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Degradation of Dacthal and Its Metabolites in Soil

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DCPA (dimethyltetrachloroterephthalate) or dacthal, a pre-emergence herbicide introduced in 1959 is used widely to control annual grass and certain broadleaf weeds in turf, ornamentals, agronomic crops and vegetables. DCPA has recently achieved notoriety by being the most common inadvertent residue detected in California (Ross et al. 1990) and the pesticide most frequently detected in a national groundwater survey (USEPA 1990). In eastern Oregon the use of DCPA in the production of onions has resulted in the contamination of an aquifer.

Although DCPA has a low vapor pressure, 2.5×10^{-6} mm Hg, its very low water solubility, 0.5 ppm (Wauchope et al. 1992) results in a Henry's Law Constant of significant magnitude that the problem of inadvertent residues has been attributed to evaporative loss (Ross et al. 1990). It is not the parent compound that is being detected in groundwater but the di-acid metabolite which has a solubility of 5780 ppm. Consequently the degradation kinetics in soil are determining in both situations. Hydrolysis to the acid metabolites will eliminate evaporative loss on the one hand and enhance the potential for movement to groundwater depending on the persistence of these metabolites.

The rate of degradation of the parent compound is influenced by temperature and soil moisture (Walker 1978). A half-life of 16.6 days was observed at 25°C and 12.6% water content. Decreasing the temperature to 5°C and the water content to 9.6% decreased the rate of degradation, giving a half-life of 289 days. A more recent study of Choi et al. (1988) confirmed these observations, reporting a half-life of 11-16 days at medium soil moisture (0.2 kg water per kg of soil) and 25°C. These investigators identified an optimum temperature range for degradation of 20-30°C. Increasing the temperature to 35°C reduced the degradation rate. These studies were concerned primarily with the herbicidal activity of the compound and focused on the degradation of the parent. The rate of production of metabolites and their stability has not been reported.

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This study was designed to define the rate of breakdown of DCPA in soil taken from fields in which onions had been raised. In addition the rate of formation and breakdown of the two acid metabolites was monitored.

MATERIALS AND METHODS

Soil used in the study was obtained from a field at the Malheur Experiment Station, Ontario Oregon in which onions had been raised. This soil had a cation exchange capacity of 23 meq/100 g, 1.59% organic matter and a pH of 8.1. After screening through a 20 mesh screen a portion of the soil was treated with DCPA in ethyl ether and mixed thoroughly. Twenty gram samples of treated soil were added to petri dishes along with 12 mL of water to achieve 50% of field capacity. The petri dishes were wrapped with polyethylene tape to minimize water loss. However the samples were monitored twice weekly to detect any water loss and additional water was added when necessary. Control, untreated samples were handled in similar fashion. Treated and control soil samples were held at room temperature (25°C) or at 38°C. At appropriate intervals 3 treated and 3 control samples were removed from storage. One control sample was used as a soil blank while the other two were spiked with either the parent or the di-acid metabolite to assess recovery efficiency.

Each sample was analyzed for the presence of the parent compound as well as the mono- and the di-acid metabolites. The 20 g soil samples were stirred with 100 mL of 0.4M HCl:acetone (20:80) making sure the pH was less than 2.0. After centrifuging, the supernatant was recovered and the residue extracted with another 100 mL of the HCl:acetone. The supernatants were combined, filtered and most of the acetone removed on a rotary evaporator. Water (100 mL) was added to the residual which was extracted with 3x100 mL aliquots of diethylether. The volume of the ether extracts was reduced to 10 mL, and treated with diazopropane to prepare the propyl esters. Hexane (10 mL) was added to the reaction mixture which was then transferred to a silica gel (4.5% de-activated) column and eluted with benzene (30 mL). The final solution was made up to volume with hexane and analyzed on a Varian Model 3700 gas chromatograph using a Supelco SPB-1 wide bore capillary column (30m x 0.75 mm i.d.) and a ^{63}Ni electron capture detector. The oven temperature was maintained at 205°C, the injection port at 250°C and the detector at 320°C. Column and sweep nitrogen flow was 18 and 25 mL per minute respectively.

RESULTS AND DISCUSSION

Resolution of the three esters derived from the parent and two metabolites is illustrated in Figure 1. Limits of detection for the 3 derivatives ranged from 10-15 picograms with recoveries of 74-85% being obtained. A linear response was demonstrated up 150 picograms.

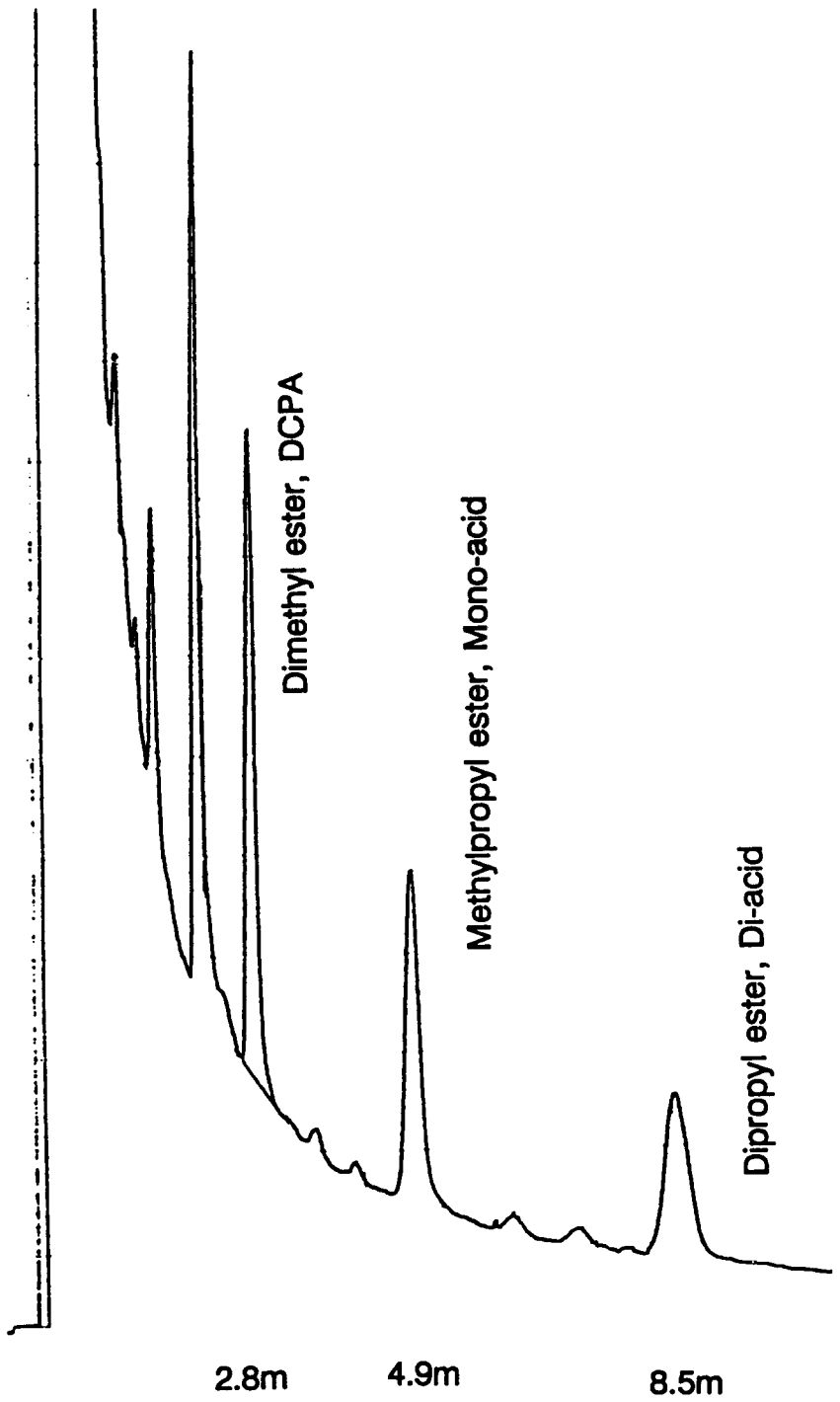

Figure 1. Chromatogram of standard dacthal and metabolites

The study was carried out using soil that had been treated with DCPA in order to avoid any adaptive lag etc. The control, unsupplemented soil contained a 2 ppm residual of the di-acid which was accounted for at each sampling. At room temperature the rate of loss of the parent compound was approximately linear for the first 30 days (Figure 2) with a half-life of 16 days consistent with previous observations (Walker 1978; Choi et al. 1988). Only small quantities of the mono-acid (0.1-0.2ppm) were detected indicating that the rate of degradation of this metabolite was much faster than that of the parent. In another study it was established that the mono-acid hydrolysed to the di-acid quite rapidly at room temperature. A first order rate constant of 0.247 ± 0.006 days^{-1} with a half-life of 2.8 ± 0.1 days was indicated. Mass balance calculations showed that little if any other metabolites were produced. The fact that virtually no loss of the di-acid metabolite could be demonstrated over 300 days is of obvious environmental significance.

At 38°C (Figure 3) the degradation of the DCPA was considerably slower as has been reported previously (Choi et al. 1988). The data conformed to a first order process with a rate constant of 0.0080 ± 0.0004 days^{-1} with a half-life of 86.6 ± 4.6 days. This decrease in rate with increase in temperature would suggest that a microbiological process was limiting. Any increase in the rate of direct hydrolysis expected with an increase in temperature was not sufficient to compensate for the loss of microbial activity. The di-acid metabolite was also very stable at the higher temperature over the 290 days.

In sterile soil (120°C for 30 min.) there was essentially no degradation of the parent compound over a 60-day period. On the other hand the mono-acid hydrolysed at essentially the same rate in sterile and non-sterile soil suggesting that this step could be mediated by microbial activity or direct chemical hydrolysis.

Despite the high pH of the soil which would tend to favor direct hydrolysis it would appear that microbial activity is responsible for the degradation of the parent. Decreased activity at higher temperatures and loss of activity in sterile soil would be consistent with this observation. Loss of activity with sterilization is not absolute proof of microbial involvement. Kearney and Kaufman (1967) have demonstrated that changes in activity can result from changes in soil structure produced by sterilization.

Hydrolysis of the mono-acid is rapid and can be effected by direct chemical process and it is assumed that microbial activity could also be involved. It is not surprising that this metabolite is susceptible to direct hydrolysis since it would be considerably more water soluble and available to react. The parent compound with a much lower solubility would be bound in soil and not readily available to the aquatic environment. It could however, partition into organisms where it would be subject to hydrolysis.

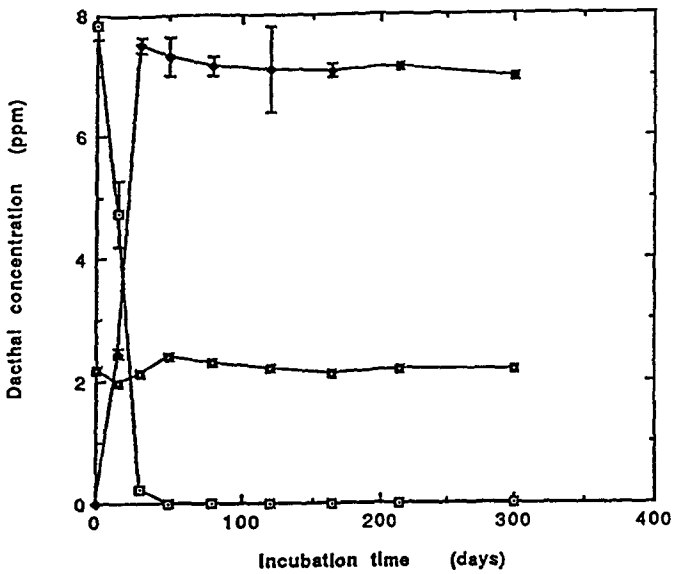

Figure 2. Degradation of dacthal at 25°C
⊡ dacthal, ◆ dacthal di-acid, ■ control

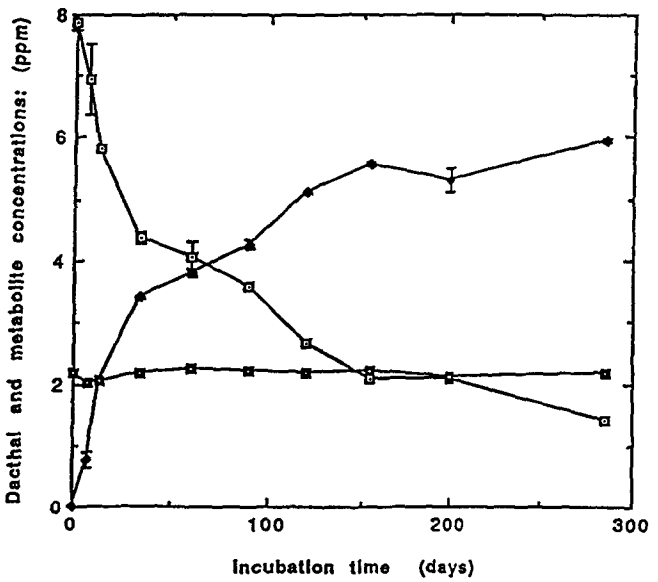

Figure 3. Degradation of dacthal at 38°C
⊡ dacthal, ◆ dacthal di-acid, ■ control

This study clearly demonstrates why the DCPA metabolite is being found in groundwater. The two major chemical factors which determine potential to move to groundwater are the K(oc) and the persistence in soil (Gustafson, 1989). The di-acid metabolite has a very low K(oc) associated with high water solubility and is very persistent both enhancing the tendency to be found in groundwater. Just how this metabolite might be further degraded is not apparent at this point.

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