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Dissipation Behavior of Malathion and Dimethoate Residues from the Soil and Their Uptake by Garden Pea *(Pisum sativum)*

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The contamination of soil by pesticide chemicals can occur through direct application to control some inhabiting insect pests of a variety of economic plants while indirect avenues can occur through aerial applications, spray drifts, wash-off from the atmosphere, treated plants through precipitation, erosion, and run-off from agricultural and forest lands (Mulla *et al.* 1981). It is obvious, therefore, why a great deal of attention must be paid to studying the many complex interactions that occur between pesticides and the soil (Harvey 1983). The fate of pesticides and their behavior in soil is influenced by several factors including adsorption, movement and decomposition (Shamahat 1980). The breakdown of pesticides in soil is brought about by a variety of biological and non-biological mechanisms; frequently total decay is due to a combination of events. The principal biological route is the microbial consumption of the pesticides as energy, carbon and/or nitrogen source (Bums and Edwards 1980). Data has been collected suggesting that organic molecules in soil slowly become sequestered within the soil matrix (Alexander 1995). The patterns of disappearance of persistent compounds in the field and laboratory studies show a declining bioavailability to microorganisms with time of residence in soil. If a chemical persists and thus remains in contact with particulate matter for some time, it becomes more and more resistant to extraction by solvents (Kelsey *et al.* 1997). This persistence leads to different behaviors: the pesticide may be stressed to a faster degradation (biological or chemical) on the active sites of particulate matter, or on the contrary, the pesticide may be protected and exhibit a longer half-life in soil (Lartiges and Garrigues 1995).

Both malathion and dimethoate are used as foliar sprays in Kenya on a wide spectrum of crops but their fate in the soil has not been studied. The objective of this study was to investigate the dissipation of malathion and dimethoate from the soil and the subsequent uptake of the same by the garden pea plant from soil treated with ^{14}C-labeled malathion and ^{14}C-labeled dimethoate. The dissipation of ^{14}C-labeled malathion at the 2nd, 3rd carbons of the diethyl mercaptosuccinate and ^{14}C-labeled dimethoate at the methoxy groups from the soil was studied under simulated tropical field conditions in the greenhouse.

MATERIALS AND METHODS

Chemicals were of analytical grade and solvents were pure grade. Solutions of pesticide emulsion concentrates were prepared in tap water. The soil used in the greenhouse had the following characteristics pH (6.5), Mn (0.28%), K (2.7%), Na (3.6%), Ca (45%) P (17.4%) and Carbon (0.9%). The garden pea seeds were procured from farmers.

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Malathion, (2^{nd}, 3^{rd} ^{14}C-labeled) with specific activity of 50 mCi/mmo1 and radiochemical purity of 99 % (by HPLC) was obtained from Sigma Chemical Company, Missouri, USA. The standards of malathion and dimethoate were obtained from Chemical Services, Box 3108, West Chester PA, 1938 USA.

Methoxy-^{14}C dimethoate was synthesized in the laboratory from the reaction of phosphorus pentasulphide (P_2S_5), N-methyl 2-chloro acetamide and labeled ^{14}C-methanol. Methoxy-^{14}C dimethoate was synthesized in the laboratory according to the method of Chen and Dauterman (197 1).

250 µCi of ^{14}C-methanol with specific activity of 50 µCi/mmol, neat liquid in a sealed ampoule was purchased from ICN Pharmaceuticals, USA. 2,5-diphenyloxazole (PPO) and 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP) in toluene, Carbo-Sorb and Permafluor® from Packard Bioscience B.V., Netherlands

The instruments used were Liquid Scintillation Counter (Canberra Packard 2500 TR) and Biological Material Oxidizer (Packard 307).

The garden pea plants were grown in 250-ml PVC pots, each filled with 170 g of dry soil and placed on trays, in a greenhouse at the University of Bayreuth in Germany. Each pot had three seedlings, which were irrigated from the trays. Metal lamps of 5x250W continuously illuminated the plants for 11 hours a day. The temperatures in the green house ranged from 10°C to 26°C. The average relative humidity was 70%. When the seedlings were 21 days old, the soil in each PVC pot was treated with 50% emulsion concentrate (EC) of malathion laced with ^{14}C-labeled malathion [S-l, 2 bis(ethoxycarbonyl) ethyl O,O-dimethyl phosphorodithioate] and in another set of experiments each PVC pot received 40% emulsion concentrate (EC) of dimethoate laced with ^{14}C-labeled dimethoate [0, O-dimethyl S-methyl carbamoyl methyl phosphorodithioate] at a rate of 15.53 µg/g. The initial radioactivity in each PVC pot was 0.412 µCi and 0.326 µCi for malathion and dimethoate, respectively in a greenhouse.

Sampling after pesticides application in the greenhouse was done after 1, 3, 5, 6, 24, 48, 96, 192, 216, 312, 384, 408, 504, 576 and 696 hours. Both whole plant and soil samples were collected (replicas of three) at the same time. The whole plant including the roots was removed after the roots were completely detached from the soil. The plant was chopped into small pieces and ground with a pestle in a mortar. The soil sample was also homogenized in a mortar. A representative sub-sample of 5 g from the homogenized soil was taken while a whole ground plant sample was taken and placed in extraction thimbles and extracted continuously by the Soxhlet extractors for four hours with 40 ml of pure methanol solvent for both malathion-treated and dimethoate-treated samples. The resulting colored extracts were concentrated to 5 ml by rotary evaporation at 35°C. The extracts were cleaned-up according to the method of Leoni *et al*, (1992). One ml of the extract was mixed with 4 ml of the cocktail (PPO and POPOP in toluene) and radioassayed in liquid scintillation counter to determine the extractable residues in the samples. The extracted plant sample was air-dried and finely ground and mixed in a Retsch Ultracentrifugal mill. The extracted soil sample was air dried and homogenized in a mortar. A representative sub-sample of 500 mg from the extracted soil and plant samples was taken separately and placed in a folded filter paper and combusted in a biological material oxidizer. The $^{14}CO_2$, released was trapped by 7 ml of Carbo-Sorb®, mixed with 7 ml of Permafluor® E cocktail and radioassayed to determine the non-extractable (bound) residues. Quench correction for the liquid scintillation counter was done by internal standardization.

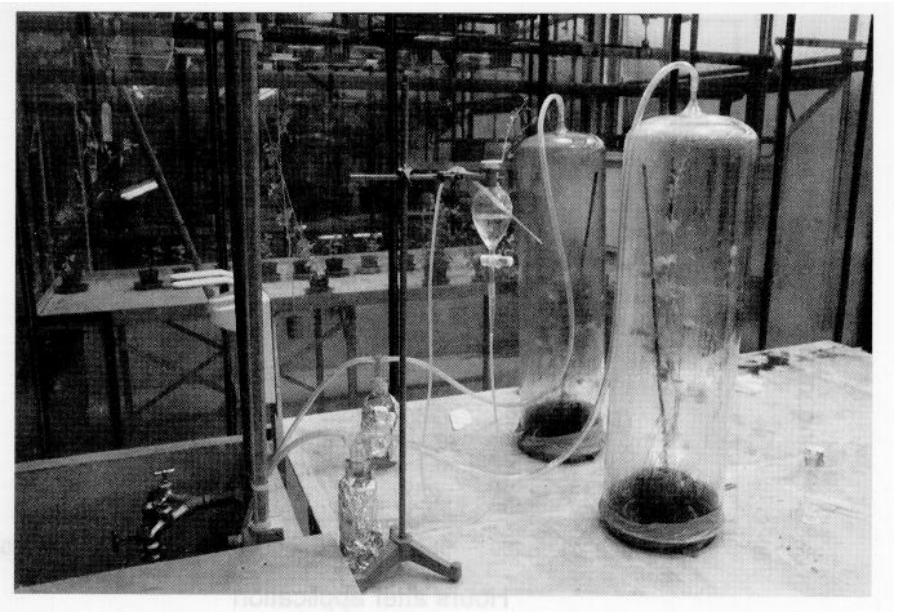

Figure 1. Experimental set up for the determination of $^{14}CO_2$ and ^{14}C-compounds in evapotranspired water from the potted garden pea plants.

To determine $^{14}CO_2$ resulting from mineralization of the pesticides in the soil and ^{14}C-compounds in evapotranspired water from the plant, potted garden pea plants were enclosed in the glass bell jar placed over a trough set up as shown in figure 1. Solutions of malathion and dimethoate emulsion concentrates in tap water were applied to soil in the PVC pots at a rate of 15.53 µg/g with initial radioactivity of 0.412µCi and 0.326 µCi respectively. The contact between the bell jar and the trough was sealed with a heavy-duty masking tape to make the system airtight. A pipe was connected from the outlet of the bell jar to the wash bottle containing ethanolamine, which trapped $^{14}CO_2$. The wash bottles were covered with an aluminum foil to protect the trapper from photodecomposition. The evapotranspired water condensed under the glass bell jar and collected in the trough. The connecting tubes were tilled with sachets of silica gel to trap the water vapor that could be drawn into the ethanolamine. To draw air through the system, vacuum was created at the outlet of the wash bottle by a vacuum pump. The ethanolamine was removed and replaced in the wash bottle every 24 hours. An aliquot of the solution was radioassayed. The evapotranspired water, which collected in the trough, was withdrawn with hypodermic syringe at an interval of 12 hours and aliquots radioassayed. The potted plants in the bell jars were watered from a separating funnel clamped to the retort stand. Water flowed by gravity.

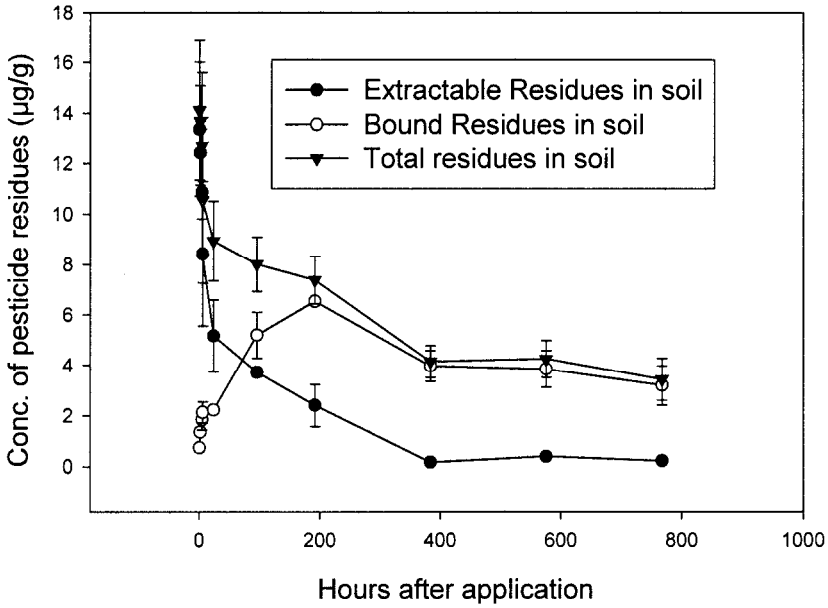

Figure 2. Dissipation of ^{14}C malathion from the soil

For each determination, two identical experiments were set up, with one acting as a control in which no pesticide was applied. The recovery rates of malathion and dimethoate from the spiked soil samples at a concentration of 15.530µg/g were 95 % and 90.5 % for malathion and dimethoate. The recovery rates from the spiked plant samples at the concentration of 2.3 µg/g were 89 % and 83.7 % for malathion and dimethoate. The results were corrected according to these recovery rates. The data has been subjected to statistical analysis according to the method of Mactaggart and Farewell (1992).

RESULTS AND DISCUSSION

Figures 2 and 3 show the results of dissipation of 2, 3 ^{14}C-malathion and methoxy- ^{14}C dimethoate from the soil. The dissipation curves for the two pesticides show that the dissipation of the extractable residues is initially fast and slow in the later stages. However, the dissipation of malathion as shown by extractable residues is faster than that of dimethoate. The loss of the extractable residues from the soil is due to the conversion of the same into bound residues in the soil, volatilization to the atmosphere, uptake by the pea plant and microbial mineralization to $^{14}CO_2$. The dissipation of both pesticides is initially fast because the processes responsible for the loss of the residues are concentration dependent; initially the concentration of the extractable residues is high. As time advances the concentration of the extractable residues decreases and this reduces the rate of dissipation of the extractable residues. The bound residues of malathion in the soil initially build up and reach a maximum concentration of 42 % of the initially applied dose and then start to decrease as time elapses.

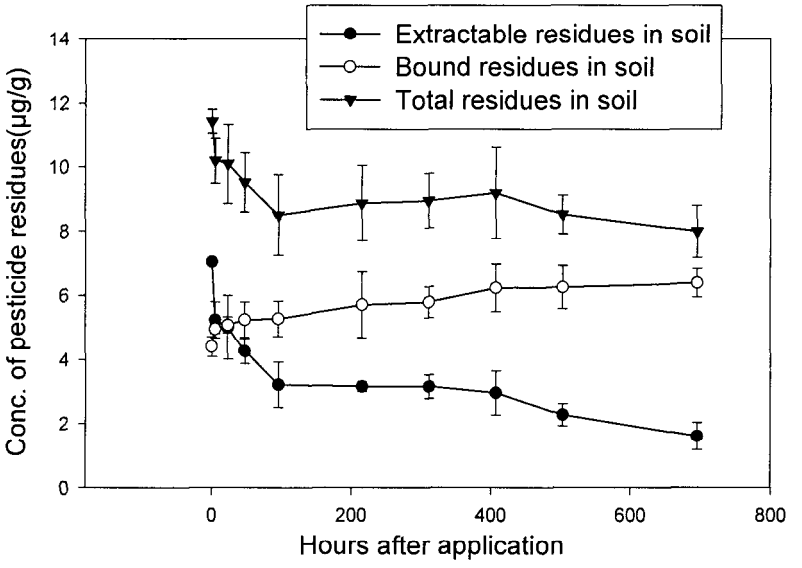

Figure 3. Dissipation of ^{14}C dimethoate from the soil

Bound residues of dimethoate in the soil showed a similar pattern but did not decrease after reaching a maximum concentration of 41.3 % of the initially applied dose. The overall dissipation patterns of the two pesticides were exponential and first order kinetics model was used to determine the half-life values of the total residues of the pesticides in the soil. The semi-log transformation of the concentration of the total residues with time in the soil gave half-life ($t_{1/2}$ value of 17 days for malathion residues and 72 days for the dimethoate residues. The results clearly show that residues of malathion dissipated faster than residues of dimethoate from the soil. The loss of the pesticides residues from the soil is due to microbial mineralization to $^{14}CO_2$, volatilization to the atmosphere, degradation of the labeled part of the original pesticide molecules into metabolites which did not bear the labeled part of the original compound, uptake by the plants and subsequent loss by the plants through evapotranspiratioin to the atmosphere. Leaching of the pesticides out of the PVC pots was not possible because the PVC pots were irrigated from the trays on which they were placed. Malathion residues dissipated faster than the dimethoate residues because the bound residues of malathion underwent microbial mineralization while bound residues of dimethoate seemed to resist this type of degradation. It has been reported from other studies that once the pesticide residues are bound to the soil, some pesticides may be protected from biological and chemical degradation and for the others, they may undergo faster degradation (Lartiges and Garrigues, 1995).

Figures 4 and 5 show the results of the uptake of the residues of malathion and dimethoate from the soil by the garden pea plants. The absorption patterns of the residues of the two pesticides from the soil by the pea plants are different. The extractable residues of malathion initially increase in the pea plant and after 6 hours

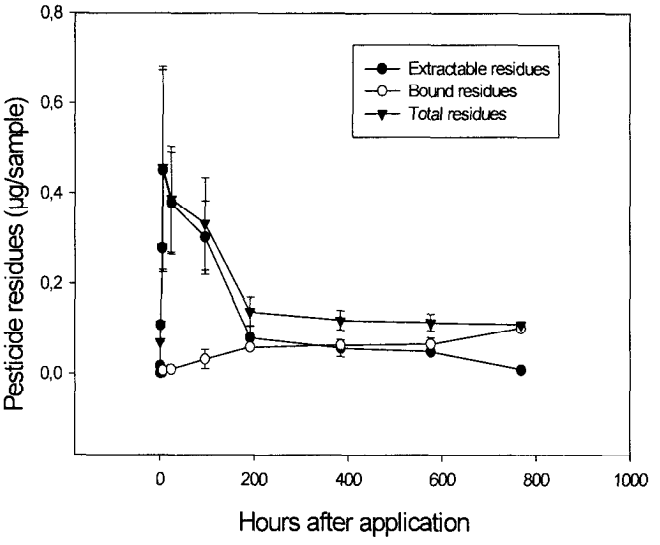

Figure 4. Uptake of malathion from the soil by the pea plant

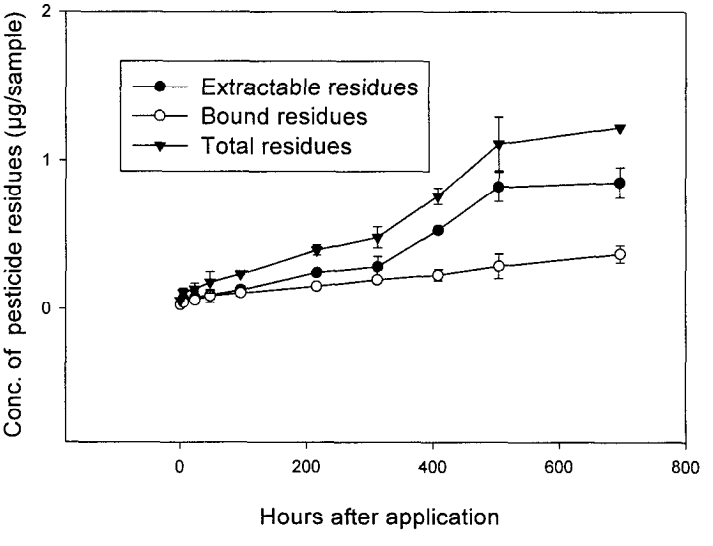

Figure 5. Uptake of ^{14}C dimethoate by the Pea plant

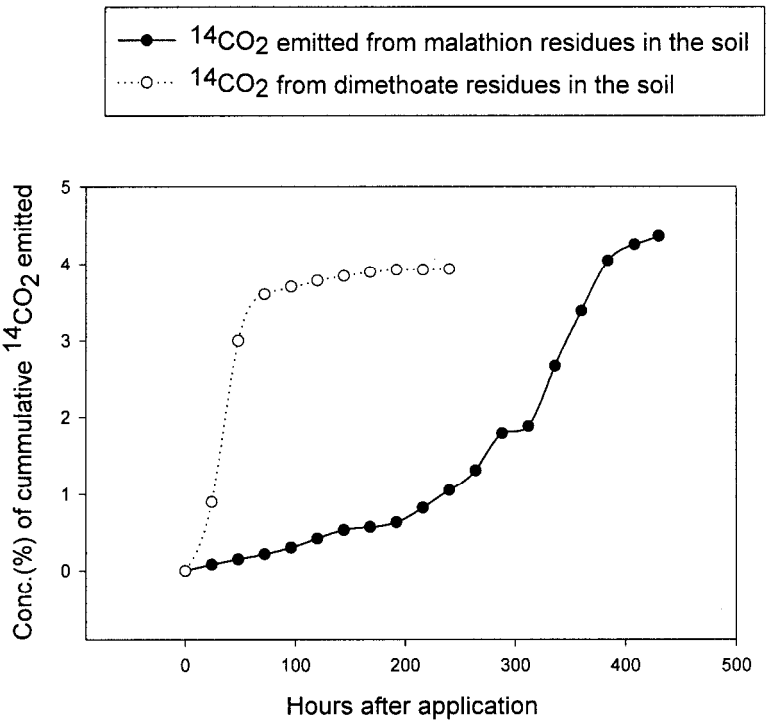

Figure 6. Cummulative $^{14}C\,O_2$ emitted from the treated soil

reach a maximum of 2.9 % of initially applied dose. Afterwards the extractable residues decrease very rapidly and then decrease more slowly after 200 hours. This is in contrast with the extractable residues of dimethoate, which increase as time goes by. The bound residues of both malathion and dimethoate increase slowly with time. The total residues of malathion in the plant initially increase rapidly in the first six hours followed by a high rate of decrease until 200 hours and then slowly decrease. The total residues of dimethoate increase in the plant throughout. Neubaur *et al.,* (1982) reported a gradual and relatively slow increase in aphid control efficiency with time on Citrus Glove leaves by dimethoate applied to the soil. This supports the present observation where the total residues of dimethoate absorbed by the pea plant from the soil builds up with time. Therefore residual concentration effectiveness would be expected to increase.

The pesticide residues are lost from the pea plant by evapotranspiration to the atmosphere. The rate at which malathion residues are lost from the plant exceeds the rate at which the same are absorbed from the soil while the rate of absorption of the residues of dimethoate from the soil by the pea plant exceeds the rate at which the pea plant loses the same by evapotranspiration. This difference is well correlated to the physical properties of the two pesticides. The value of log Ko/w of dimethoate is 0.78 and its solubility in water is 25,000 mg/l at 20°C while log Ko/w for malathion is 2.36 and its

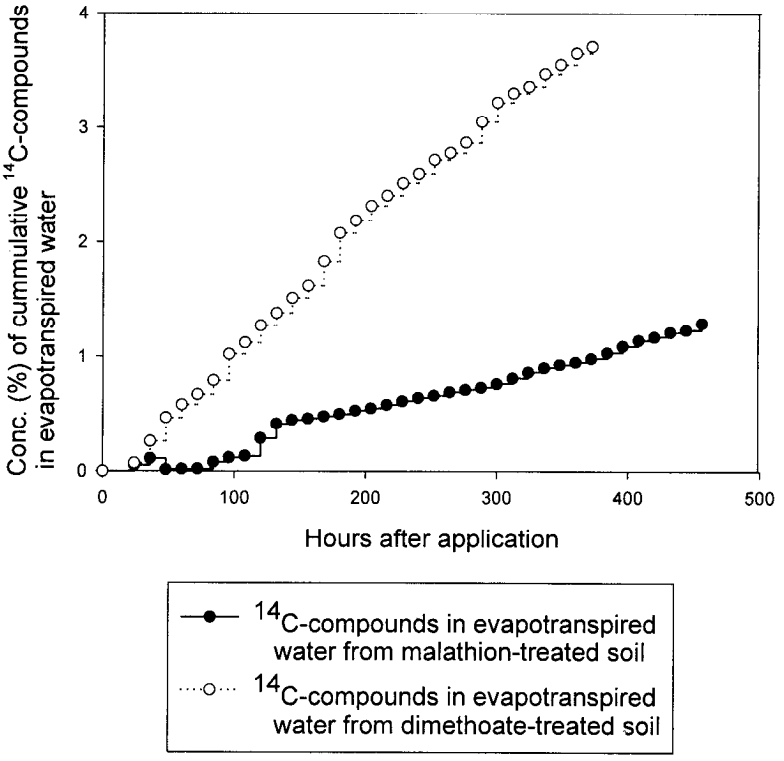

Figure 7. ^{14}C-compounds in the evapotranspired water

solubility in water is 143 ppm (Howard *et al.* 1991). Malathion is therefore more lipophilic than dimethoate and follows a symplastic pathway from the soil to reach the plant while dimethoate, which is less lipophilic, moves mainly by water mass flow through the apoplast (Sicbaldi *et al.* 1997). Figure 6 shows results of $^{14}CO_2$ produced from the soil when it was treated with the pesticides. Production of $^{14}CO_2$, from both pesticides is exponential although the initial production of the gas from dimethoate is higher and further releases of $^{14}CO_2$, ceases within 216 hours. The production of the gas from malathion in the soil increases slowly as time elapses. 192 hours later when the bound residues of malathion in the soil start decreasing, there is an upsurge in $^{14}CO_2$ production as shown in figure 6. The observation supports the earlier suggestion put forward to explain the decrease in bound residues of malathion in the soil as shown in figure 2. Production of $^{14}CO_2$ from dimethoate in the soil is as a result of mineralization of the extractable residues only.

Figure 7 shows results of the ^{14}C-compounds in evapotranspired water from the pea plant grown on the soil treated with the pesticides.

The concentration of the accumulated ^{14}C-compounds in evapotranspired water increases with time from plants grown on both malathion-treated and dimethoate-treated soils. There was higher concentration of the compounds in evapotranspired water from plants grown in dimethoate-treated soil. This is because of the higher solubility of dimethoate in water than that of malathion and due to the fact that dimethoate takes a shorter route to move from the soil to the leaves where evapotranspiration takes place. The low solubility of malathion in water and its longer pathway while moving from the soil to the leaves reduces its availability in the evapotranspired water.

The results show that dimethoate is more persistent than malathion in the soil. Faster dissipation of malathion is accelerated by the degradation of the bound residues, which would normally increase the persistence of a pesticide in the soil since they are sequestered in the soil. Malathion is not efficiently absorbed from the soil by the pea plant due to its low solubility in water and high log Ko/w. Dimethoate in the soil is readily available to the pea plant by water mass flow through the xylem.

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