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Influence of Metam Sodium on the Dissipation and Residual Biological Activity of the Herbicides EPTC and Pebulate in Surface Soil under Black Plastic Mulch

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Metam sodium is a potential replacement for methyl bromide, which is used to control soil pests. Metam sodium rapidly breaks down in the soil to form methylisothiocyanate (MITC). Dissipation of the herbicides EPTC and pebulate in a silt loam soil under plastic mulch in the absence and presence of metam sodium was examined in field experiments in 1998 and 1999 at Knoxville, Tennessee. EPTC half-life (DT_{50}) was 9 d, but when applied in conjunction with metam sodium DT_{50} increased to 22 d. Similarly, average pebulate DT_{50} was 8 d and increased to 23 d when applied in conjunction with metam sodium. This increase in herbicide DT_{50} with the addition of metam sodium is thought to be due to a reduction in soil microorganisms that degrade EPTC and pebulate. EPTC applied with metam sodium injured tomato plants and reduced total crop yield more than EPTC, pebulate, or pebulate with metam sodium. The increased tomato injury may have been related to the greater and prolonged activity of EPTC and slower EPTC dissipation in the presence of metam sodium or MITC.

Keywords: *Methyl bromide replacement; Vapam; metam sodium; pebulate; EPTC; soil; persistence; weed control; tomato; MITC*

INTRODUCTION

Preplant soil fumigation with methyl bromide has been an effective standard practice in plasticulture tomato production (Bhella, 1988; Teasdale and Abdul-baki, 1995; Noling, 1997). Methyl bromide controls weeds and other soil-borne pests. However, as a result of its potentialcontribution to stratospheric ozone depletion, methyl bromide use in preplant soil fumigation is being phased out (USDA, 1999). This phase-out has encouraged research into alternatives for methyl bromide for control of weeds and other soil-borne pests and diseases.

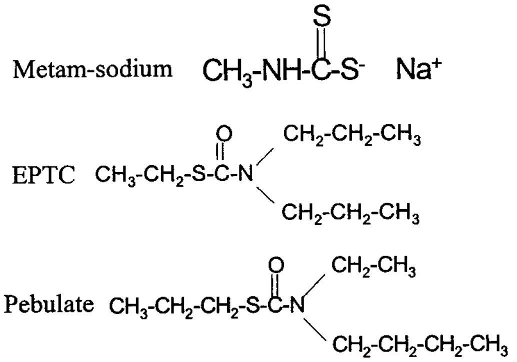

Figure 1. Chemical structures for metam sodium, EPTC, and pebulate.

This research focused on one potential alternative to methyl bromide in plasticulture tomato production. Metam sodium (sodium salt of methylcarbamodithioic acid) is a soil fumigant that is labeled for use in numerous crops including tomatoes (Figure 1). Like methyl bromide, metam sodium provides broad spectrum activity to nematodes and soil-borne pests, such as weeds. Bewick (1989) also reported that metam sodium increased tomato yield comparable to that obtained with methyl bromide. With respect to weed control, Koster and van der Meer (1990) found that in The Netherlands, soil treatment with metam sodium led to 90% yellow nutsedge control. The combination of the herbicide pebulate and metam sodium resulted in improved control of yellow nutsedge compared to metam sodium alone (Locascio et al., 1997). Metam sodium use can also reduce Fusarium crown and root rot in tomato (McGovern et al., 1998), suppress parasitic nematode populations (Fallahi et al., 1998), and reduce weed growth especially when covered with polyethylene film (Csinos et al., 1997).

Metam sodium must be incorporated or injected into soil to prevent rapid loss of its highly volatile breakdown product, methylisothiocyanate (MITC) (van den Berg et al., 1999). Metam sodium (42% w/w aqueous sodium salt) is miscible in water. MITC has a vapor pressure of 3.2 KPa at 25 °C (Ahrens, 1994). The LD_{50} for rats is 1300 mg/kg, and the dermal LD_{50} in rabbits is 1000 mg/kg. Applications should be made using proper personal protective equipment.

Once in the soil, the released MITC is toxic to organisms. The released gas penetrates weed seeds and other nonresistant plant propagules, such as stolons or rhizomes, before emergence from soil. Dormant seeds or those with impermeable seed coats may not always be completely controlled. Although the mode of action of this chemical is not fully understood, MITC is absorbed into the organism where it may disrupt

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internal biochemical pathways, perhaps interacting with nucleophilic centers (Ahrens, 1994).

EPTC (S-ethyl dipropyl carbamothioate) and pebulate (S-propyl butylethyl carbamothioate) are in the carbamothioate herbicide family which is used primarily for grass and sedge control (Figure 1). The compounds in this family are considered to be meristematic inhibitors (Barrett and Harwood, 1998b), which suggests that thiocarbamates are oxidized to their sulfoxide derivatives for full herbicidal activity (Barrett and Harwood, 1998a). This sulfoxide inhibits very long chain fatty acid synthesis and subsequent surface wax synthesis. Metam sodium also must be hydrolyzed to form the toxic moiety, MITC. EPTC and pebulate are mono-carbamates and metam sodium is a dithiocarbamate (Figure 1). From a mammalian toxicology perspective, Staub et al. (1995) reported that these three carbamates formed S-methyl thiocarbamates, which are potential aldehyde dehydrogenase inhibitors, indicating a similar metabolic pathway.

The thiocarbamates are known to be volatile. Koren et al. (1969) found that mechanical incorporation of the thiocarbamates increased their activity by reducing volatilization. Similarly, if a plastic mulch layer is placed directly over the treated soil, losses due to volatilization should be further reduced. Greater chemical persistence would promote higher concentrations which could prolong the lethal concentration for an extended interval, thus maximizing efficacy. Mixing metam sodium into the soil consistently reduced Fusarium crown and root rot in tomato, while metam sodium application using drip irrigation systems, soil injection, or surface application failed to consistently reduce disease in soil not covered with plastic (McGovern et al., 1998).

Thiocarbamates are readily degraded by microorganisms (Fang et al., 1961; Moorman et al., 1992). Harvey et al. (1987) found that when a soil previously treated with EPTC was compared to a soil with no previous EPTC exposure, the dissipation was more rapid in soils previously treated and the EPTC half-life was decreased from 14 to 3 d. The addition of dietholate (O,O-diethyl O-phenyl phosphorothioate) can extend EPTC persistence and weed control, apparently by inhibiting metabolism of the carbonyl linkage of EPTC (Moorman et al., 1992), thus preventing microbial adaptation. EPTC degradation in soil is dominated by bacteria and not fungi, and a range of microorganisms capable of degrading thiocarbamates is typically present in soil (Tal et al., 1990).

We hypothesize that if microorganism populations can be reduced by use of a soil fumigant, then the dissipation rate of a microbially degraded herbicide may also be reduced. A potential result would be improved weed control later in the season. However, a potential risk is that tomato injury may also increase.

The influence of a soil fumigant or plastic mulch soil-covering on the dissipation rate of a herbicide has not been researched extensively. When using a soil fumigant, complete control of all deleterious organisms is desired. When metam sodium is used many soil microorganisms are reduced, perhaps including those responsible for the breakdown of the thiocarbamates. Hamm and Clough (1998) reported significant reductions in microorganisms with the use of metam sodium. Toyota et al. (1999) demonstrated that metam sodium fumigation altered soil microbial community structure and function, and some changes were persistent. However, the effects on broad-scale properties such as total or culturable bacterial numbers were less enduring, with recovery in treated soils to levels prevailing in control soils 26 d after fumigation. Macaladay et al. (1998) reported persistent changes (at least 126 d) in heterotrophic activity and the fatty acid composition of the microbial biomass. This suggests that metam sodium use has the potential to alter important microbially mediated functions, such as herbicide degradation.

The objectives of this research were to characterize EPTC and pebulate dissipation under field conditions in surface soil under a black plastic mulch and to determine the influence of metam sodium on their dissipation rates. Additional research examined the effect of metam sodium on the observed herbicidal activity of EPTC and pebulate under field conditions.

MATERIALS AND METHODS

CAUTION. Because of the toxicity of metam sodium it is vitally important that personal protective equipment be worn: full-body spray suit, goggles, and respirator. Metam sodium, and to a lesser degree EPTC and pebulate, has a strong pungent odor which can cause headache or nausea if exposure occurs. Additionally, odor from metam sodium can accumulate on the applicator's clothing (even through spray suits), so laundering of contaminated clothing should be performed accordingly.

Field Bioassay. Field experiments were conducted in 1998 and 1999 in Knoxville, TN on a Sequatchie loam soil (fine-loamy, siliceous, thermic Humic Hapudult) with a pH of 6.5, organic matter of 1.3%, cation exchange capacity of 7 cmol/kg, and sand/silt/clay percentages of 39/46/15, respectively. The experiments were initiated May 26, 1998 and April 14, 1999. The experimental area was mechanically tilled to bury previous crop residue. The area had been cropped for more than 10 years in corn or soybeans and no persistent herbicides had been used on the area.

The experiment was a 2 by 3 factorial of metam sodium application rate (0 or 110 kg active ingredient (ai)/ha) and herbicide treatment (EPTC at 3.4 kg ai/ha, pebulate at 6.7 kg ai/ha, or untreated control). Treatments were arranged in a split plot design with four replications. The main plots were the absence or presence of metam sodium at 110 kg ai/ha. Metam sodium was applied as a broadcast treatment to the appropriate plots. Herbicide treatments were subplots (2.6 m wide by 6.1 m long). Herbicide applications were made with a CO_2-pressurized backpack sprayer in 170 L/ha of water carrier. Immediately after application two passes were made with a field cultivator to mechanically incorporate the chemicals to a depth of 10 cm. Immediately after incorporation, a Rainflo 2600 plastic mulch layer formed a 20 cm tall soil bed and stretched black polyethylene mulch over the top of the bed and buried the plastic on each side to prevent volatilization loss. The plastic mulch material was Rain-Flo black, 1 mil, embossed, high-density polyethylene. The plastic was cut at the plot ends and covered with soil to isolate each individual plot from possible chemical movement and to reduce outgassing.

A plant-back interval of 14 to 28 d is required after metam sodium application to allow MITC to dissipate to reduce crop injury. Mountain Fresh cv. tomato was used in both years. In 1998, tomatoes were hand planted 23 d after chemical application. In 1999, the tomatoes were mechanically transplanted 36 d after chemical application using a Kenco 130 G bed wheel planter. In-row plant spacing in both years was 46 cm with 10 plants per plot. Plants were staked and tied throughout the season. A commercial fungicide and insecticide spray program was utilized (Bost et al. 1998). Plants were irrigated and fertigated through the drip irrigation system throughout the growing season. All production practices were typical for commercial tomato production under Tennessee conditions using the plasticulture system (Rutledge et al., 1998).

Biological response (crop yield and phytotoxicity) of tomato plants to the various chemical treatments was evaluated. Crop phytoxicity was visually estimated using a 0 to 100 percent scale, with 0% indicating no injury and 100% being plant death. Fruit was hand harvested at the mature green stage from the center six plants of each plot. This is when the fruit has 10−30% of the surface showing a definite change in color from green to yellow or a combination of pink and red. Yields (four harvests in 1998 and three harvests in 1999) were recorded for total yield and also graded for marketable yield (data not shown). Data were subjected to analysis of variance for comparison between years and among treatments and subtreatments. Treatment means were separated by least significant difference (LSD) test (0.05).

Herbicide Dissipation. Field experiments separate from the field bioassay experiments were conducted in 1998 and 1999 in Knoxville, TN to examine EPTC and pebulate dissipation from soil in the absence and presence of metam sodium. Methods for experimental design and plot establishment were the same as the field bioassay, although no plants were grown in the plots. Because most of the sampling interval was prior to when the tomato plants would have been planted (because of the required waiting period after metam sodium application), the lack of crop presence would not have altered the results. Separate field experiments were used to maintain plot integrity for each respective objective. Planting dates, application and plot establishment techniques, and soils were the same in the two sets of field experiments. Each herbicide−metam sodium combination was examined in separate treatments which were replicated four times. Untreated control plots were also sampled to determine background interferences.

Soil cores were collected from each plot, using an 8-cm diameter plugger type sampler to a depth of 8 cm at 0, 1, 2, 4, 8, 16, 21, and 28 d after treatment (DAT) in 1998 and 0, 1, 2, 4, 7, 14, 26, 35, 43, and 57 DAT in 1999. Two soil cores were collected at each sampling date from each plot and mixed to form a composite sample. Care was taken to minimize contamination between samples and to collect a representative sample from each plot. To prevent herbicide degradation, all samples were immediately frozen after collection and immediately transferred to storage at −10 °C. Freezing the sample effectively stops microbial degradation, which is the major loss mechanism for these herbicides (Puchalski et al., 1999). After sampling, the black plastic was "re-sealed" with duct tape to maintain plot integrity.

For extraction, soils were thawed and mixed by shaking the bag to homogenize soil. Because of the volatility of these chemicals, soil samples were not air-dried and sieved as in other herbicide dissipation studies (Mueller and Blumhorst, 1997). To reduce losses to volatility and degradation, sample preparation was done quickly (<4 h). Field plot replicate sample integrity was maintained throughout sample collection, preparation, and chemical analysis. A representative 50-g sample (moist soil basis) was extracted with 100 mL of methanol by placing the soil and methanol into a 250-ml low-density polyethylene screw top bottle. The bottle was then placed on a reciprocating shaker which was then operated at 80 cycles per minute for 16 h. The bottles were removed from the shaker, allowed to statically equilibrate for 1 h, and then the methanol extract was filtered through two pieces of qualitative filter paper (Whatman #1). An aliquot of the soil extract was placed into a 2-ml autosampler vial for analysis.

Herbicide concentrations were determined using a Hewlett-Packard 5890 gas chromatograph equipped with a nitrogen−phosphorus detector. The analytical method utilized an Econo-Cap SE−30 mega-bore column (30 m length, 0.54 mm i.d., 1.2 μm film thickness). Chromatographic conditions consisted of an injection port at 250 °C, oven ramped from 110 °C to 190 °C at 5 °C per minute, and detector operated at 230 °C. A Hewlett-Packard (San Fernando, CA) chemstation software program was used to control the instrument and capture data. On the basis of an external standard technique examining fortified soil samples, EPTC recovery was 86 ± 7% with a retention time of 5.37 min and the recovery of pebulate was 94 ± 5% with a retention time of 6.87 min (data and chromatograms not shown). Each herbicide concentration was corrected for soil moisture, dilution of extracting solvent, and recovery.

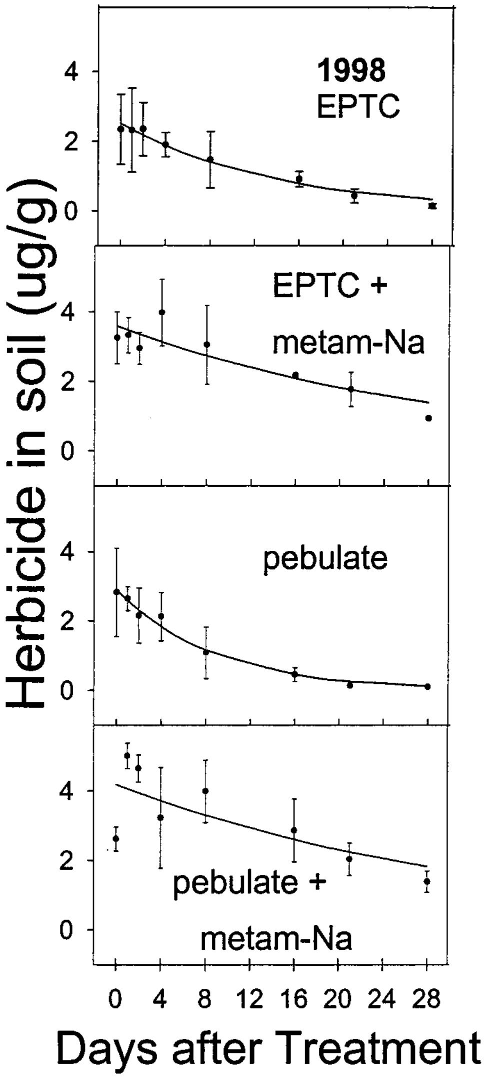

Figure 2. Pebulate and EPTC concentrations in soil as a function of days after treatment during 1998. Solid line represents the first-order kinetics expression. Data point is mean of four replications. Error bars on each data-point represent the standard error at that sampling interval.

Herbicide concentrations were determined using a first-order nonlinear regression procedure (Brown et al., 1996). The data were regressed against time in days. The analysis provided a first-order dissipation rate constant (k) and upper and lower confidence intervals. A disappearance time to 50% of initial concentration or half-life (DT_{50}) value for each treatment was calculated using the equation

$$DT_{50} = \ln 0.50/k$$

where DT_{50} is the herbicide half-life in days and k is the first-order dissipation rate constant (Walker 1987). A "corrected" r^2 value was determined by the formula

$$r^2 = [1 - (\text{residual sums of squares}/\text{corrected total sum of squares})]$$

Herbicide concentrations were plotted against time for each data point with error bars representing the mean and standard error and the line representing the predicted values (Figures 2 and 3).

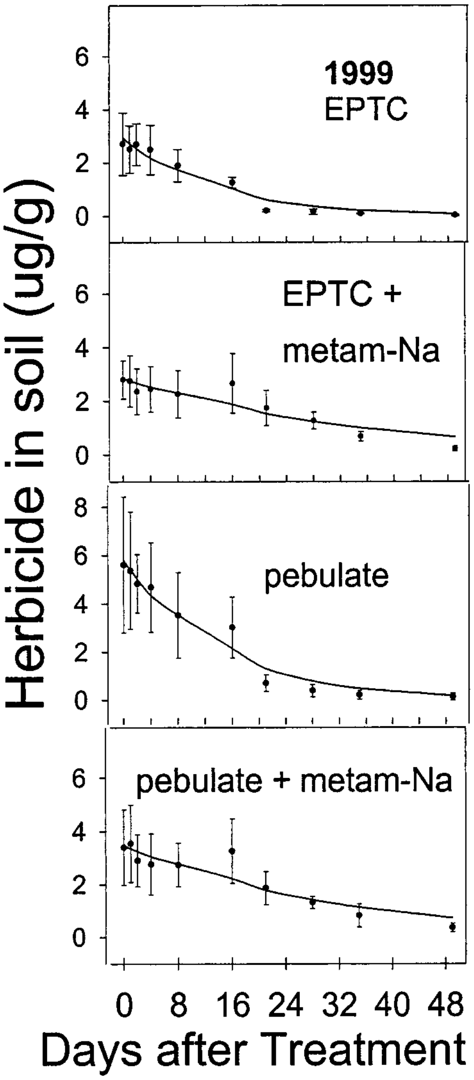

Figure 3. Pebulate and EPTC concentrations in soil as a function of days after treatment during 1999. Solid line represents the first-order kinetics expression. Data point is mean of four replications. Error bars on each data-point represent the standard error at that sampling interval.

Table 1. Tomato Injury in Knoxville, TN in 1998 as Affected by Application of Metam Sodium and the Herbicides EPTC and Pebulate[a]

metam sodium rate (kg ai ha^{-1})	herbicide treatment	herbicide rate (kg ai ha^{-1})	days after planting			
			11 d	25 d	40 d	51 d
0	untreated	0	3%	0%	1%	1%
0	EPTC	3.4	11%	8%	5%	4%
0	pebulate	6.7	11%	9%	11%	11%
110	untreated	0	9%	0%	0%	0%
110	EPTC	3.4	33%	45%	34%	18%
110	pebulate	6.7	14%	13%	3%	0%
		LSD (0.05)	13%	11%	6%	7%

[a] Data presented are mean of 4-replications and are based on a 0–100 percent scale (0%, no injury; 100%, plant death).

RESULTS AND DISCUSSION

Field Bioassay. In 1998, application of EPTC did not injure the tomatoes (Table 1). EPTC with metam sodium injury was >30% from 11 DAP to 40 DAP and was the most severe injury of all treatments. This was the only treatment that reduced total and marketable tomato yield (data not shown). Pebulate application with or without metam sodium did not injure tomatoes as determined by comparison to the untreated control (Table 1).

Table 2. Tomato Injury in Knoxville, TN in 1998 as Affected by Application of Metam Sodium and the Herbicides EPTC and Pebulate[a]

metam sodium rate (kg ai ha^{-1})	herbicide treatment	herbicide rate (kg ai ha^{-1})	days after planting			
			13	29	35	44
0	untreated	0	1%	1%	4%	5%
0	EPTC	3.4	5%	11%	9%	6%
0	pebulate	6.7	3%	8%	11%	11%
110	untreated	0	0%	0%	1%	5%
110	EPTC	3.4	15%	18%	33%	20%
110	pebulate	6.7	4%	6%	15%	6%
		LSD (0.05)	6%	8%	9%	7%

[a] Data presented are mean of 4 replications and are based on a 0–100 percent scale (0%, no injury; 100%, plant death).

Table 3. First-Order Dissipation Rate Constants (k) and Half-lives (DT_{50}) of EPTC and Pebulate under Field Conditions as Influenced by Metam Sodium in 1998 and 1999

year	herbicide	$k \pm SE^a$	$DT_{50}{}^b$	r^2
1998	EPTC	.0725 ± 0.0074	9.6 (7.6, 12.8)	.98
1998	EPTC + metam	.0341 ± 0.0086	20.3 (12.6, 53.3)	.81
1998	pebulate	.1137 ± 0.0113	6.1 (4.9, 8.1)	.98
1998	pebulate + metam	.0298 ± 0.0131	23.3 (11.2, 315)	.56
1999	EPTC	.0755 ± 0.011	9.2 (6.9, 13.9)	.96
1999	EPTC + metam	.0296 ± 0.006	23.4 (16.0, 43.9)	.86
1999	pebulate	.0711 ± 0.0088	9.8 (7.5, 13.6)	.97
1999	pebulate + metam	.0317 ± 0.0063	21.9 (15, 40.3)	.86

[a] Rate constant ± standard error. [b] Half-life in days, lower and upper limits of 95% confidence interval in parentheses.

Tomato injury was similar in 1999, with EPTC and metam sodium application causing the most severe crop injury (Table 2) and again reducing crop yield (data not shown). Pebulate did not injure tomatoes.

Herbicide Dissipation. In this study several factors affecting herbicide dissipation from soil were minimized. The soil was covered with plastic mulch immediately after incorporation of the herbicide, therebyreducing volatilization losses. MITC losses to the atmosphere, which can be substantial, are due to its high vapor pressure (van den Berg et al., 1999). Rainfall infiltration was prevented by the plastic so leaching was reduced, although leaching of MITC constituted only a small fraction of the amount applied even under conditions favoring leaching (Saeed et al., 1996). The fumigant and the herbicides were applied and mixed into the soil such that they were in the same area in the soil. Thus, use of the plastic mulch should have maximized any potential effect of metam sodium on the subsequent dissipation of EPTC or pebulate.

In 1998, samples were taken through 28 d and in 1999 the sampling interval was extended through 49 d. Variation within each sampling day was typical for field studies (Mueller and Blumhorst, 1997). First-order kinetics provided an acceptable empirical fit to the data, with $r^2 > 0.80$ for most curves (Table 3).

When not coapplied with metam sodium, the DT_{50} for EPTC and pebulate was <10 d (Table 3). When metam sodium was used in combination with EPTC and pebulate, the DT_{50} increased to >20 d. This difference was largely due to slower herbicide dissipation 0 to 8 DAT in the presence of metam sodium (Figures 2 and 3). This trend was more evident for pebulate dissipation than for EPTC dissipation.

These results on EPTC and pebulate dissipation in the absence of metam sodium in surface soil reasonably agree with previous studies (Koren et al., 1968). Obrigawitch et al. (1982) reported a half-life for EPTC of 18 d. Pebulate was previously reported to have a DT_{50} of approximately two weeks (Ahrens 1994).

Given that thiocarbamate herbicides are primarily degraded in soil by microorganisms, the data suggest that metam sodium application to soil reduces microbial activity and thus reduces herbicide dissipation. However, microbial activity apparently rebounds fairly quickly once the fumigation effect is suspended (Toyota et al., 1999). Our data suggest this recovery in microbial activity, in that thiocarbamate dissipation later in the sampling interval may have been less affected by the initial presence of metam sodium (Figures 2 and 3). Although MITC levels were not evaluated in this research, it would be expected that the most pronounced fumigation effect would be immediately after application. As soil microorganisms recover from the fumigation event, microbially mediated herbicide degradation would intensify.

An important agronomic consideration is the amount of herbicide remaining in the soil at the time of crop transplanting and immediately thereafter. This is a critical time for weed control, becausethe crop is not as competitive as it will be once fully established. Additionally, transplant seedlings are more vulnerable or susceptible to herbicide injury. Those treatments where metam sodium was coapplied exhibited greater herbicide concentrations at the time of crop establishment (Figures 2 and 3).

Nelson et al. (1999) have previously reported an antagonistic effect of metam sodium and 1,3-dichloropropene on pebulate activity. They suggested that decreased tomato yield in metam sodium and 1,3-dichloropropene and pebulate treated plots was most likely due to reduced nutsedge control, thus pebulate activity was antagonized by the fumigant. Our findings indicate no antagonism based on the crop response of tomato under field conditions. Additionally, the pebulate dissipation data provide no basis for reduced herbicidal activity when pebulate is applied in conjunction with metam sodium. However, there is variability in that soil microflora, moisture, and temperature in our field study were different from those in Nelson et al. (1999).

The application of metam sodium in conjunction with EPTC or pebulate increased the persistence of each herbicide in soil. This may improve mid- to late-season weed control, but may also cause greater crop injury. Another potential outcome of slower herbicide dissipation would be reduction of herbicide application rates if these herbicides are to be used in conjunction with metam sodium, because the herbicidal activity is protracted. Further research is needed to evaluate the potential of decreased herbicide rates for comparable weed control, especially difficult-to-control weeds such as yellow nutsedge, and improvements in crop response.

ABBREVIATIONS USED

DT_{50}, herbicide half-life; DAT, days after treatment; MITC, methylisothiocyanate.

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