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Effect of Soil Conditions on the Degradation of Cloransulam-Methyl

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ABSTRACT

Herbicide efficacy and environmental fate are often controlled by soil conditions. Aerobic soil laboratory studies were undertaken to determine the degradation of the herbicide cloransulam-methyl [*N*-(2-carbomethoxy-6-chloro-phenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo [1,5-*c*]pyrimidine-2-sulfonamide] for a range of soil factors. Treatments included soil temperature (5, 15, 25, 40, and 50°C), moisture (20, 40, and 60% water filled pore space), and soil type. The soils under study were a Drummer silty clay loam (fine-silty, mixed, superactive, mesic Typic Endoaquolls) and a Cisne silt loam (fine, smectitic, mesic Vertic Albaqualfs). Variability in molecular degradation was investigated using two radiolabeled forms ([*Phenyl*-UL-^{14}C] and [*Pyrimidine*-7,9-^{14}C]). Dissipation of parent compound in soil solution and sorbed phases, formation of radiolabeled metabolites, ^{14}C mineralization, total microbial respiration, and bound residue formation were measured for up to 120 d. Dissipation of parent and formation of bound residues in Drummer soil increased with greater temperatures. The influence of temperature on ^{14}C mineralization, however, was dependent on position of radiolabel, suggesting that distinct groups of microorganisms degrade different parts of the molecule at higher temperatures. Only ^{14}C mineralization was influenced by moisture, with response depending on soil type. Increasing moisture resulted in more ^{14}C mineralization in Drummer, but not Cisne soil, which was attributed to increased microbial access to pesticide at greater moisture contents in Drummer soil. Reduced availability, suggested by greater sorption in Drummer soil, may explain persistence of parent in this soil. Bound residues were more extensive and exhibited greater dependence on biological activity in Cisne soil, owing to enhanced dissipation of parent compound in this soil.

CLORANSULAM-METHYL [*N*-(2-carbomethoxy-6-chloro-phenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo [1,5-*c*]pyrimidine-2-sulfonamide] (CAS Registry No. 147150-35-4), recently developed for the control of broadleaf weeds in soybean [*Glycine max* (L.) Merr.], is a triazolopyrimidine sulfonamide herbicide (Fig. 1) that functions by inhibition of the plant enzyme acetolactate synthase (ALS). Notable characteristics of the compound include a low application rate (label rates of 17.5 and 44 g ha^{-1}, preplant and preemergent, respectively), low pK_a (4.81), a short half-life ($t_{1/2}$ = 13–28 d), solubility in water of 184 mg L^{-1} (pH 7), and apparent K_d ranging from 0.19 to 4.89 L kg^{-1} (Wolt et al., 1996). Little published data, with limited degradation studies, exist on the behavior of cloransulam-methyl, making this research important for understanding the environmental fate of this new xenobiotic compound.

The study of herbicide degradation and fate is vital for both maintaining environmental quality and optimizing agricultural practices. Herbicidal activity and environmental behavior are both affected by the influence of environmental conditions on soil processes. Herbicide fate processes (e.g., sorption and desorption, volatilization, chemical hydrolysis, biodegradation, and bound residue formation) exhibit variability that can be dependent on factors such as soil temperature, moisture, redox potential, and pH. Of general importance are data relating the effects of moisture and temperature conditions on fate of xenobiotics in soil.

Temperature responses for environmental fate processes are variable, and range from temperature independence observed for some sorption phenomena (Hassett and Banwart, 1989) to hyperbolic (Mervosh et al., 1995a) or exponential functions (Lemley et al., 1988). Temperature optima are often associated with biological systems, whereas chemical processes generally exhibit exponential increases with temperature. For example, an Arrhenius plot of mesophilic bacterial growth in pure culture exhibited a response maximum at approximately 40°C, with reduced rates at higher and

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lower temperatures (Ingraham, 1958). Thus, pesticide degradation controlled by biological factors would be expected to display temperature optima.

The relative importance of chemical and biological degradative processes can be investigated by examining activation energy values from degradation studies over a range of temperatures. The activation energy is obtained by regressing the natural logarithm of the rate constant against $1/t$ according to the Arrhenius equation:

$$\ln K = -(E_a/RT) + \ln A$$

Where K is the degradation rate constant, A is an empirical constant, t is temperature (K), R is the universal gas constant (8.3145 J K^{-1} mol^{-1}) and E_a (kJ mol^{-1}) is the activation energy for the reaction. The temperature responsiveness of various degradation mechanisms has been characterized using the E_a of the system (Burnside, 1965; Hance, 1967; Lemley et al., 1988). Activation energy values greater than 60 kJ mol^{-1} are frequently reported for chemical and physical reactions of xenobiotics in soil (Burnside, 1965; Hance, 1967; Lemley et al., 1988), whereas biological reactions typically result in E_a values less than 30 kJ mol^{-1} (Meikle et al., 1973; Thirunarayanan et al., 1985). Meikle et al. (1973) suggested that the catalytic nature of biological reactions results in a lower energy requirement and hence, a diminished response to temperature. An objective of this study is to determine temperature dependence of cloransulam-methyl dissipation mechanisms.

Soil moisture content affects both biological and abiotic environmental fate processes. A general trend of reduced degradation rates at low moisture contents has been observed for many pesticides, such as picloram (Meikle et al., 1973), imazaquin and imazethapyr (Flint and Witt, 1997), trifluralin (Zimdahl and Gwynn, 1977), clomazone (Mervosh et al., 1995a), and chlorsulfuron (Thirunarayanan et al., 1985). Factors such as limited diffusion of the substrate (xenobiotic), increased toxicity (higher solution concentration), and greater sorption at low moisture contents may result in less dissipation. At low enough water contents, physiological constraints result in reduced or no microbial activity, leading to retarded degradation, whereas reduced availability of oxygen may occur at higher moisture contents (Helweg, 1987; Flint and Witt, 1997). Therefore, aerobic microbial activity is often maximal at a water content where substrate diffusion and oxygen supply are optimized (Skopp et al., 1990). Abiotic processes, such as sorption, transport, and volatilization, may also be dependent upon diffusion kinetics, and thus are also expected to respond to water content. This study investigates the importance of soil moisture on cloransulam-methyl fate processes, including dissipation of parent in sorbed and solution pools, bound residue formation, and mineralization, using a range of moisture contents optimal for soil microbial activity.

Sorption of hydrophobic organic compounds is usually greater in soils with more organic carbon, often resulting in bioavailability limitations for pesticide degradation (Sims et al., 1991, 1992). Though hydrophobic sorption may be intrinsically temperature-independent at equilibrium (Hassett and Banwart, 1989), the extent of sorption and resulting bioavailability constraints may be strongly influenced by temperature in the nonequilibrium conditions present in unsaturated soils (Mervosh et al., 1995b). Owing to sorption nonequilibrium, the solution phase is typically depleted, preferentially over the sorbed phase in unsaturated soils (Mervosh et al., 1995b). However, movement of substrates into inaccessible pore space may be more important than sorption in limiting bioavailability in many soils (Pignatello, 1989). The relative importance of physical inaccessibility in xenobiotic biodegradation appears to be a function of water content (Johnson et al., 1998). The role of bioavailability in soil degradation of cloransulam-methyl was investigated as a function of temperature and moisture.

The degradative characteristics of cloransulam-methyl have not been extensively determined in relation to temperature and soil moisture. The goal of this research was to demonstrate the important dissipation mechanisms of the xenobiotic cloransulam-methyl through soil pools and the influence of soil temperature and moisture on these processes and pathways. The study employs a range of moisture conditions throughout which bioavailability constraints should be more important than physiological stress (Harris, 1981; Skopp et al., 1990) and temperature conditions spanning the range expected at or near the soil surface where the pesticide is applied.

MATERIALS AND METHODS

Chemicals

Two forms of [^{14}C]cloransulam-methyl were utilized: [*Phenyl*Phenyl-UL-^{14}C] (1.24 × 10^6 Bq $mmol^{-1}$, radiochemical purity 96.9%) and [*Pyrimidine*-7,9-^{14}C] (1.23 × 10^6 Bq $mmol^{-1}$, radiochemical purity 98.1%). Labeling patterns are depicted in Fig. 1. The primary impurity in both labeled samples was cloransulam, which is formed by hydrolysis of the methyl ester group and is the most important transformation product in soil or water (Wolt et al., 1996). These compounds, along with

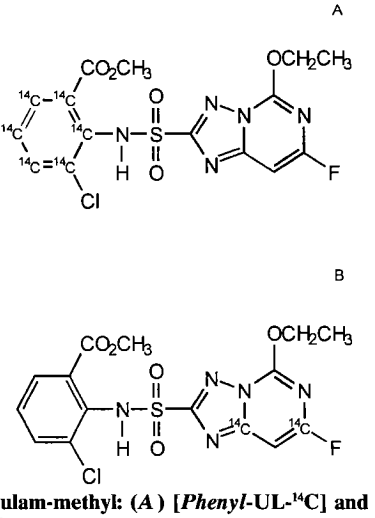

Fig. 1. Cloransulam-methyl: (*A*) [*Phenyl*-UL-^{14}C] and (*B*) [*Pyrimidine*-7,9-^{14}C].

analytical grade cloransulam-methyl and metabolites (purity > 98%), were gifts from Dow AgroSciences, Indianapolis, IN. Organic solvents and water were Optima grade (Fisher Scientific, Pittsburgh, PA).

Soils

Soils included the top 10 cm of both a Drummer silty clay loam, collected near Champaign, IL, and a Cisne silt loam, collected from Brownstown, IL. Soil was sieved through a 4-mm screen, mixed, and stored at 5°C. Soil properties are described in Table 1.

Experimental Design

Temperature and Moisture

Degradation of cloransulam-methyl [*Phenyl*-UL-^{14}C] was measured in soil as a function of temperature and moisture conditions. Herbicide was applied at a rate of 138 ng g soil^{-1} (equivalent to a field application rate of 35 g ha^{-1} as described by Wolt et al., 1996). Only the Drummer soil was subjected to a range of temperatures (5, 15, 25, 40, and 50°C) in this study. Both Drummer and Cisne soils were subjected to a range of moisture contents (20, 40, and 60% water filled pore space, WFPS) by addition of 0.09, 0.20, and 0.30 kg H_2O kg^{-1} for the Drummer soil and 0.08, 0.17, and 0.25 kg H_2O kg^{-1} for the Cisne soil. In each experimental treatment, field moist soils (equivalent to 50 g air-dry material) were added to triplicate mason jar biometers to produce a bulk density of approximately 1.2 g cm^{-3} (Mervosh et al., 1995a). Soils were spiked with the herbicide (in 100 μL methanol) then gently mixed (approximately 1 min). Each jar was fitted with a glass vial containing 10 mL 0.2 *M* NaOH to trap CO_2. Soils in the temperature study were extracted at 0, 2, 7, 14, 28, and 56 DAT (days after treatment) and soils from the moisture study were extracted at 0, 2, 7, 14, 28, and 96 DAT, as described in the analytical section. Also, CO_2 traps from both studies were sampled weekly. Analysis included determination of: parent and radiolabeled degradation products in soil solution and sorbed phases, ^{14}C mineralization, formation of bound residues (unextractable ^{14}C), and total microbial respiration.

Radiolabel Position

Drummer soil samples (equivalent to 50 g air-dry material) were spiked separately with both forms of labeled cloransulam-methyl (in 100 μL methanol) and Cisne soil samples received [*Phenyl*-UL-^{14}C] only. Herbicide applications were 242 ng g soil^{-1} for [*Phenyl*-UL-^{14}C] and 293 ng g soil^{-1} for [*Pyrimidine*-7,9-^{14}C]. Herbicide was applied at three temperatures (5, 25, and 50°C), in triplicate. The CO_2 traps were sampled weekly for analysis of ^{14}C mineralization as described below.

Sterile Controls

Sterile conditions were achieved by subjecting Drummer and Cisne soils to radiation from a ^{60}Co source with a total exposure of 6 Mrad in a dose applied over 2 h (Isomedix, Chicago, IL). Sterility was verified at the end of the incubation by dilution plate counting on agar containing 0.8 g nutrient broth L^{-1} (Difco Laboratories, Detroit, MI). Both sterile and nonsterile Drummer and Cisne soils were spiked with cloransulam-methyl at a rate of 242 ng g soil^{-1} [*Phenyl*-UL-^{14}C]. Herbicide was applied at three temperatures (5, 25, and 50°C), in triplicate. At 2, 8, 26, and 40 DAT soils were prepared for bound residue analysis by organic solvent extraction, and the NaOH traps were sampled weekly. Only ^{14}C mineralization and bound residue formation were investigated in this study.

Sorption Isotherm

An equilibrium batch sorption isotherm study was conducted with the Cisne and Drummer soils. Soils were air-dried and sieved to pass through a 0.23-mm screen. A 1:4 soil to solution ratio was used (2.5 g soil and 10 mL solution). Solution phase consisted of 0.01 *M* $CaCl_2$, with one of four cloransulam-methyl [*Pyrimidine*-7,9-^{14}C] concentrations (21, 26, 54, and 83 ng mL^{-1}). Soil and solution were mixed for 24 h on a horizontal reciprocating shaker at 25°C. Preliminary studies had shown that 24 h was a sufficient mixing time to reach equilibrium and that cloransulam-methyl did not degrade during this time (verified by high pressure liquid chromatography [HPLC] as described below). The samples were centrifuged for 10 min at 7800 *g* and two 1-mL aliquots analyzed via liquid scintillation spectrometry (LSS) for total radioactivity.

Analytical Methods

Extraction

At each sampling time triplicate soil samples, ranging from 1.5 to 10 g, were placed in separate Teflon centrifuge tubes and 0.01 *M* $CaCl_2$ solution (containing 50 mg L^{-1} $HgCl_2$ as an inhibitor) was added to each to obtain a 1:1 ratio of soil to solution. Soil sample size was increased to 10 g to improve cloransulam-methyl detection at later sample dates. The tubes were placed on a shaker for 24 h and then centrifuged at 7800 *g* for 5 min to remove solids. Based on a preliminary study, a reproducible endpoint was obtained by repeating the extraction process two additional times. This extract is subsequently referred to as the solution pool. An organic extraction (ace-

Table 1. Properties of Cisne silt loam and Drummer silty clay loam.

Select chemical properties†			Exchangeable nutrients†		Base saturation†		Moisture release curve‡		Particle size fraction†	
Property	Units	Value	Nutrient	Concentration	Element	Fraction of CEC	Pressure	Moisture	Size fraction	%
				mg kg^{-1}			M Pa	%		
Drummer										
OC¶	g kg^{-1}	17	P	6	H		−0.03	26.3	Sand	19
pH		7.5	K	101	K	1.3	−0.1	21.2	Silt	45
SMP¶			Mg	650	Mg	27.5	−0.5	18.0	Clay	36
CEC¶	cmol kg^{-1}	19.7	Ca	2800	Ca	71.2	−1.5	15.2		
Cisne										
OC	g kg^{-1}	10	P	15	H	4.5	−0.03	25.6	Sand	19
pH		6.7	K	82	K	2.8	−0.1	18.3	Silt	55
CEC	cmol kg^{-1}	7.6	Ca	1100	Ca	72.0	−1.5	9.2		

† Analyses performed by A&L Laboratories, Ft. Wayne, IN.
‡ Performed as described by Klute (1986).
¶ OC, organic carbon (w/w); SMP, buffer pH; CEC, cation exchange capacity.

tone to water to acetic acid 99:0.5:0.5 [v/v/v] for the temperature study and acetone to water 80:20 [v/v] with 0.01% acetic acid for other studies) was carried out in the same manner. The organic extract, minus the solution pool, is subsequently referred to as the sorbed pool. Extracts were filtered though a 0.45 μm PTFE filter (Alltech Associates, Deerfield, IL). Water extracts underwent solid phase extraction (Alltech Vacuum Manifold, Extract-Clean C_{18} 200 mg columns) followed by resuspension in 2 mL water and acetonitrile (60:40). These samples, as well as the organic extracts, were then evaporated (Pierce Reacti-Therm Heating Module, Rockford, IL) and made up to a specified volume (300–500 μL) with the latter acetonitrile solution.

Extraction Analysis

Cloransulam-methyl and radiolabeled degradation products were determined with reverse phase radiochromatic HPLC (Hewlett Packard Series 1050, San Fernando, CA) equipped with a Flow Scintillation Analyzer 500TR Series (Packard Instrument Company, Meriden, CT). Conditions were: injection volume, 0.2 mL; mobile phase flow rate, 1 mL min^{-1}; UV detector wavelength, 274 nm. We used a 5 × 250 mm reverse phase C_{18} column (Alltech Econosil C_{18}) and Ultima Flo M cocktail (Packard Instrument Company, Meriden, CT). A multiple-step mobile phase gradient of acetonitrile and water was used to facilitate separation of parent compound from degradation products. The gradient (% water/% acetonitrile) was as follows (gradient change was linear during unspecified time intervals): 0 to 3 min, 100/0; 8 to 13 min, 60/40; 16 to 18 min, 0/100; 21 to 24 min, 100/0. Total radioactivity present was determined by adding 15 mL of Biosafe II (Research Products International Corp., Mt. Prospect, IL) to 50 μL of concentrated extract and then using LSS (Packard 1900TR liquid scintillation analyzer, Packard Instrument Company, Meriden, CT).

Bound Residue Analysis

Total ^{14}C in soil was determined by combusting three 0.3-g subsamples of dried, extracted soils (organic solvent extraction) from each biometer in a Harvey OX-500 biological oxidizer that trapped $^{14}CO_2$ in ^{14}C cocktail (R.J. Harvey Instrument Corp., Hillsdale, NJ). The cocktail sample was then analyzed using LSS.

Mineralization and Respiration

The CO_2 traps were analyzed for ^{14}C mineralization of radiolabeled herbicide and degradation products by LSS with correction for chemiluminescence. Microbial respiration in soil was determined by titration of 1-mL samples from NaOH traps as follows: carbonate was precipitated with 0.5 mL of 1.5 *M* $BaCl_2$ and the unreacted NaOH was titrated with 0.1 *M* H_2SO_4, using phenolphthalein as an indicator (Anderson, 1982).

Statistical Analysis

Statistical analyses were conducted using SAS (SAS Institute, 1996) and the data analysis tools in Microsoft Excel.

RESULTS AND DISCUSSION

The average mass balance for all three studies over the duration of incubation was 82.3 ± 15% of applied ^{14}C for Cisne soil and 77.7 ± 15% of applied ^{14}C for Drummer soil. Cloransulam-methyl was rapidly redistributed from the solution phase to other soil pools, the solution pool being preferentially depleted over the sorbed pool during the formation of degradation products and bound residues (Fig. 2 and 3). Results reported in these figures are expressed as a fraction of recovered materials to simplify presentations. In most treatments, partial depletion of the sorbed pool was observed by the end of the incubation period. Preferential depletion of the solution phase has been reported previously for 4-hydroxybenzoic acid (Johnson et al., 1998) and clomazone (Mervosh et al., 1995b). A summary of the overall fate of cloransulam-methyl (25°C, 40% WFPS) in the two soils is presented in Fig. 2.

Soil Type

In Cisne soil there was less parent compound remaining in solution by 28 DAT (4.6 ± 9.6% of applied parent) compared with the Drummer soil (30.9 ± 9.6%) (Fig. 2). Similarly, there was less parent in the sorbed phase in Cisne (2.5 ± 3.9%) compared with Drummer (44.5 ± 22.3%). As would be expected, the increased dissipation of parent in Cisne soil was accompanied by greater occurrence of radiolabeled degradation products (41.3 ± 23.5% of applied radioactivity by 28 DAT), in contrast to Drummer (23.3 ± 0.55%). In addition,

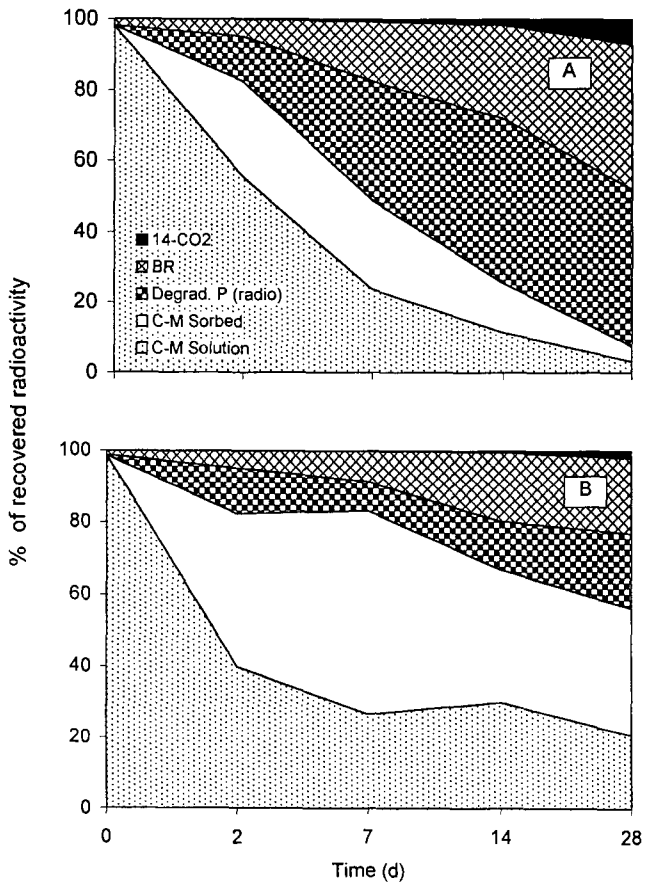

Fig. 2. Summary of herbicide fate (phenyl label) to radiolabeled carbon dioxide ($^{14}CO_2$), bound residues (BR), radiolabeled degradation products (Degrad. P (radio)), parent in sorbed (C-M Sorbed), and solution (C-M Solution), in two soils at 40% water filled pore space (WFPS); (*A*) Cisne and (*B*) Drummer.

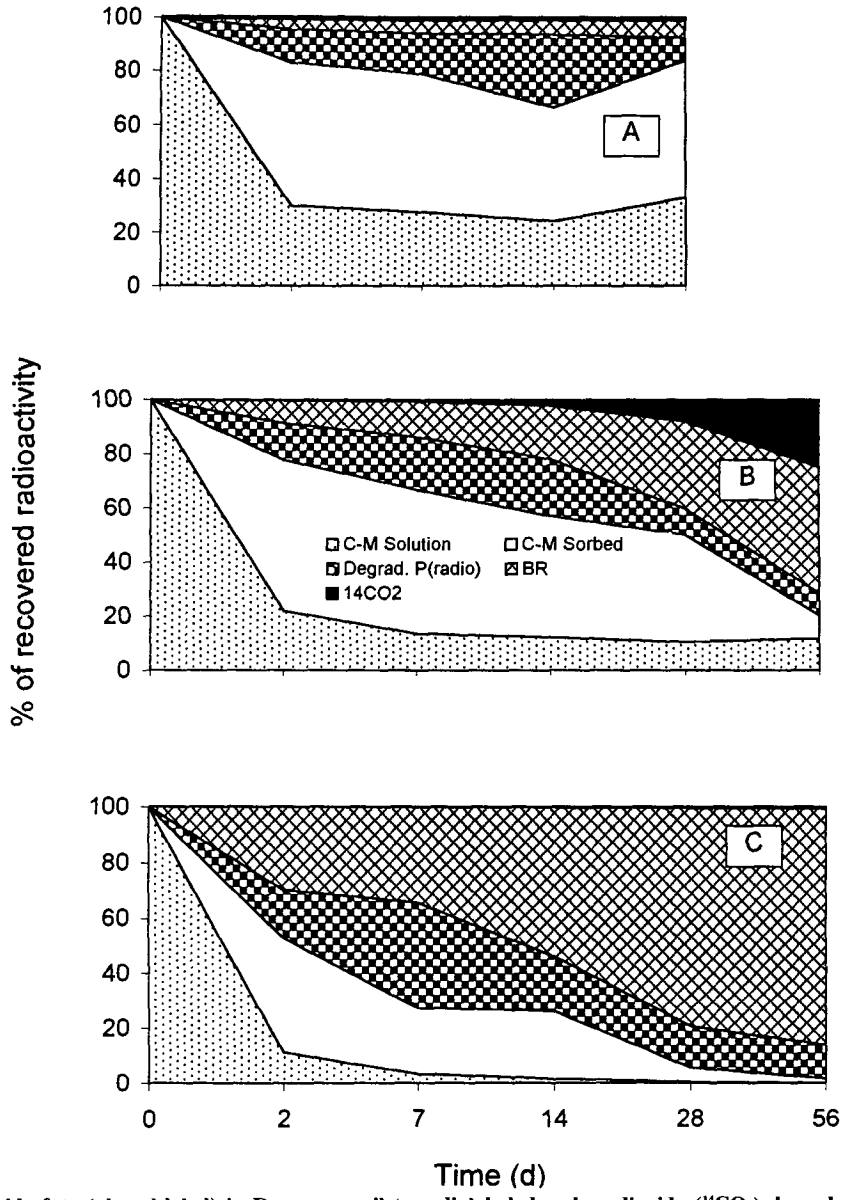

Fig. 3. Summary of herbicide fate (phenyl label) in Drummer soil to radiolabeled carbon dioxide ($^{14}CO_2$), bound residue (BR), radiolabeled degradation products (Degrad. P. (radio)), parent in sorbed (C-M Sorbed), and solution (C-M Solution), at three temperatures: (*A*) 5°C, data reported only to 28 days after treatment (DAT) due to excessive experimental error at 56 DAT; (*B*) 25°C; and (*C*) 50°C.

mineralization and bound residue formation were both more significant in Cisne (4.5 ± 0.1% and 26.0 ± 6.8%, respectively) compared with the Drummer soil (1.4 ± 0.1% and 13.8 ± 1.1%, respectively).

Sorption isotherms were well-represented by the Freundlich equation ($r^2 = 0.99$)

$$\log C_w = 1/n \log C_s + \log K_d$$

where C_w and C_s are the concentrations of cloransulam-methyl remaining in solution (ng mL^{-1}) and sorbed (ng g soil^{-1}), respectively, n is a correction factor, and K_d is the equilibrium sorption coefficient (mL g soil^{-1}). Using this equation, K_d values calculated for the Cisne and Drummer soils were 0.45 and 1.40 mL g^{-1}, respectively. Greater sorption in the Drummer soil was attributed to the higher organic matter content and a sorption process dominated by hydrophobic partitioning (Hultgren et al., 1998). The greater persistence of parent compound in soil solution in Drummer soil compared with Cisne soil throughout the incubation ($p < 0.01$) (Fig. 2) can be attributed to inaccessibility of pesticide present in the extensive fine pore space expected for the finer textured soil. A similar persistent solution pool was noted for *p*-hydroxybenzoate, and was attributed to physical inaccessibility (Johnson et al., 1998). Bound residue formation (Fig. 4, inset) was greater in Cisne compared with Drummer soil. Greater parent compound degradation in Cisne soil perhaps led to more degradation products that were capable of binding.

The concentrations of cloransulam-methyl in sorbed and 0.01 *M* $CaCl_2$ phases were used to calculate a non-equilibrium, or *apparent* sorption coefficients (K_{da}) according to the equation

$$K_{da} = C_{sa}/C_{wa}$$

where C_{sa} is the sorbed phase and C_{wa} is the solution phase (Mervosh et al., 1995b). It is important to recognize that K_{da} is not an estimate of K_d, but rather an

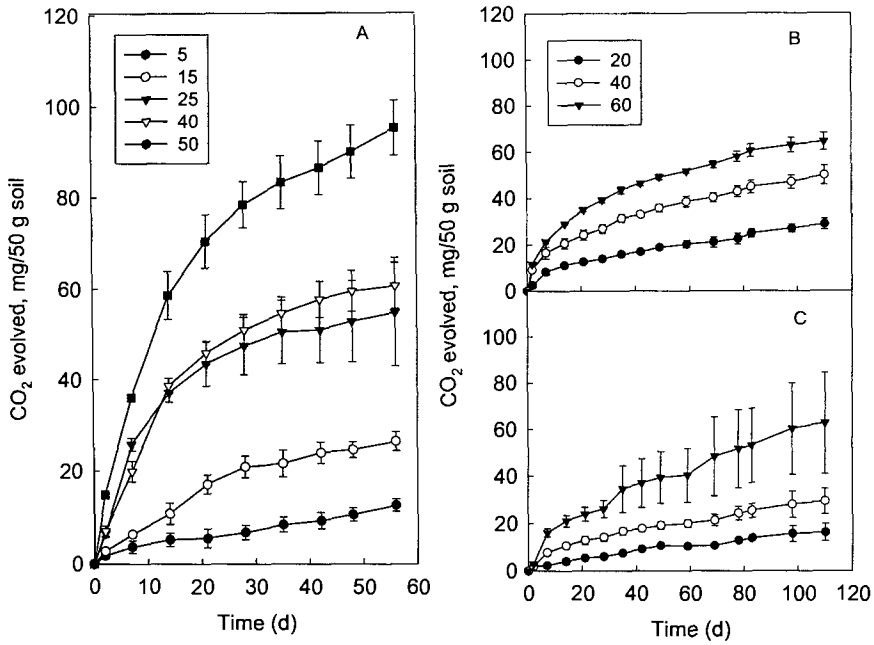

Fig. 4. Microbial respiration (*A*) as a function of temperature (°C) in Drummer and (*B*) as a function of moisture (% water filled pore space [WFPS]) in Cisne and (*C*) Drummer soil. Bars indicate standard deviation.

indicator for sorption nonequilibrium in the system, and may be useful in predicting bioavailability constraints. In Cisne soil, K_{da} (0.48 mL g^{-1}) approached K_d within 2 d of incubation, and increased to 1.38 mL g^{-1} after 28 d. Drummer soil equilibrated more slowly, with K_{da} (1.06 mL g^{-1}) significantly less than K_d at 2 d, and a final K_{da} (1.71 mL g^{-1}) only slightly greater than K_d at 28 d. The slow response of sorption in the Drummer soil may be attributed to diffusion constraints in the fine- textured soil.

Temperature

Effect of temperature on cloransulam-methyl mass balance in Drummer soil is depicted in Fig. 3. Parent compound in soil solution declined as temperature increased, from 26.8 ± 3.0% of applied parent at 5°C to 8.1 ± 2.1% at 25°C and 0.4 ± 0.4% at 50°C at 28 DAT. No parent or metabolites remained in solution at 50°C. Wolt et al. (1995) observed slower degradation of cloransulam-methyl at 5°C than at 25°C. A similar pattern was observed for sorbed parent (for example, at the same sampling time, 41.0 ± 6.9% at 5°C, 35.5 ± 7.8% at 25°C, and 4.0 ± 3.7% at 50°C), though this phase was more persistent. The resulting time-averaged K_{da} determined from these values increased with temperature from 1.73 mL g^{-1} at 5°C to 9.35 mL g^{-1} at 50°C. This trend may be explained by a greater response to temperature for processes depleting the solution phase than for replenishing the solution by desorption.

The fraction of parent remaining in Drummer soil over the temperature conditions 15, 25, 40, and 50°C was used to determine E_a with a degradation rate constant determined from first order kinetics. An Arrhenius diagram of these data is presented in Fig. 5. As noted in the introduction, E_a values in the range of less than 30 kJ mol^{-1} (Meikle et al., 1973; Thirunarayanan et al., 1985) are thought to represent biological mechanisms with values greater than 60 kJ mol^{-1} being frequently reported for chemical reactions of xenobiotics in soil (Burnside, 1965; Hance, 1967; Lemley, et al., 1988). An activation energy of 70.8 kJ mol^{-1} was obtained for dissipation of parent from solution, suggesting that chemical and physical mechanisms are important in the overall fate of cloransulam-methyl in Drummer soil.

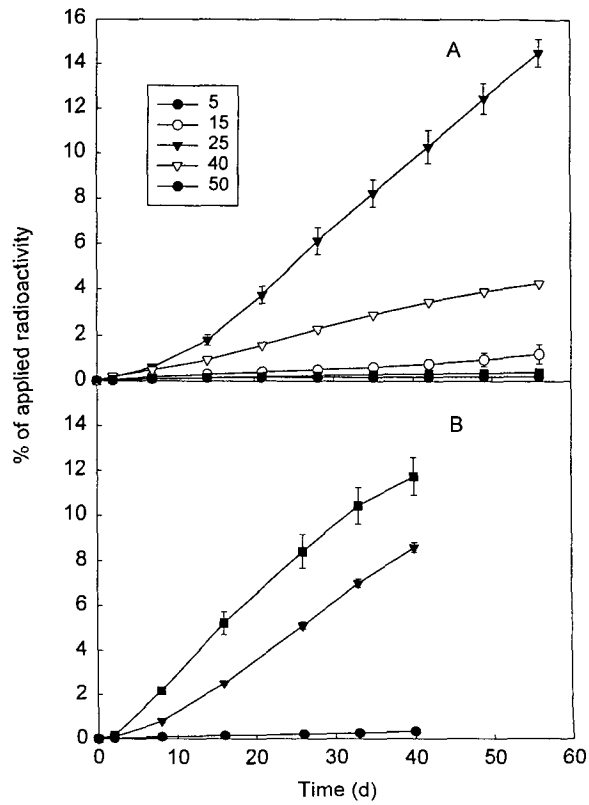

Fig. 5. Mineralization of (*A*) phenyl-labeled and (*B*) pyrimidine-labeled cloransulam-methyl as a function of temperature (°C) in Drummer soil. Bars indicate standard deviation.

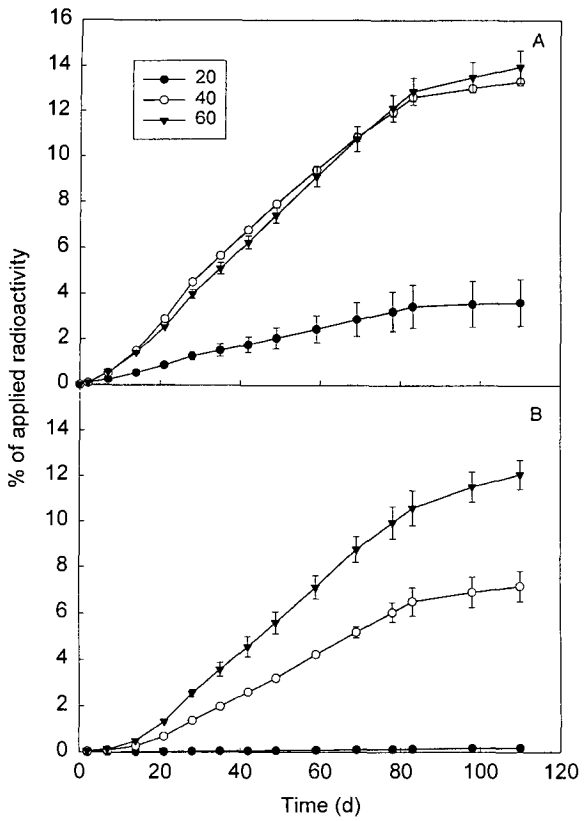

Fig. 6. Mineralization of phenyl labeled cloransulam-methyl as a function of soil moisture (% water filled pore space [WFPS]) in (*A*) Cisne and (*B*) Drummer soil. Bars indicate standard deviation.

Bound residue formation increased with temperature and reached 77.4 ± 4.7% at 50°C (Fig. 3). Increased bound residue formation with temperature has been reported for other xenobiotics (Helweg, 1987; Lehmann et al., 1993; Mervosh et al., 1995a). Higher temperature also resulted in greater respiration by the soil microbial community (Fig. 4a). Growth of any particular species of microorganism is thought to be restricted to a range spanning approximately 40°C (McMeekin et al., 1988), thus the increase in respiration between 40 and 50°C is probably due to a shift in species dominance as temperature increased beyond the mesophilic range. In contrast to this, ^{14}C mineralization rates were at an optimum at 25°C and declined at higher and lower temperatures (Fig. 5a) in all incubations with phenyl-labeled material regardless of soil type. Similar results were reported for the herbicide clomazone, though lack of temperature response above 25°C could also have been attributed to volatilization losses at higher temperatures in that study (Mervosh et al. 1995a). The vapor pressure of cloransulam-methyl (4×10^{-14} Pa at 25°C), however, is negligible (Wolt et al., 1996). In contrast, data from the pyrimidine-labeled compound illustrated a different trend (Fig. 5b), with mineralization increasing with temperature throughout the range employed. These results suggest that distinct groups of microorganisms are degrading different parts of the molecule at higher temperatures. Its appears that the organisms responsible for degrading the phenyl ring are unresponsive above 25°C. For both soils and pesticide label patterns, temperature treatments producing the maximum mineralization rates exhibited accelerating kinetics indicative of growth. Apparent growth responses to xenobiotics have been reported for concentrations as low as 75 ng g soil^{-1} (Alexander and Scow, 1989), well below the rate employed herein. It should be noted that an increase in degrader population may have occurred in this study due to factors other than the addition of cloransulam-methyl (e.g., adjustment of soil moisture and introduction of carrier solvent).

Moisture

Soil moisture had no influence on the concentration of parent in solution (data not shown). The moisture range was apparently not large enough to have an effect on parent disappearance processes. Mervosh et al. (1995b) also reported no effect of soil moisture on clomazone in solution or apparent K_d over an incubation period of 84 d. Biodegradation rates of other herbicides, however, have been influenced by soil moisture conditions through several mechanisms, including reduced oxygen availability at higher moisture contents and reduced diffusion of the substrate at lower moisture contents (Chapman et al., 1986; Flint et al., 1997; Helweg, 1987; Meikle et al., 1973; Walker, 1978). Analogous to parent disappearance, formation of bound residues was not affected by soil moisture. A larger moisture range may have produced an effect, as the influence of moisture conditions on bound residue formation has already been noted for other pesticides (Helweg, 1987; Kruger et al., 1993, 1997; Ou, 1984; Ou et al., 1982). In contrast, soil moisture did influence both respiration (Fig. 4b and 4c) and ^{14}C mineralization (Fig. 6). The response of ^{14}C mineralization to changing moisture conditions differed between the two soils. At the two higher moisture contents the microorganisms are not thought to be at a physiological disadvantage (Skopp, 1990), therefore differences in mineralization should be attributed largely to bioavailability limitations (Harris, 1981). In Drummer soil, ^{14}C mineralization kinetics slowed considerably with a change in moisture content from 60 to 40% WFPS, and mineralization was virtually eliminated at 20% WFPS, suggesting reduction in microbial access to cloransulam-methyl (Fig. 6b). Inasmuch as the results of differential labeling studies suggested involvement of more than one group of organisms in biodegradation of cloransulam-methyl, mineralization should be dependent upon microscale transport of the herbicide among microbial colonies. Pesticide transport through Drummer soil is restricted (Mervosh et al., 1995c) due to the high clay and organic carbon content, thus explaining the response of mineralization to moisture content. The result at the lowest water content may also be explained by reduced physiological well-being of the degrading microorganisms. Conversely, no effect from decreasing moisture was observed with Cisne soil until a content of 20% WFPS was achieved (Fig. 6a). These results support the previous observation that parent was significantly depleted from solution in Cisne soil, whereas

much remained in Drummer soil throughout the experiment.

Importance of Biological Processes

The effect of soil sterilization was examined for bound residue formation and mineralization only. As would be expected, significantly less mineralization occurred under sterile conditions. The influence of abiotic conditions on bound residue formation, however, differed between soils. Introduction of sterile conditions reduced formation of this pool in Cisne soil but had little influence in Drummer soil. These data suggest that biological processes are important in Cisne soil while abiotic processes are the main mechanism for formation of this pool in Drummer soil. This hypothesis is supported by more extensive accumulation of degradation products in Cisne soil (Fig. 2a). A detailed review of processes contributing to bound residue formation was presented by Calderbank (1989). A substance may bind to soil through a stable chemical linkage (Hsu and Bartha, 1976). Intraorganic matter diffusion (IOMD) may occur (Brusseau and Rao, 1989), which describes the diffusive mass transfer of sorbate into the interior of organic matter. Pignatello (1989) suggests that physical occlusion may be responsible for the detainment of compounds in soil, due to entrapment in soil micropores that should have been more prevalent in the Drummer soil used here. In summary, bound cloransulam-methyl residues may be a result of any combination of these processes, both chemical and biological (Getzin, 1981) and dominance of any single process could depend on factors such as soil type and environmental variables.

CONCLUSIONS

Cloransulam-methyl disappearance was a function of temperature and soil type, but was insensitive to soil moisture in the range of conditions used in this study. Soil environmental variables influenced mineralization and bound residue formation to varying degrees. The effect of temperature on mineralization differed between the two radiolabeled forms of the herbicide. The contrasting temperature responses of the two labels suggests that more than one group of organisms is involved in degradation, and furthermore illustrates the importance of label position in environmental fate studies. Increasing soil moisture resulted in greater mineralization in Drummer soil, however in Cisne soil there were no differences in mineralization at the two highest moisture contents. The effect in Drummer soil was attributed to increased moisture improving microbial access to pesticide. Temperature and soil type both affected bound residue formation; greater formation of this pool occurred at higher temperatures for both soils and more accumulated in Cisne soil, possibly due to great accumulation of degradation products. Inclusion of sterile controls revealed that both biological and abiotic processes contributed to bound residue formation. Relative contribution of biological processes depended on soil type. Finally, we note that formation of bound residues and mineralization responded differently to temperature, illustrating the variability in response between dissipation processes during changing environmental conditions. In summary, this study depicts the significance of chemical structure, soil type, soil temperature, and moisture on cloransulam-methyl dissipation mechanisms.

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