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Dissipation and Transport of Clopyralid in Soil: Effect of Application Strategies

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ABSTRACT: At present there are no herbicide uses registered for broadleaf weed control in buckwheat. Clopyralid, mixed with desmedipham, was anticipated to provide early-season broadleaf weed suppression with minimal crop injury. However, field trials resulted in limited success, which brought into question the fate and availability of clopyralid for weed control. A 4-year field study was conducted in Lithuania to evaluate the dissipation of clopyralid in Haplic Luvisol sandy loam soil and the influence of application rate, application timing, and coapplication with desmedipham on its degradation and transport. Clopyralid dissipation was rapid; 50% dissipation times, in the surface 5 cm, averaged over the 4 years of the study, were <7 days. Application rate (90 versus 180 g ai ha^{-1}), timing (pre-emergence versus postemergence), and coapplication with desmedipham (360 g ai ha^{-1}) did not significantly influence clopyralid dissipation. Clopyralid dissipation by leaching was not a significant factor; at 7−21 days after application, <8 μg kg^{-1} was found at the 10−20 cm depth. Understanding the dissipation of herbicides and the influence of application strategies on herbicide fate will allow for informed decisions and improved efficacy of weed control. On the basis of the results of this research, weed scientists can now determine whether increased rates of clopyralid would provide sufficient residual chemical for adequate weed control without crop injury.

KEYWORDS: clopyralid, desmedipham, soil dissipation, leaching, buckwheat

INTRODUCTION

Clopyralid (3,6-dicloropicolinic acid or 3,6-dichloro-2-pyridine-2-carboxylic acid) is a selective systemic herbicide absorbed by plant leaves and roots and is used for postemergence control of many annual and perennial broad-leaved weeds in pastures, turf, and a variety of crops.[1] For broadleaf weed control in buckwheat in the Northern Plains of the United States or northern Europe, there are no currently registered herbicide uses. It was thought that clopyralid, an auxin-type herbicide, possibly mixed with desmedipham, a photosynthetic inhibitor-type herbicide, as an early low-dose application would provide early-season broadleaf weed control with limited crop injury.[2] However, application of clopyralid with or without desmedipham had limited success for early-season weed suppression in buckwheat.[2] The question arises as to whether clopyralid persisted long enough in the soil for early-season broadleaf weed control, particularly when applied at low rates. Clopyralid may have dissipated through transport or degradation processes to levels that would not provide weed suppression.

On the basis of laboratory experiments, clopyralid is considered to be relatively mobile and could be transported out of the zone for weed control. For instance, clopyralid has reported K_{oc} values ranging from 40 to 300 L kg^{-1}.[3−6] In a 6-year study using field lysimeters to characterize comparative leaching of clopyralid with pendimethalin, mecoprop, and dicamba following fall and spring application in soil cropped to winter rye, clopyralid was the most mobile of the tested herbicides.[7] Under a variety of climatic conditions, mass loss of clopyralid was <3% of the amount applied except for one season, in which sporadic leaching resulted in >20% loss of the fall-applied clopyralid. In contrast, in a study conducted in Sweden, Bergström et al.[8] reported that 24% of applied clopyralid remained 56 days after application (DAA) in the top 20 cm of soil; two samples of drainage water collected from lysimeters at a 1 m depth had detectable levels of clopyralid, presumably due to preferential flow in macropores. In another lysimeter study with overall precipitation and leachate amounts similar to those of the present study, no clopyralid was detected in leachate during the 11 month period following spring application.[9] However, other reports of clopyralid concentrations in lysimeter leachate at depths ≥50 cm[10,11] and at >1.5 m depths in lysimeter leachate and tile-drain effluent[12,13] following spring herbicide application have also been published.

In addition to transport processes, clopyralid can dissipate by microbial degradation processes.[5,14,15] Clopyralid degradation has been shown to be affected by temperature, soil properties, crop rooting characteristics, tillage, soil moisture, amount and timing of water application, and other factors. For instance, half-lives in laboratory incubation studies ranged from 44 days at 10 °C to 26 days at 30 °C in sandy loam soil and from 42 days at 10 °C to 10 days at 30 °C in a clay soil.[14] Ahmad et al.[15] found similar temperature responses in laboratory studies, half-life = 46 days at

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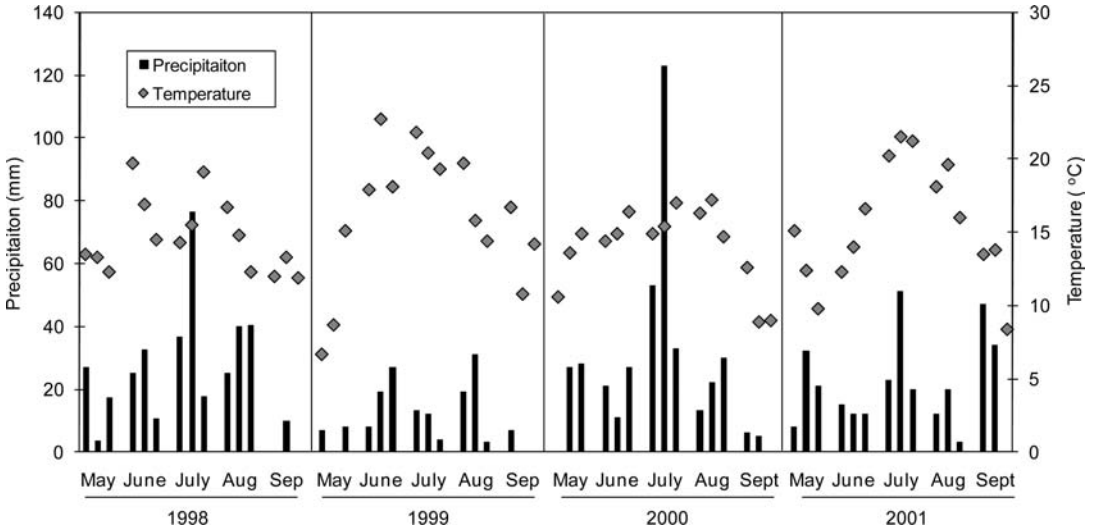

Figure 1. Air temperature (10 day averages) (diamonds) and precipitation (10 day totals) (bars) reported during the growing seasons of the experiment (May−September 1998, 1999, 2000, and 2001).

10 °C and 4 days at 30 °C. They also found field half-lives ranging from 5 to 72 days, depending on whether the field was pasture or bare ground and shaded or unshaded. In a field study, Pik et al.[5] found dissipation was fastest in moist soils with warm temperatures where there was least sorption, with half-lives ranging from ∼56 to >90 days.

In view of the wide range in published values for half-life under variable conditions, field dissipation studies were needed to determine whether clopyralid persisted long enough for adequate early-season broadleaf weed control in the cool climates of northern Europe. The objective of this four-year research project was to determine the soil dissipation of two rates of clopyralid, applied alone or combined with a single rate of desmedipham. Most applications were applied at the one true leaf stage of crop growth; however, one rate of clopyralid was applied pre-emergence (PRE) in two of the four years.

MATERIALS AND METHODS

Study Site. Experiments were conducted under natural climatic conditions from 1998 to 2001 at the Traku Voke Branch of the Lithuanian Institute of Agriculture. The surface soil (0−20 cm), a Haplic Luvisol sandy loam, had the following properties: pH 6.1; organic carbon (OC), 0.97%; total nitrogen (N), 0.13%; silt, 36%; and clay, 11%. The soil, which had no history of prior clopyralid use, was plowed to a depth of 20 cm in the fall and cultivated once in the spring prior to seeding with buckwheat (*Fagopyrum esculentum*) cultivar 'Smuglianka', which was planted in late May at a rate of 80 kg ha^{-1}. Winter rye was the crop prior to buckwheat in 1998, 2000, and 2001, whereas in 1999 buckwheat followed buckwheat. Fertilizer was applied annually at a rate of 30/60/60 kg ha^{-1}, $N/P_2O_5/K_2O$, after spring cultivation. Additional details of the study location and experimental conditions can be found elsewhere.[2]

Pesticide Application. In each of the four years, clopyralid (formulated as Lontrel 300) was applied at 90 or 180 g ai ha^{-1} postemergence (POST), with or without desmedipham at 360 g ai> ha^{-1} (formulated as Betanal AM). In 2000 and 2001, clopyralid was also applied pre-emergence (PRE) alone at 180 g ha^{-1} (not incorporated). POST treatments were applied when buckwheat was at the one true leaf stage, in early June, whereas PRE applications occurred in late May. The herbicides were applied with a backpack or bicycle sprayer having nozzles 50 cm on center and calibrated to deliver 200 L ha^{-1} of spray solution at 276 kPa. Individual treatment areas were 50 m^2.

The experimental design was a randomized complete block with each treatment replicated four times annually. Analysis of variance and least-squares means were used to evaluate significant differences between treatments: application rates of clopyralid, 90 versus 180 g/ha, applied with or without desmedipham; application timing, one-leaf stage of crop growth versus prior to emergence of the crop.

Sample Collection and Extraction. Multiple soil core samples were collected using a 5 cm diameter split core sampler from each treatment area (50 m^2) at 1, 7, 14, and 21 DAA. At the completion of the sampling day, soil cores were divided into three layers by depth (0−5, 5−10, and 10−20 cm), air-dried overnight to allow for uniform mixing, and composited by depth into one sample for each treatment replicate. Composite soils were stored at −25 °C (<180 days) until thawed for extraction (stored at 4 °C <10 days).

The extraction method from soil was similar to that previously used for plant material.[7] Clopyralid was extracted from the soil (20 g) using 1 N NaCl solution (50 mL) and 0.1 N NaOH solution (6 mL). After 1 h of shaking in a horizontal shaker, the samples were centrifuged at 3000 rpm for 30 min and the supernatant was decanted. The soil was extracted again as described above, and the decantates were combined, acidified to pH <2 with 50% H_2SO_4, and then extracted three times with 3.0 mL of ethyl acetate by liquid−liquid extraction. The combined extracts were dried with anhydrous Na_2SO_4, and the sample was then evaporated at 40 °C to ∼0.5−1.0 mL using a vacuum rotary evaporator. The remaining solution was evaporated just to dryness with an air stream.

Analysis. Analysis of clopyralid was the same as previously reported for plant and water samples.[7] Derivatization of clopyralid to the ethyl ester of 3,6-dichloropicolinic acid was performed by adding 1.0 mL of concentrated H_2SO_4 and 5.0 mL of ethanol, briefly shaking the solution, and then heating the sample for 15 min at 70 °C in a water bath. The solution was then cooled to room temperature, and after slight shaking with 1.0 mL of *n*-hexane, the aqueous and organic phases were separated and the organic phase was retained for analysis. Derivatization of analytical standards and samples was performed at the same time.

Gas−liquid chromatographic analyses of the ethyl ester of clopyralid were performed using a Hewlett- Packard model 5890, equipped with an electron capture detector and a 30 m long × 0.32 mm diameter × 0.25 μm film thickness 5% phenyl−methyl silicone (HP-5) column. Carrier gas (N_2) flow rate was 35 mL min^{-1}. Clopyralid analysis used an

injection port temperature of 220 °C, a detector temperature of 240 °C, and an oven temperature starting at 70 °C, followed by an increase of 30 °C min^{-1} to 180 °C, and held for 10 min. The retention time of the ethyl ester of 3,6-dichlorpicolonic acid was 6.5−7.8 min. Quantitation used external standards. The limit of quantification was 5 $\mu g\ kg^{-1}$ in soil. Recoveries of clopyralid standards ranged from 85% (at 5 $\mu g\ kg^{-1}$) to 102% (at 100 $\mu g\ kg^{-1}$).

Calculations and Statistical Analyses. The dissipation of clopyralid was calculated on the basis of first-order kinetics using the equation

$$ln\ C = ln\ C_0 - kt \quad (1)$$

where C_0 is the initial concentration, C is the concentration of clopyralid after time t, and k is the first-order rate constant.[16] The natural log of concentrations of extractable clopyralid was plotted against time of sampling (1, 7, 14, and 21 DAA) to give a straight line with a slope proportional to the rate constant. Time for 50% dissipation (DT_{50}) was calculated by using the formula

$$DT_{50} = 0.693/k \quad (2)$$

RESULTS AND DISCUSSION

Climate Conditions. Monthly air temperatures from 1998 through 2001 were similar to the 30-year average.[7] Air temperatures ranged from 7 to 23 °C during the growing seasons (May−September) with averages of 15 ± 2 °C in 1998, 16 ± 5 °C in 1999, 14 ± 3 °C in 2000, and 16 ± 4 °C in 2001 (Figure 1). Precipitation was variable during the study with 361, 158, 399, and 310 mm of rainfall measured during the summer growing season (May−September) for 1998, 1999, 2000, and 2001, respectively (Figure 1). Total precipitation for May and June, the time when soil residues of clopyralid were present, was 116 mm in 1998, 69 mm in 1999, 114 mm in 2000, and 100 mm in 2001.

Clopyralid Dissipation in Soil. *Effect of Application Rate (Figure 2).* The greatest concentrations of clopyralid (mass of clopyralid (μg) per dry weight mass of soil (kg)) were found at the 0−5 cm soil depths 1 DAA, which ranged from 36 to 95 $\mu g\ kg^{-1}$ for the 90 g ai ha^{-1} application and from 78 to 243 $\mu g\ kg^{-1}$ for the 180 g ai ha^{-1} application over the 4 years; these respectively represented 83 ± 15 and 91 ± 5% of the clopyralid residues measured 1 DAA to a 20 cm depth (Figure 2). Trace amounts (<7 $\mu g\ kg^{-1}$) of clopyralid were found at the 10−20 cm depth 1 DDA in 1998 and 2001. In both years clopyralid was applied to wet soil in contrast to 1999 and 2000 when clopyralid was applied to very dry soil. For those two years, during the 24+ h after application until sampling, some clopyralid may have diffused to a depth of >10 cm. However, the low detections may have also been an artifact of the sampling protocol as a result of very wet soil conditions.

Clopyralid dissipated rapidly; at 21 DAA, the percentage of applied clopyralid measured at the 0−20 cm depth dropped to <10% of applied chemical with no observed accumulation at lower depths: 90 g ai ha^{-1} application, 5 ± 4% in 0−5 cm, 3 ± 3% in 5−10 cm, 2 ± 3% in 10−20 cm; 180 g ai ha^{-1} application, 7 ± 2% in 0−5 cm, 4 ± 3% in 5−10 cm, 1 ± 2% in 10−20 cm. The times required for half of the applied clopyralid to dissipate (DT_{50}) from the top soil (0−5 cm) and soil column (0−20 cm) were statistically similar for the 90 and 180 g ai ha^{-1} application rates; DT_{50} values ranged from 5.2 to 6.5 days, with the exception

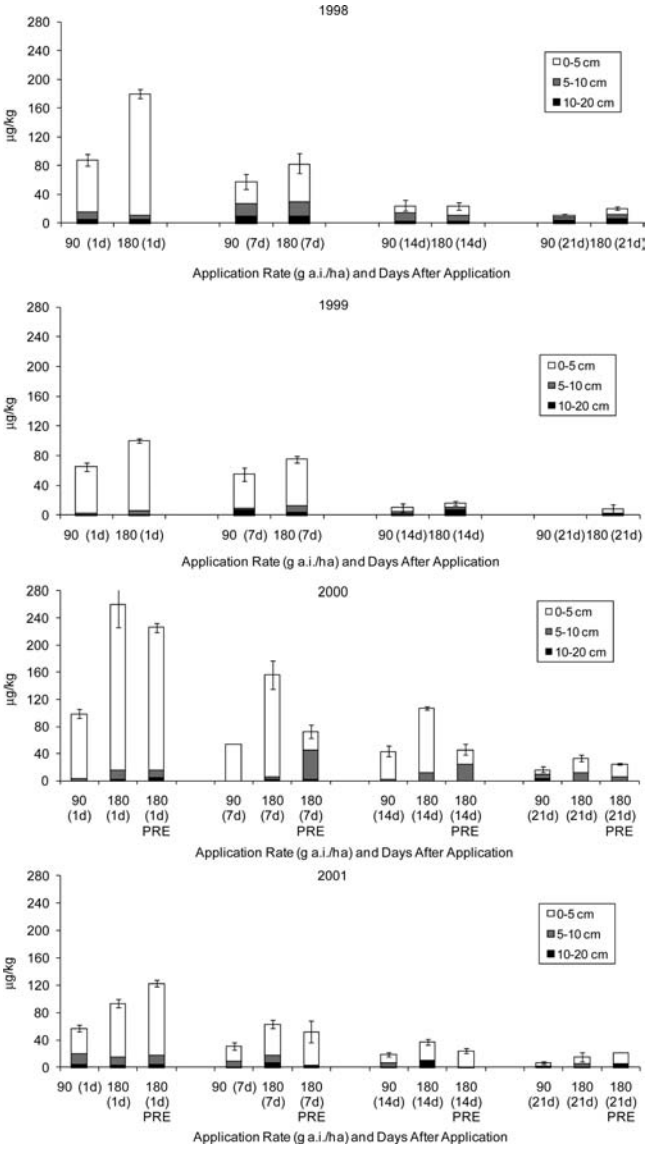

Figure 2. Dissipation and transport of clopyralid as influenced by application rate (90 versus 180 g ai ha^{-1}) and application timing (pre-emergence (PRE) = late May prior to emergence of buckwheat; post-emergence (all data not labeled PRE) = early June when buckwheat was at the one true leaf stage). Pesticides were applied using a backpack or bicycle sprayer. Variations in pesticide application rates from year to year resulted from variations in the operator's application speed or technique.

of the 0−20 cm soil column at 90 g ai ha^{-1} (DT_{50} = 13.9 days) (Table 1).

Influence of Application Timing. Application of clopyralid prior to buckwheat emergence (pre-emergence, PRE, late May) or shortly after buckwheat emergence (one true leaf stage, postemergence, POST, early June) had no influence on the dissipation rate of clopyralid in the top soil (0−5 cm) or the soil column (0−20 cm) (Table 1; Figure 2). At 21 DAA the percentages of applied clopyralid measured in the soil column (0−20 cm) were 14 ± 5 and 14 ± 2% for PRE and POST, respectively (PRE, 11 ± 3% in 0−5 cm, 2 ± 1% in 5−10 cm, 2 ± 3% in 10−20 cm; POST, 9 ± 1% in 0−5 cm, 6 ± 1% in 5−10 cm, < 1% in 10−20 cm). DT_{50} values were not significantly different for dissipation for PRE and POST clopyralid

Table 1. Time (Days) for 50% Dissipation of Clopyralid in 0−5 and 0−20 cm Soil When Applied at Two Rates with or without Desmedipham Post- and Pre-emergence[a]

	postemergence application				pre-emergence application
	clopyralid (90 g/ha)		clopyralid (180 g/ha)		
soil depth (cm)	desmedipham (0 g/ha)	desmedipham (360 g/ha)	desmedipham (0 g/ha)	desmedipham (360 g/ha)	desmedipham (0 g/ha)
0−5	5.2 ± 1.6 a[b]	6.0 ± 2.7 ab	5.2 ± 1.2 a	5.3 ± 1.2 a	6.9 ± 0.7 ac
0−20	13.9 ± 2.5 d	7.2 ± 1.9 bce	6.5 ± 1.2 ae	6.4 ± 1.4 ae	7.3 ± 0.9 bce

[a] Average DT_{50} value ± standard deviation (days) reported in 1998, 1999, 2000, and 2001. [b] DT_{50} values followed by the same letter are not statistically different ($p = 0.05$).

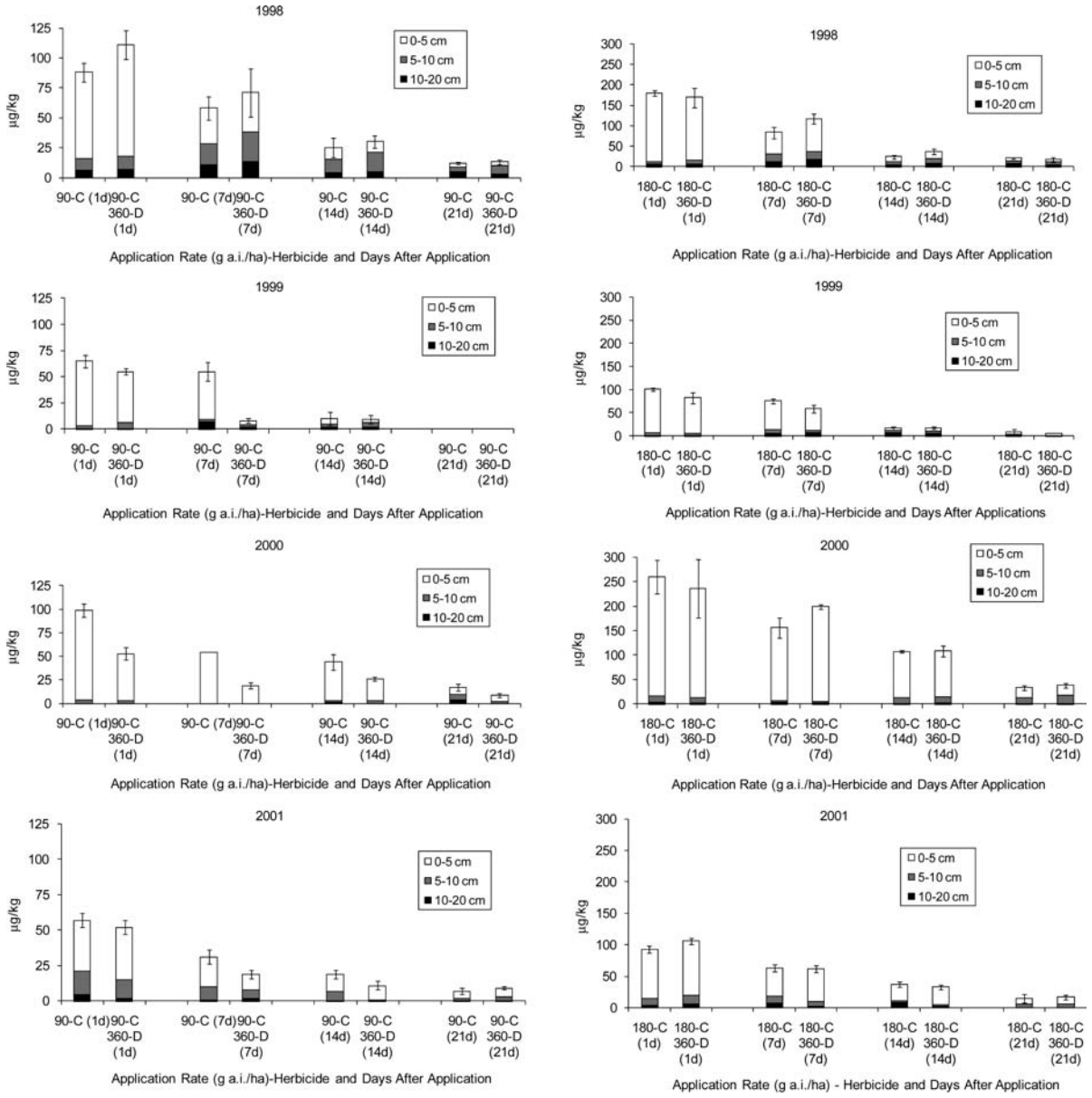

Figure 3. Dissipation and transport of clopyralid (C) as influenced by application rate (90 or 180 g ai ha^{-1}) with or without simultaneous application of desmedipham (D, 360 g ai ha^{-1}). Pesticides were applied using a backpack or bicycle sprayer. Variations in pesticide application rates from year to year resulted from variations in the operator's application speed or technique.

application in the 0−5 cm (6.9 versus 5.2 days) or the 0−20 cm (7.3 versus 6.5 days) soil depths.

Coapplication with Desmedipham. Simultaneous application of the active ingredient desmedipham with clopyralid had no

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significant effect on the dissipation of clopyralid in the sandy loam soil (Figure 3). With one exception (clopyralid at 90 g ai ha^{-1} and desmedipham at 0 g ai ha^{-1}, 0−20 cm soil depth) the DT_{50} for clopyralid was <10 days regardless of the application of clopyralid alone (90 or 180 ai ha^{-1}) or with 360 g ai ha^{-1} desmedipham (Table 1). At 21 DAA the percentages of applied clopyralid measured at different depths in the soil column were similar with or without the concurrent application of desmedipham: 90 g ai ha^{-1} clopyralid, 0−5 cm, 5 ± 4% [clopyralid, C] versus 5 ± 6% [clopyralid and desmedipham, C + D], 5−10 cm, 3 ± 3% [C] versus 4 ± 3% [C + D], 10−20 cm, 2 ± 3% [C] versus 1 ± 2% [C + D]; 180 g ai ha^{-1} clopyralid, 0−5 cm, 7 ± 2% [C] versus 7 ± 3% [C + D], 5−10 cm, 4 ± 2% [C] versus 3 ± 3% [C + D], 10−20 cm, 1 ± 2% [C] versus 1 ± 1% [C + D].

Comparative Dissipation. In general, dissipation has been shown to be dependent on soil type and climatic conditions. In a Swedish field dissipation study, which had daily maximum and minimum temperatures of 15−25 and 5−12 °C, respectively, when clopyralid was applied at 120 or 240 g ha^{-1}, there was very little dissipation in the top 30 cm soil during the first 30 days after application.[8] At 56 DAA in a clay soil 11 and 24% of applied chemical were present in the 0−10 and 10−20 cm soil depths, respectively. In a clay loam soil, there was less dissipation at 56 DAA as compared to the clay soil. In a Canadian study of clopyralid at locations with different soil types, temperatures, and moistures, disappearance ranged from rapid (56−84 days) in two soils to slow (385 days) in another soil at the same location; at a separate location with cooler, drier conditions, however, 40% of the applied clopyralid remained in soil after the end of the second growing season.[5]

In New Zealand, half-lives varied from 24 to 72 days in shaded bare ground and pasture, respectively,[15] whereas >99% of the applied chemical dissipated in 90 days in Texas.[10] In contrast, in 3 of the 4 years of the present study, average May and June temperatures were 13 and 15 °C, respectively, yet DT_{50} in the upper 20 cm of soil ranged from 6 to 13 days, regardless of the applied amount, timing, or coapplication with desmedipham.

Dissipation from surface soils in some field studies has been attributed as previously discussed to preferential flow leaching through macropores.[8,12,13] Dissipation through leaching does not appear to be a significant process. In a companion field lysimeter study, <1% of applied clopyralid was found in leachate at a 1 m depth.[7] Also, there were no precipitation events greater than 33 mm within 21 DAA; the largest rainfalls occurred in July (1998, 76 mm; 2000, 123 mm; 2001, 51 mm; the exception was 1999, with largest rainfall of 31 mm in August).

It appears that despite the cool, moist conditions after application, the rapid dissipation was due to microbial degradation as previously reported by others.[5,14,15] Degradation is dependent on the availability of the pesticide to the degrading microorganism and the presence and activity of a degrading microbial population. The short DT_{50} values were presumably due to a population of active microbial degraders. These results help explain the limited success for early-season weed suppression by clopyralid in buckwheat.[2] Further research is needed to determine whether increased rates of clopyralid can persist long enough for early-season broadleaf weed control without affecting buckwheat tolerance.

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