damaging levels (5,9). Furthermore, the performance of chloropicrin relative to the methyl bromide/chloropicrin mixture did not diminish with repeated use on the same ground in a strawberry-lettuce rotation (9). Although chloropicrin can also be effective in bed applications that require less material, results for strawberry production at a coastal site near Watsonville have been variable. For example, shank applications of chloropicrin to two-row beds provided 117 and 77% of the yields obtained with methyl bromide and chloropicrin in 1997 and 1998, respectively (Fig. 3). Earlier treatments of the same plots with chloropicrin gave relative yields of 90 and

109% in 1995 and 1996, while the relative yields without fumigation ranged from 45 to 82% of that obtained with a methyl bromide/chloropicrin standard (10). All of the bed fumigation treatments in these experiments provided a high and equivalent level of *Verticillium* wilt control and other factors are likely to have contributed to the year-to-year variation in the relative effectiveness of chloropicrin (10). In other experiments, bed fumigation with chloropicrin at 224 or 280 kg/ha resulted in yields approximately 12% less than the standard methyl bromide/chloropicrin control (14). A survey of earlier fumigation trials for strawberry production in California suggests that soil fumigation with chloropicrin alone in place of methyl bromide mixed with chloropicrin will result in an average yield loss of 9.6% (25). The same survey suggests that high rates of chloropicrin are more effective and that the performance of chloropicrin may decline with consecutive years of use on the same ground for strawberries. While the latter result is doubtful, we clearly need better data on the minimum rates of chloropicrin needed for effective soil treatment, especially where major pathogens are present in soil. For example, elimination of *V. dahliae* in field soil at 15 cm depth required 140 kg/ha, but control equivalent to that obtained with methyl bromide and chloropicrin at 50 cm depth required 224 kg/ha (J. M. Duniway, *unpublished data*). Even the higher rate provided only partial control of buried inoculum of *Phytophthora cactorum* (G. Browne, *unpublished data*). Although chloropicrin is registered and available now for use as a soil fumigant in California, there is resistance by regulators in some counties to the use of the high rates known to be most effective and the actual regulations on its use are still evolving. In addition, methods to apply chloropicrin as an emulsion in water through drip irrigation systems are under development (27). Although chloropicrin has considerable utility as a stand-alone fumigant in soil, it is more likely to be used in mixtures with 1,3-D or in sequential applications with metam sodium (9,10,27).

1,3-D. This compound was initially developed to be a soil nematocide in a mixture with 1,3-dichloropropane (D-D) (13,19).

Fig. 2. Yields of fresh market strawberries obtained in 1996 from replicated field plots where the soil was not treated or was fumigated with 67% methyl bromide and 33% chloropicrin at 361 kg/ha, chloropicrin at 353 kg/ha, or 70% Telone II (1,3-dichloropropene) and 30% chloropicrin at 484 kg/ha, or Telone II at 340 kg/ha. Yields with different letters are significantly different at $P = 0.05$. Fumigants were injected at 20 cm depth (standard broadcast treatment), and the soil was immediately covered with polyethylene, which was removed after 5 days. Beds were raised, and strawberry cv. Selva was transplanted (two rows per bed) in November 1995. Conventional practices for annual strawberry production and pest management for the area were followed. Berries were picked for fresh market at least twice weekly for several months by normal grower practice. These plots were part of a larger set of experiments on alternatives to methyl bromide conducted over 4 years in commercial fields farmed with a strawberry-lettuce rotation just inland from Watsonville, CA (9).

Early in its development, however, D-D exhibited activity against some oomycota (13), and with additional use of 1,3-D as a fumigant, its known spectrum of activity has grown to include certain plant pathogenic fungi and bacteria (24). 1,3-D is available as a fumigant under the brand name Telone (Dow AgroSciences LLC, Indianapolis), either as a stand-alone fumigant (Telone II, 94% 1,3-D) or in mixtures with 17 or 35% chloropicrin (Telone C-17 and Telone C-35, respectively). As distributed in the United States, 1,3-D is a mixture of *cis* and *trans* isomers, with the *cis* isomer being the more biologically active of the two. Although 1,3-D is volatile and somewhat mobile in the soil as a gas, it is less volatile and mobile than methyl bromide.

Telone II is not likely to be used as a stand-alone soil fumigant in strawberry production. Nevertheless, the author and coworkers did apply it in one field experiment near Watsonville, CA, to determine if it would give general growth and yield increases in strawberry. When applied by standard broadcast methods at 340 kg/ha, Telone II increased subsequent strawberry yields significantly over those obtained without soil fumigation (Fig. 2) (9). Neither plant pathogenic nematodes, *V. dahliae*, nor *Phytophthora* spp. were significant factors affecting strawberry in this experiment and the results suggest that Telone II causes many of the shifts in soil microbiology associated with the positive response of strawberry to soil fumigation with methyl bromide and chloropicrin reviewed above. A mixture of 70% Telone II and 30% chloropicrin in the same experiment at 484 kg/ha, however, provided significantly higher yields than Telone II alone (Fig. 2). In fact, the Telone/chloropicrin mixture approximately doubled yields relative to nonfumigated soil in a manner similar to standard fumigation with methyl bromide and chloropicrin (Fig. 2) (9).

Although a survey of earlier fumigation trials for strawberry production in California suggests that soil fumigation with Telone mixed with chloropicrin is no better than fumigation with chloropicrin alone (25), more recent experiments with Telone C-35 have shown it to be a highly effective fumigant for strawberry produc-

tion in California. For example, shank applications to preformed beds with Telone C-35 at 476 kg/ha (treated bed area) often resulted in yields equivalent to those obtained with methyl bromide/chloropicrin (Fig. 3) (10). Shank application to beds at a lower rate of 308 kg/ha nearly doubled yield over that obtained without fumigation, but the resulting yield was 12% less than the methyl bromide/chloropicrin standard (14). Relative to broadcast application, fumigation of preformed beds requires less chemical, e.g., approximately 40% less for two-row strawberry beds. Perhaps more important is the recent evolution of methods to emulsify Telone C-35 in water for delivery into preformed beds through drip irrigation systems under plastic mulch (27). This method was tried first in other cropping systems, but results from early trials in strawberries showed it to be highly effective. For example, when applied as an emulsion, Telone C-35 provided berry yields equivalent to those obtained with standard bed or broadcast fumigations with methyl bromide/chloropicrin (Fig. 3) (10). Numerous experiments and grower trials have now been conducted with drip and/or shank applied Telone C-35 for strawberry and it is likely to become one of the preferred alternatives to methyl bromide/chloropicrin for strawberry production in California. Furthermore, in part because of its strong nematocidal activity, Telone may also become an important component of soil fumigation practices for nursery production of runner strawberry plants in California. In addition, Telone C-17 is one of the likely alternatives to methyl bromide for tomato production in Florida, where nematode control is important; however, where nutsedge is a problem, an additional herbicide will be required (16).

The complex history of recent regulatory reviews and requirements for reregistration of 1,3-D as a soil fumigant is reviewed elsewhere (24). Regulatory concerns include potential ground water contamination, worker exposure, air emissions for potential chronic exposure, and a California Proposition 65 listing as a carcinogen. As of this writing however, Telone II, Telone C-17, and Telone C-35 are all registered and available for use nationally and in California. An emulsified version of Telone C-35 is approaching registration under the brand name InLine (Trademark of Dow AgroSciences LLC). Although registered and available, some of the regulations to mitigate risks of human exposure are cumbersome and actually limit the utility of 1,3-D products. These include extensive buffer zone requirements (e.g., cannot be shank applied within 90 m of occupied structures), personal protective equipment to limit worker exposure, and in California, a cap on the amount of 1,3-D that can be applied in 1 year per township (93 km²) to mitigate potential for chronic exposure. Large buffer zones are a limitation in many areas of strawberry production that are near or abut urban areas. Because of the heat at the usual time of soil treatment, the personal protective equipment requirements are difficult to implement in Florida. The township cap in California, which varies with the season and method of application, will restrict the availability of 1,3-D as a full replacement for methyl bromide in some areas of concentrated strawberry production (4). Fortunately, methods of application of 1,3-D products to soil are evolving that further reduce worker exposure (e.g., drip delivery of emulsified 1,3-D [1]) and air emissions (e.g., low permeability plastic mulches [36]). Even with the current restrictions in place, it is likely that 1,3-D, when used in combination with chloropicrin, will become one of the preferred alternatives to methyl bromide for strawberry production in California.

Methyl isothiocyanate. Metam sodium (sodium *N*-methyl di-thiocarbamate) degrades rapidly to methyl isothiocyanate (MITC) in soil, and has been distributed as a soil fumigant in a stabilized aqueous solution under a variety of trade names since the 1950s (e.g., Vapam HL, 42% metam sodium, Amvac Chemical Corp., Newport Beach, CA). MITC is the primary active agent of metam sodium in soil and is a broad-spectrum fumigant with activity against plant pathogenic nematodes, weeds, oomycota, and a variety of plant pathogenic fungi (13). The behavior of metam sodium

Fig. 3. Yields of fresh market strawberries obtained in 1997 and 1998 from replicated field plots at a coastal site near Watsonville, CA, where the soil was not treated or was broadcast or bed fumigated with 67% methyl bromide and 33% chloropicrin at 364 kg/ha, bed fumigated with chloropicrin at 336 kg/ha, or bed fumigated with Telone C-35 at 476 kg/ha. Strawberry was grown every year, *Verticillium dahliae* was present in the soil, and the broadcast fumigation treatment (rate per total ground area) was applied in September 1996 and 1997. Two-row beds were then shaped, fumigated by shank injection (two shanks per bed, 15 to 20 cm deep, rates given per unit of treated bed area), and covered with black plastic mulch. Telone C-35 was also applied to beds as a water emulsion through the drip irrigation lines after the plastic mulch was in place. 'Selva' was transplanted through the plastic mulch 1 month later and conventional practices for annual strawberry production and pest management for the area were followed. Berries were picked for fresh market at least weekly for several months by normal grower practice.

and MITC in soil has been investigated extensively (26), and current application practices rarely achieve an optimum distribution or the ideal conditions of soil temperature and moisture for MITC to kill all stages of plant pests and pathogens. Although metam sodium is registered, available to growers, and has been used widely, it has a reputation of being unreliable if not used carefully. Metam sodium and its active derivatives are not very mobile in soil and the product must be delivered to the volumes of soil targeted for treatment either by mechanical placement or by water infiltration. For most applications, water is used to move the material in soil, but this needs to be done without leaching too deeply or the volatilization of irritant and smelly vapors. Some sort of surface seal, either applied as water or plastic, is usually required.

Metam sodium has been used on a limited scale as a stand-alone fumigant for strawberry production in California for a long time, but the results have been variable and yields are generally significantly lower than those obtained with methyl bromide and chloropicrin. Whereas some of these applications have been done in part by sprinklers, most have delivered metam sodium into preformed beds through drip lines under plastic mulch. With this latter method, more recent studies have shown metam sodium at approximately 280 liters/ha of treated bed area to give about half the yield increase induced by standard fumigation with methyl bromide and chloropicrin (25,27). Unfortunately, metam sodium probably reacts with chloropicrin and 1,3-D in aqueous solutions and simultaneous or combined applications of metam sodium with these other fumigants have not been very successful (27). Sequential applications separated by several days in time, however, can be effective. For example, shank applications to beds of chloropicrin at 224 and 280 kg/ha or Telone C-35 at 308 kg/ha, when followed 2 weeks later by drip applications of metam sodium, provided strawberry yields nearly equivalent to those obtained following standard fumigation with methyl bromide and chloropicrin (14). Although sequential treatments take more time, they may facilitate soil treatments that are effective with less chloropicrin or 1,3-D. Furthermore, a sequential treatment with metam sodium can provide an added increment of weed and soilborne pathogen control, although these benefits are more likely following chloropicrin than Telone C-35 (G. T. Browne and J. M. Duniway, *unpublished data*).

MITC can also be generated in soil using the granular product dazomet (Trade name Basamid; BASF Corp., Mount Olive, NJ). As is the case for metam sodium, dazomet is not likely to be used as a stand-alone fumigant for strawberry production, but may be a useful addition to other fumigants in sequential applications. For example, applying Basamid at 168 to 224 kg/ha over the tops of beds and furrows, with an appropriate series of overhead sprinkler irrigations to activate the product and seal the soil, either before or after shank fumigations with Telone C-35 (314 to 400 kg/ha) increased strawberry yields somewhat, but more important, provided a high level of weed control (28). Although dazomet can potentially be used as a more general soil fumigant at higher rates, the optimum sequence of soil moisture for full activation following application without residual phytotoxicity is difficult to achieve. Furthermore, dazomet is currently registered in the United States only on nonbearing (e.g., nursery) crops. Experimentation is currently being done, however, to use dazomet in sequential applications with other fumigants for the production of runner strawberry plants in nurseries. The idea is to use other fumigants for general pathogen and nematode control in soil and use dazomet to augment control of weeds and volunteer strawberry plants in the upper layers of soil. Control of volunteer strawberry seedlings is needed to maintain trueness to type in runner plant production. Metam sodium and dazomet will continue to have useful applications in strawberry production, but most likely they will be used in conjunction with other soil fumigants that provide greater or more consistent pathogen control.

Chemical alternatives requiring further development. Among the growing list of chemicals proposed as alternatives to methyl bromide for soil fumigation (Table 1), methyl iodide and propargyl bromide currently stand out for having chemical reactivity and known spectrum of biological activity in soil that are similar to those of methyl bromide. Both were considered to be prospective fumigants several decades ago, but were overshadowed by the growing availability and utility of methyl bromide at that time. Neither methyl iodide nor propargyl bromide has significant potential for transport to the stratosphere and they are not considered to be stratospheric ozone depleting compounds (21). Methyl iodide can be applied to fumigate soil by conventional shank methods and both can be applied by evolving methods of delivery in water through drip systems. It is important to note, however, that neither methyl iodide nor propargyl bromide has been registered with the U.S. EPA as a pesticide or soil fumigant. As of this writing, there has been more development activity and there is more information available on methyl iodide than on propargyl bromide.

Methyl iodide. Considerable research is underway to further develop and register methyl iodide as a soil fumigant under the name Iodomethane or Midas (Tomen Agro Inc., now Arvesta Corp., San Francisco). The basic properties of methyl iodide are reviewed elsewhere (11,21). Although methyl iodide has efficacy equal to or better than methyl bromide against fungi, nematodes, and weeds on an equimolar basis (21), it also has a much higher molecular weight (142 versus 95) and may require higher rates on a weight basis. Although the toxicology data needed for registration of methyl iodide are still being gathered, its toxicology is likely to be similar to that of methyl bromide. Methyl iodide, however, is listed on the California Proposition 65 list as a carcinogen. Methyl iodide does have a safety advantage over methyl bromide in being liquid rather than gas at normal handling temperatures, but it is sufficiently volatile and mobile in soil to act as a true fumigant (11).

In one of the early trials of methyl iodide as a fumigant for strawberry production, when shank applied in beds at 403 to 448 kg/ha, methyl iodide worked as well as the methyl bromide/chloropicrin standard in increasing berry yields and controlling Verticillium wilt (7,8). Like methyl bromide, methyl iodide appears to have some synergy with chloropicrin in killing fungi (12), and most recent trials of methyl iodide for strawberry have used 50/50 mixtures of methyl iodide with chloropicrin. For example, when this mixture was drip applied into beds at 224 to 336 kg/ha, it gave berry yields almost equivalent to those obtained with standard methyl bromide/chloropicrin fumigation (H. Ajwa, *personal communication*). Similar drip applications also reduced the numbers of viable *V. dahliae* microsclerotia buried at depths of 15 and 30 cm, but control at deeper depths was somewhat less than with the methyl bromide (J. M. Duniway, *unpublished data*). However, in strawberry nursery experiments where a 50/50 mixture of methyl iodide and chloropicrin was shank applied by standard broadcast methods, it worked as well as the methyl bromide/chloropicrin standard in reducing inoculum of *V. dahliae* buried in soil and nearly as well for runner plant production (J. M. Duniway, *unpublished data*). There are numerous trials being done to further develop methyl iodide as a soil fumigant for strawberries and other crops. No doubt, methods for its application will be further optimized to improve pathogen control while reducing risks of residual phytotoxicity. Barring unforeseen complications, methyl iodide is likely to become an important alternative to methyl iodide for soil fumigation.

Propargyl bromide (3-bromopropyne). While there is considerable recent activity to further develop propargyl bromide as a soil fumigant (35), there are few published reports to date on its effectiveness in soil. Propargyl bromide is physically unstable and in recent years has been formulated in 20% toluene for handling, but more acceptable carriers are currently under development.

Recent trials show that propargyl bromide can be a very effective soil fumigant. For example, injections of propargyl bromide into soil microplots in Florida at 168 kg/ha controlled root knot nematode damage to tomato and increased yield in the same manner as methyl bromide applied at 448 kg/ha (20). Propargyl bromide has also been applied in water through drip systems for strawberry production in California. For example, in an experiment near Watsonville, application of 202 kg/ha to preformed beds by this method provided berry yields nearly equivalent to those obtained with methyl bromide/chloropicrin at 420 kg/ha; propargyl bromide also gave a high level of *Verticillium* wilt control in this experiment (H. Ajwa, *personal communication*). Given its very high level of activity as a biocide in soil, considerable development work is being done to further stabilize propargyl bromide for safe distribution, and field research is under way to further optimize it as a soil fumigant. However, the status of the toxicology information needed for U.S. EPA registration is unclear, and there are many hurdles to overcome for propargyl bromide to become a registered and available soil fumigant.

Concluding remarks. Among the known chemical alternatives to methyl bromide, chloropicrin, 1,3-D, and metam sodium are the only ones currently registered and available in the United States that have enough broad-spectrum activity to be considered as current replacements for methyl bromide in soil fumigation. None of these three, however, can be considered an equivalent replacement for methyl bromide in most soil applications, and they are likely to be used in mixed or sequential applications. Two additional alternatives, methyl iodide and propargyl bromide, have strong fumigant activities in soil that approach those of methyl bromide. Although these compounds are currently being developed as soil fumigants, they are not registered and we do not know when or even if they will actually become available as commercial fumigants. No doubt, the list of possible chemical alternatives to methyl bromide will continue to grow as other compounds and methods of soil treatment are explored. Any new chemical alternatives identified in the near future, however, are several years from commercial application and are not likely to help offset reductions in methyl bromide scheduled between now and 2005. Improved methods of soil fumigation (e.g., drip application and less permeable plastics) with the alternatives known at this time are more likely to be important in the next few years. The preferred fumigant and method of application, however, are likely to vary among cropping systems.

The phase-out of methyl bromide has heightened public awareness of fumigants in general, and the regulatory environment for the large-scale use of known and new fumigants is also changing at this time. Chloropicrin is registered, but guidelines for its use in California are still evolving and some county agricultural commissioners in California are not allowing applications at the higher rates known to be most effective. In the case of 1,3-D, the cumbersome worker protection and buffer zone requirements, as well as the township caps in California, have already been noted. There is also little doubt that metam sodium will come under further review, and new broad-spectrum fumigants such as methyl iodide and propargyl bromide are likely to face stiff resistance from some quarters. Unfortunately, much of the soil fumigation that is done for production of high-value horticultural crops is done in areas of mixed urban and agricultural land use. The growing proximity of urban populations, along with an increased awareness of the toxicology of soil fumigants, is likely to lead to further restrictions on the use of soil fumigants. Therefore, it is imperative that research continue to further improve fumigation technology to reduce human exposure and to further optimize agricultural production systems that now rely on methyl bromide so that they can remain economically viable using less, and perhaps in some cases, no soil fumigants.

Hopefully the importance of soil fumigation for nursery production of certain planting materials is given sufficient consideration

in the future development and regulation of soil fumigants. For example, the production of vigorous and largely pathogen-free runner strawberry plants on a few thousand acres of fumigated soils in California has very large and long-term benefits, including reductions of pesticide use, for strawberry production on nearly 10,000 ha within the state and additional acreage elsewhere. Furthermore, a large portion of this nursery production is for export to other countries and must meet strict phytosanitary requirements. Although nursery production of strawberry runner plants will likely always require some treatment of soil to reduce or eliminate harmful pathogens, chemical alternatives to methyl bromide are currently less developed for strawberry runner plant production than they are for berry production. Although there is information on strawberry runner production with chloropicrin and 1,3-D/chloropicrin (15), we currently know very little about the potential risks of pathogen damage and contamination of nursery materials grown without methyl bromide. Additional nursery research is underway, however, and some of the more active new fumigants, such as methyl iodide and propargyl bromide, may have important applications in nursery production systems. Although exemptions to allow continued use of methyl bromide in soil after 2005 will be hard to obtain (2), they should be considered for certain nursery situations where it will otherwise be difficult, if not impossible, to produce high quality, pathogen-free planting materials.

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