EVIDENCE FOR ACCELERATED DEGRADATION OF METHAM-SODIUM AND DAZOMET IN ISRAEL

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INTRODUCTION

Metham-sodium (MS) (sodium *N*-methyl dithiocarbamate) and dazomet (DAZ) (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione) have been proposed as alternative soil fumigants to replace methyl bromide in Israel and elsewhere. When applied to moist soil, these fumigants are decomposed to methyl-isothiocyanate (MITC), which is an effective wide-spectrum soil fumigant for controlling various soilborne pests (fungi, nematodes, soil insects and weeds). In Israel, MS is commonly applied on a large scale, at rates ranging from 500 to 1000 L ha $^{-1}$, to control several soilborne plant pathogens in regions with intensive potato, peanut and other cropping systems. In recent years, we found cases in which repeated applications of MS to commercial potato fields in various locations in Israel, have resulted in less effective control of potato Verticillium wilt, caused by *Verticillium dahliae.* In such situations, farmers usually react by applying higher dosages and the results may be an upwards spiral in chemical usage and costs, without improved pest control.

A possible explanation to the reduced effectiveness of MS, resulting from repeated applications, is an accelerated degradation due to enrichment in soil of microbial populations which degrade this pesticide. This phenomenon had been observed with a variety of pesticides, especially herbicides and fungicides (Katan and Aharonson, 1989). Cases of accelerated degradation of metham-sodium in field soils in the Netherlands and in Australia with histories of previous treatments with this fumigant has been reported (Smelt *et al*., 1989; Warton and Matthiessen, 2000).

The objectives of the present study were to determine the possible occurrence and the widespread of the problem of accelerated degradation of MITC in various field soils in Israel, and first assessing prevention strategies in order to delay and/or control the development of the phenomenon.

We studied the relationship between rate of degradation of MITC after application of the fumigants in history (soil with previous application of MS or DAZ) compared to non history soils and the failure of MS or DAZ fumigants to adequately control assay organisms (such as *V. dahliae* and *Fusarium oxysporum* f. sp. *radicis-lycopersici)*, under controlled environment conditions.

MATERIALS AND METHODS

The soil samples were collected from a number of field sites with known MS or DAZ use history in different locations of Israel. At each site, soil was collected from the MS or DAZ pre-treated site, and from an adjacent site with a similar soil type but with no history of MS or DAZ use.

The accelerated degradation of MITC was investigated by comparing fumigant degradation kinetics in history and non history soils in a fumigation chamber (narrow-neck glass containers). The glass containers were each filled with 1 kg of soil and nylon net-bags containing the assay organisms (bioassay) were buried in the soil. Metham-sodium or DAZ was added to the soil and the fumigation apparatus were incubated at 25^{o}C for 7 days. Concentrations of MITC in the headspace of the containers were measured using the Solid-Phase Micro-Extraction (SPME) method and analysed by gas chromatography. Following the soil treatments, the propagules were retrieved from the bags (7 days after incubation), the viability of the organisms was tested by appropriate methods, and percentage of mortality calculated by comparing to untreated control.

RESULTS

After first application, (i.e. nonhistory soil) the maximum concentration of MITC was reached 36 hours after application of DAZ (Fig. 1 A) and 2 hour after application of MS (Fig. 1 B). The concentration of MITC maintained a detectable level even 168 hrs after the treatment. Dazomet, at the same dose applied, to soil which was previously treated with DAZ (history soil), gave a maximum concentration of MITC at 6 hours after application of DAZ, and no MITC was detectable after 48 hours (Fig. 1 A). Metham sodium at the same dose, applied to history soil (second and third application), gave a maximum concentration of MITC two hours after application of metham sodium, and no MITC was detectable after 48 hours. As shown in Fig. 1 B, accelerated degradation of MITC became evident, already after the second application. The accelerated MITC degradation shortened the Concentration x Time (C x T) period for pathogen exposure and therefore this phenomenon is the likely cause of poor control of *V. dahliae* and *Fusarium oxysporum* f. sp. *radicis-lycopersici* propagules. Indeed, Fig. 2 shows that after application of MS to history soil (second and third application), percent mortality of both pathogens was significantly reduced, when compared to the application of MS to nonhistory soil (first application).

Application of formaldehyde to soil where the accelerated MITC degradation phenomenon was observed, resulted in an improved performance of MS application. This indicates to the possibility that accelerated degradation is associated with microbial activity. The mechanisms of accelerated enhanced MITC degradation have yet to be elucidated.

DISCUSSION AND CONCLUSIONS

In our study, MITC dissipated more rapidly from history soils previously treated with MS or DAZ. We found that the phenomenon was correlated with the concentration of metham–sodium applied as a pretreatment, and with soil pH. In general, high soil pH increases the risk of the accelerated MITC degradation onset.

This phenomenon has important practical implications and further emphasizes the importance of alternating pesticides and avoiding frequent application of the same pesticide.

The potential of soils to degrade fumigants rapidly, and thus to reduce their efficacy is shown in this study for MITC. The phenomenon should be studied also for other fumigants in order to prevent the rapid loss of efficacy of these chemicals.

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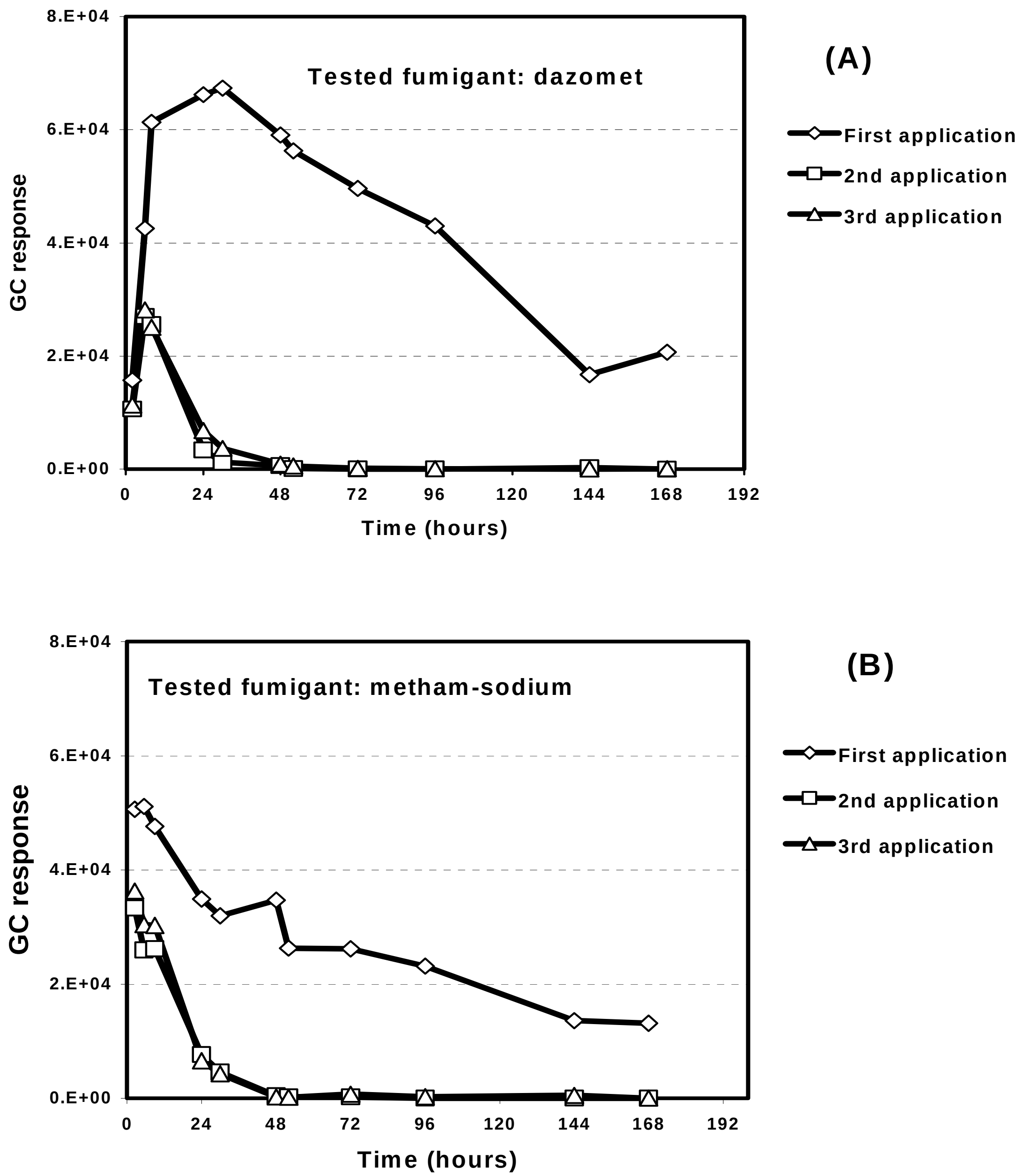

Fig. 1. Degradation of MITC, generated from dazomet or metham-sodium applied to non history Rehovot soil (first application) or previously treated with dazomet as indicated. Pre-application (first application) was done with dazomet (29 mg a.i./kg dry soil). The tested compounds dazomet **(A)**, at a rate of 29 mg a.i./kg dry soil, or metham-sodium at a rate of 16.3 mg a.i./kg dry soil **(B)** were applied after it was determined that no residues of MITC from previous application to the soil remained.

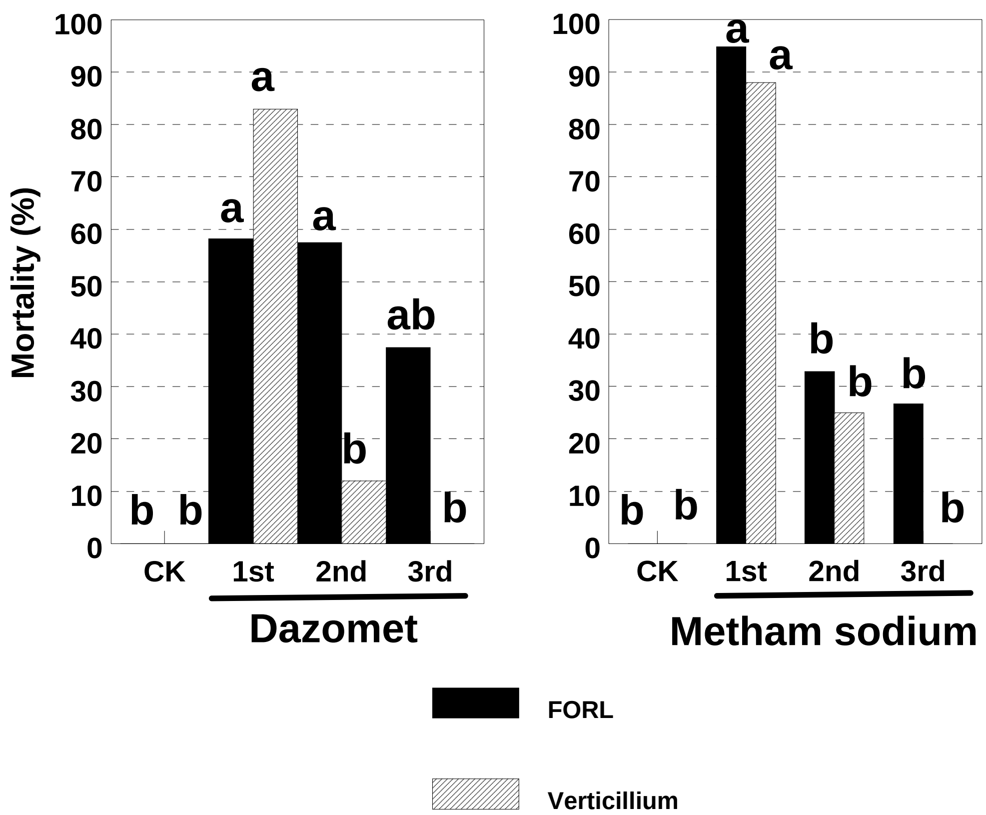

Fig. 2. Effect of exposure to dazomet or metham-sodium applied to Rehovot non history (first application) or history soil (second and third application) on *Verticillium dahliae* and *Fusarium oxysporum* f. sp. *radicis-lycopersici* propagules mortality. The challenge compounds dazomet or metham-sodium were applied at a rate of 29 mg a.i. or 16.3 mg a.i./kg dry soil, respectively. For each pathogen, columns topped with different letters are significantly different ($P \leq 0.05$). CK = Soil nontretaed with dazomet or metham-sodium.