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REVIEWS AND ANALYSES

Soil Depth and Temperature Effects on Microbial Degradation of 2,4-D

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ABSTRACT

Numerous soil factors and climatic conditions affect the degradation rate of pesticides in soils. A major soil factor influencing herbicide degradation is the composition and abundance of the microbiota, which has been shown to vary considerably with soil depth. Another important variable affecting microbial growth and degradation kinetics is temperature. Soil samples from 0- to 30-, 30- to 60-, and 60- to 120-cm depths of two Montana soils were placed in reaction flasks and treated with ^{14}C-labeled 2,4-D at representative field use rates at temperatures of 10, 17, and 24°C. A carrier gas was used to continuously evacuate evolved $^{14}CO_2$ into NaOH traps as a measure of 2,4-D degradation. Comparisons of the effects of soil depth and temperature were made by fitting experimental data to both first-order and logistic kinetic models. Degradation rates of 2,4-D decreased significantly with increasing soil depth and were positively correlated with bacterial plate counts. Effects of temperature on degradation rate constants were adequately described using the Arrhenius equation. Degradation rates of 2,4-D and bacterial enumerations were positively correlated with changes in soil organic C as a function of soil depth. These results support the idea that changes in organic C with soil depth could be used as a parameter for estimating changes in degradation rate as a function of soil depth. Efforts to model the transport of 2,4-D in soils should account for variation in degradation rate as a function of soil depth and temperature.

MICROBIAL DEGRADATION is an important process controlling the fate and transport of contaminants in soil systems. Traditionally, microbial numbers have been assumed to decrease with soil depth, thus increasing the likelihood of persistence of mobile compounds that readily move out of the biologically active surface layer. This assumption has been supported by studies in which the maximum degradation rate of organic contaminants like phenol (Dobbins et al., 1987) and metribuzin (4-amino-6-*tert*-butyl-3-(methylthio)-*as*-triazin – 5(4*H*)-one) (Moorman and Harper, 1989) has been shown to decrease significantly with increasing soil depth. Lower relative degradation rates in subsurface soils have been attributed to differences in temperature, soil water content, soil type, and decreasing microbial populations with depth (Kempson-Jones and Hance, 1979; Dobbins et al., 1987). Soil water content directly influences soil oxygen content and microbial activity and therefore can influence pesticide persistence. For example, the half-life of alachlor (2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide) increased from 23 d in surface soil (aerobic conditions) to >100 d in the vadose zone (anaerobic conditions) (Pothuluri et al., 1990). In addition, the aerobic environment of an upland Maahas clay soil promoted greater 2,4-D (2,4-dichlorophenoxyacetic acid) degradation than in the same soil in a submerged condition (Yoshida and Castro, 1975). One of the established enzymatic degradation pathways of 2,4-D by *Arthrobacter* sp. (Loos et al, 1967; Bollag et al., 1968; Tiedje and Alexander, 1969) proceeds by an oxidative process. Consequently, degradation rates may be lower in subsurface soil horizons as a result of reduced O_2 content.

Although subsurface environments were often thought to be devoid of microbial activity, recent studies show considerable microbial activity in aquifers and sediments. For example, at a depth of 7 m below the water table, Hirsch and Rades-Rohkohl (1983) characterized 90 microbial morphotypes of which 72 were identified as bacteria, 10 as protozoa, and 8 as fungi. Bacteria isolated in this study grew well at groundwater temperature (9°C) and developed best on oligotrophic media. Other studies indicate that appreciable numbers of microbes exist in subsurface aquifer sediments (Ghiorse and Balkwill, 1983; Beloin et al., 1988; Bone and Balkwill, 1988; Konopka and Turco, 1991). These microbial populations were characterized as entirely different from those found to be dominant in the surface soils and generally much lower in total biomass; they were nutritionally versatile and adapted to survive under low-nutrient stress. Turco and Konopka (1989) reported that microbes isolated from a depth of 26 m in a sandy aquifer had the capability to degrade C sources equal to that of the population in the overlying surface soil. The most microbially active strata were those associated with the aquifer, which had organic C levels >1.6% and also higher amounts of total N and P compared with much lower levels found near the surface (0.37% organic C at 1.8 m). This implied that microbial activity was nutrient-limited in the vadose zone. These findings together with the observations that pesticide degradation rates decrease with soil depth in the rooting zone (Moorman and Harper, 1989; Pothuluri et al., 1990; Adams and Thurman, 1991) suggest that: (i) soil depth is an important variable for predicting the fate of pesticides in soils, and (ii) the dependence of degradation rate on soil depth may be partially related to organic C content.

Temperature has also been shown to significantly affect

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Abbreviations: CFU, colony forming units; GIS, geographical information system.

degradation kinetics of organic contaminants in soils. Walker and Zimdahl (1981) studied the effects of temperature on the persistence of atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) and metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide) in three soil types and linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea) in two different soils. For temperature treatments that increased from 5 to 35°C, corresponding half-lives decreased for atrazine by factors ranging from 7 to 9, for metolachlor by factors ranging from 6 to 8, and for linuron by a factor of about 4.5. Ou (1984) found that the degradation rate of 2,4-D in two soils was reduced at 35°C compared with 25°C. Padilla et al. (1988) used the Arrhenius and Van't Hoff equations in a one-dimensional, finite elements transport model, MELEF-3v (Padilla and Gelinas, 1988), to predict the effect of temperature variations on the concentration profile of atrazine in a subsurface environment. Two model simulations with respective temperature gradients of 15 to 5°C and 25 to 15°C from the soil surface to a 1-m soil depth were used to predict atrazine concentration profiles after 1 yr. When these results were compared with atrazine concentration profiles generated assuming uniform profile temperatures (5 and 15°C), the predicted atrazine peak concentrations increased by 70 and 90%, respectively. Consequently, temperature effects may increase the persistence of pesticides in soils and groundwater in temperate climates, where dramatic seasonal temperature variations occur. In northern latitudes many soils are classified in the frigid or cryic temperature regimes. Mean annual soil temperature (50 cm) in these soils is <8°C; therefore, increased persistence of pesticides can be expected, especially if leaching into the subsurface occurs.

Accurate assessment of the degradation kinetics of organic contaminants in soils is critical to transport model predictions. Boesten and van der Linden (1991) investigated the effects of degradation rate on predicted pesticide leaching and persistence. They reported that changing the degradation rate by a factor of 2 changed the fraction of pesticide leached by about a factor of 10. A sensitivity analysis of an unsaturated zone transport model, PRZM (Carsel et al., 1984), performed by Villeneuve et al. (1988) showed that a 15 to 22% variation in the degradation constant led to a 100% uncertainty in the various simulation results of the amount of aldicarb (2-methyl-2-(methylthio) propionaldehyde *O*-methylcarbamoyloxime) leached below the root zone. Cohen et al. (1984) discussed the effectiveness of the one-dimensional transport model, PESTANS (Enfield et al., 1983), and suggested that models of this type must allow the user to vary the depth-dependent transformation rate of a contaminant to account for differences in parameters such as dissolved oxygen and microbial populations that occur in heterogeneous (layered) systems.

Of the herbicides used extensively in Montana, 2,4-D is still the most commonly used for broadleaf weed control in cereal grain production. Regional groundwater monitoring programs (DeLuca et al., 1989) have shown a number of wells contaminated with 2,4-D; consequently, there is significant concern about the fate and transport of 2,4-D under regional environmental conditions in surface and vadose zone soils. The ability to reasonably predict the fate of 2,4-D in soils depends on accurate estimates of degradation rates and knowledge of how they vary seasonally and within the soil profile. Thus, the objective of the current study was to determine the simultaneous effects of soil depth and soil temperature on the degradation rates of 2,4-D in representative Montana soils.

MATERIALS AND METHODS

Soils

Soil samples were taken at two agricultural sites in Montana from the 0- to 30-, 30- to 60-, and 60- to 120-cm depths (corresponding approximately to the A, B, and C horizons of each soil) air-dried, and passed through a 2-mm sieve. One of the soils was an Amsterdam silt loam (fine-silty mixed Typic Haploboroll) sampled from the Post Agricultural Research Station (Bozeman, MT); the other was a Haverson silt clay loam (fine-loamy mixed (calcareous) Mesic Ustic Torrifluvent) sampled from the Montana State University Southern Agricultural Research Station (Huntley, MT) (Table 1). Previous exposure of the exact sampling locations to applications of 2,4-D is probable but uncertain. Each soil was analyzed for particle size (Day, 1965), total organic C (Snyder and Trofymow, 1984), cation exchange capacity (CEC) (Chapman, 1965), and soil pH using a 1:1 soil/water ratio.

Degradation Experiments

Subsamples of 75 g from each soil type and depth were weighed into 250 mL Erlenmeyer side-arm flasks to include 3 replicates and 1 control for each soil type/depth treatment. Three separate experiments were conducted at 10, 17, and 24°C (±1°C) by incubating the flasks in a constant temperature water bath (Fig. 1).

A 25-mL solution of 2,4-D was applied to each flask to

Table 1. Characteristics of soils used in the degradation experiments and associated bacterial plate counts.

Soil type and (classification)	Soil depth	Clay	Silt	Sand	Organic C	Soil pH (1:1)	CEC	R2A media	2,4-D media	% 2,4-D degraders
	cm	g kg^{-1}					mmol$_c$ kg^{-1}	CFU†/g soil × 10^5		
Amsterdam silt loam (Typic Cryoboroll)	0-30	231	606	163	10.6	6.9	0.21	123.0	31.7	25.8
	30-60	300	610	90	8.1	7.4	0.21	26.3	2.3	8.7
	60-120	280	650	70	4.7	8.0	0.17	17.4	2.2	12.6
Haverson silty clay loam (Mesic Ustic Torrifluvent)	0-30	404	414	182	10.1	7.1	0.24	174.0	12.0	6.9
	30-60	500	360	140	6.1	7.8	0.25	34.7	–‡	–‡
	60-120	530	390	80	4.4	8.3	0.26	10.6	0.5	4.7

† CFU = colony forming units.
‡ Data not reported; CFU in control media (i.e., mineral salts media without 2,4-D) > CFU in presence of 2,4-D.

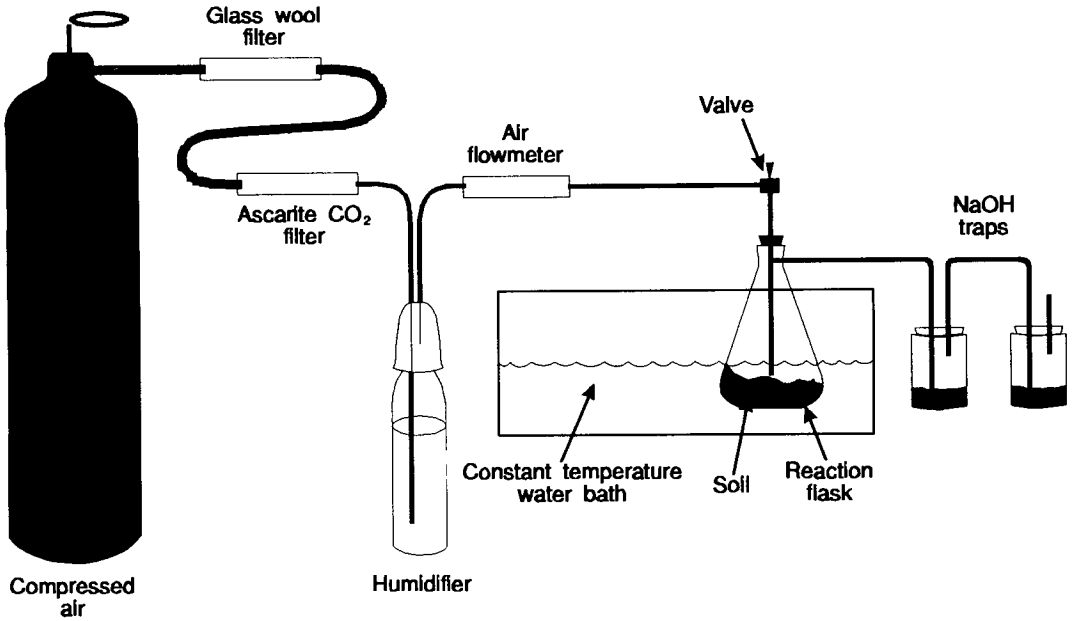

Fig. 1. Schematic of apparatus used in 2,4-D degradation experiments.

approximate a normal field rate application of 0.67 kg ha^{-1} (0.75 lb $acre^{-1}$) and a gravimetric water content of 33% (dry soil basis). Final moisture contents were not determined. The applied solution per flask included approximately 0.145 μCi (5349 Bq) of carboxyl-^{14}C-labeled 2,4-D (specific activity = 8.5 mCi $mmol^{-1}$ (3.145×10^8 Bq $mmol^{-1}$); Sigma Chemical Company, St. Louis, MO), 28.56 μg of unlabeled 2,4-D (99% purity), and 0.11 mg of $CaCl_2$ at a pH of 7.3.

Each reaction flask was subjected to a flow rate of 1.9 mL min^{-1} of humidifed, CO_2-free, compressed air. In continuous gas flow (evacuation) experiments such as these, it is commonly assumed that the humidified air maintains a constant moisture content within each reaction flask. Evolved $^{14}CO_2$ was collected in a series of two 10 mL, 0.5 *M* NaOH traps. One-milliliter aliquots from each trap were sampled every 24 h for the duration of the experiment (generally 10–12 d), added to 6 mL of scintillation cocktail (ScintiVerse E, Fisher Scientific), and analyzed using a 2200CA Tri-Carb Liquid Scintillation Analyzer (Packard Instrument Company, Laguna Hills, CA). At the termination of each experiment, 1 to 2 g of soil from each reaction flask (duplicate subsamples) were combusted at 800°C for 4 min in a biological oxidizer (Model OM300, R.J. Harvey Instrument Corp., Hillsdale, NJ). Evolved $^{14}CO_2$ was trapped in liquid scintillant (OX-161 Carbon-14 cocktail, R.J. Harvey Instrument Corp., Hillsdale, NJ) and analyzed as described above. The average recovery of ^{14}C-labeled material (residual ^{14}C plus evolved $^{14}CO_2$) in the degradation experiments was 92%.

Logistic Equation and First-Order Kinetics

Cumulative $^{14}CO_2$ evolved was graphed as a function of sampling time (d). The resulting degradation curves were interpreted by fitting these data using SAS (SAS NLIN procedure, SAS Inst., 1985) to solve the integrated form of a logistic equation (Characklis, 1990), which can be used to describe accumulation of various components in batch reactor systems. The differential form of the equation is as follows:

$$\frac{dX}{dt} = k_1 X\left(1 - \frac{X}{X_m}\right) \qquad [1]$$

where X is the component produced (known), k_1 is the effective process rate coefficient (fitted), X_m is the maximum attainable product level (fitted), and t is time (known). The integrated form of Eq. [1] is:

$$X = \frac{X_0\, e^{k_1 t}}{1 - [(X_0/X_m)(1 - e^{k_1 t})]} \qquad [2]$$

where X_0 is the initial reactor component concentration. This form of the logistic equation does not assume any particular dependence of growth rate on substrate concentration (other than to state that X_m cannot be exceeded) and therefore cannot be used as a growth rate equation. However, despite this limitation the above form of the logistic equation can be used for empirically describing the accumulation rate (or evolution) of various components in a reactor (Characklis, 1990). A mathematically equivalent expression of Eq. [2] can be derived using the phenomenological logistic equation of Simkins and Alexander (1984) in which k_1 includes effects of both growth rate and total substrate availability and X_m results directly from substrate availability.

The applicability of first-order degradation kinetics was also investigated by determining a rate constant from the equation:

$$\ln\frac{A}{A_0} = -kt \qquad [3]$$

where A is ^{14}C-labeled 2,4-D remaining at time t (which can be assumed to equal [A_0] − cumulative $^{14}CO_2$ evolved), A_0 is the initial amount of ^{14}C-labeled 2,4-D added to the reaction flask, t is time, and k is the first-order rate constant. Half-lives were then calculated for all treatments using the following relationship for a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \qquad [4]$$

where $t_{1/2}$ is half-life (d) and k (d^{-1}) is the first-order rate constant.

Bacterial Plate Counts

A relative estimate of total bacterial numbers was determined for each soil type and depth utilizing an oligotrophic plating

Table 2. Comparison of rate constants (k_1 [=] h^{-1}; 95% confidence intervals in parentheses) and r^2 values (sample population number in parentheses) obtained by fitting degradation curves (Fig. 2 and 3) to a logistic equation.

Soil depth	Temperature	Amsterdam silt loam k_1†	Amsterdam silt loam r^2†	Haverson silty clay loam k_1†	Haverson silty clay loam r^2†
cm	°C				
0–30	10	0.034 (0.002)	0.99 (11)	0.024 (0.011)	0.99 (11)
	17	0.045 (0.017)	0.99 (12)	0.062 (0.004)	0.99 (12)
	24	0.080 (0.017)	0.99 (6)	0.104 (0.012)	0.99 (6)
30–60	10	0.014 (0.015)	0.99 (11)	0.014 (0.003)	0.99 (11)
	17	0.038 (0.006)	0.99 (12)	0.033 (0.008)	0.99 (12)
	24	0.053 (0.037)	0.99 (10)	0.038 (0.030)	0.99 (10)
60–120	10	0.017 (0.016)	0.99 (11)	0.009 (0.012)	0.94 (11)
	17	0.032 (0.017)	0.99 (12)	0.030 (0.007)	0.99 (12)
	24	0.036 (0.004)	0.99 (10)	0.035 (0.008)	0.99 (10)

† k_1 and r^2 values represent the average of three fits of the logistic model to independent sets of experimental data.

medium, R2A (Difco Laboratories, Detroit, MI). The number of bacteria capable of utilizing 2,4-D as a sole C source was determined using mineral salts medium consisting of 12 g L^{-1} Noble agar (Difco Laboratories, Detroit, MI), 7 g L^{-1} K_2HPO_4, 3 g/L KH_2PO_4, 1 g L^{-1} $(NH_4)_2SO_4$, 0.1 g L^{-1} $MgSO_4$, and 0.46 mg L^{-1} 2,4-D, which approximated the initial concentration of 2,4-D applied to the soil in the reaction flasks. Control samples for each soil type and depth were also plated using the mineral salts medium in the absence of 2,4-D, so that final enumeration of 2,4-D degraders was obtained by difference.

Two 5-g subsamples of each soil type and depth were diluted in 9 mL of sterile deionized water and vortexed for approximately 3 min. Seven serial 1:10 dilutions were performed, and 100 μL aliquots of each serial dilution were transferred to triplicate plates of each medium. The plates were incubated at 24°C for 4 d (R2A) and 6 d (Noble agar). Colony forming units (CFU) per gram soil were determined from geometric means of plate counts for dilutions that ranged from about 30 to 300 CFU per plate.

RESULTS AND DISCUSSION

Two empirical kinetic models (i.e., logistic and first-order) based on dissimilar degradation mechanisms (Alexander and Scow, 1989) were used to fit the experimental degradation data. The logistic equation of Characklis (1990) provided excellent fit to the experimental data (r^2 = 0.99) (Table 2). The fit of degradation curves to the first-order kinetic model was poorer as indicated by lower r^2 values for all treatments (Table 3). One would expect a better fit of the logistic model on the basis of its three fitted parameters, compared with the first-order model with only one fitted parameter. Another reason for better fit of the logistic model is that it describes microbial degradation kinetics typically observed when a population is exposed to a new substrate (i.e., a lag phase yielding S-shaped degradation curves) (Fig. 2 and 3). Generally, the regression r^2 values for the first-order model were poorest at the low temperature (10°C). This is probably due to the fact that our experiments were terminated before the onset of log phase growth in the

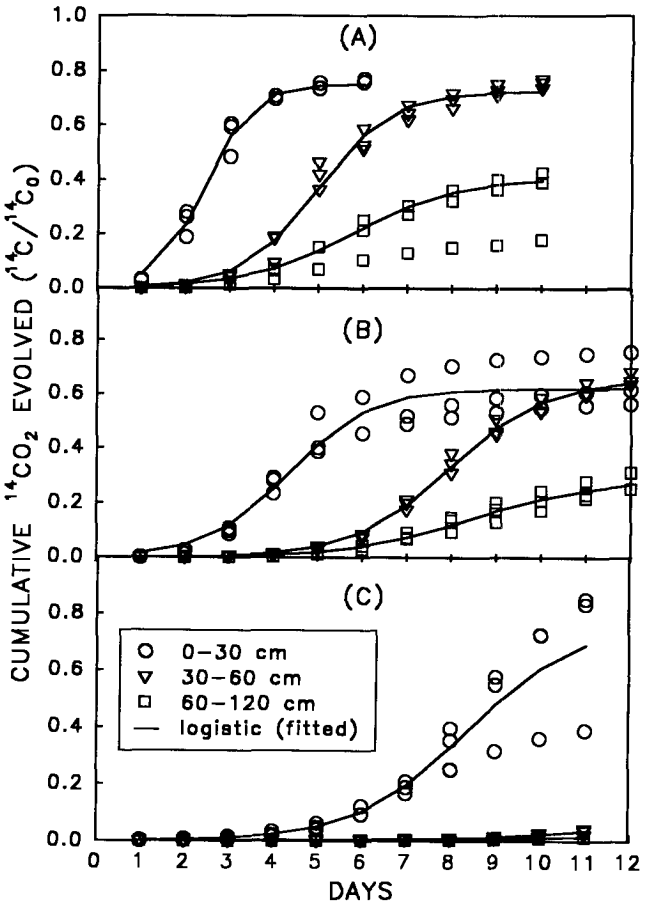

Fig. 2. Soil depth effects on 2,4-D degradation rates (expressed as cumulative $^{14}CO_2$ evolved) in Amsterdam silt loam at (*A*) 24°C, (*B*) 17°C, and (*C*) 10°C.

Table 3. Rate constants (k [=] h^{-1}; 95% confidence intervals in parentheses), half-lives ($t_{1/2}$ [=] d), and r^2 values (sample population number in parentheses) calculated from fit of first-order kinetics to degradation curves in Fig. 2 and 3.

Soil depth	Temperature	Amsterdam silt loam k†	Amsterdam silt loam $t_{1/2}$	Amsterdam silt loam r^2†	Haverson silty clay loam k†	Haverson silty clay loam $t_{1/2}$	Haverson silty clay loam r^2†
cm	°C						
0–30	10	0.0053 (0.0065)	7	0.80 (11)	0.0031 (0.0032)	11	0.71 (11)
	17	0.0046 (0.0036)	7	0.92 (12)	0.0035 (0.0011)	8	0.84 (12)
	24	0.0127 (0.0009)	2	0.93 (6)	0.0110 (0.0042)	3	0.86 (6)
30–60	10	0.00012 (0.00009)	273	0.74 (11)	0.00009 (0.00003)	352	0.89 (11)
	17	0.0044 (0.0008)	8	0.87 (12)	0.0013 (0.0007)	25	0.80 (12)
	24	0.0077 (0.0012)	4	0.96 (10)	0.0041 (0.0015)	8	0.95 (10)
60–120	10	0.00005 (0.00002)	593	0.83 (11)	0.00002 (0.00001)	1691	0.91 (11)
	17	0.0013 (0.0005)	25	0.89 (12)	0.0011 (0.0011)	31	0.79 (12)
	24	0.0022 (0.0025)	12	0.97 (10)	0.0031 (0.0007)	10	0.94 (10)

† k and r^2 values represent the average of three fits of the logistic model to independent sets of experimental data.

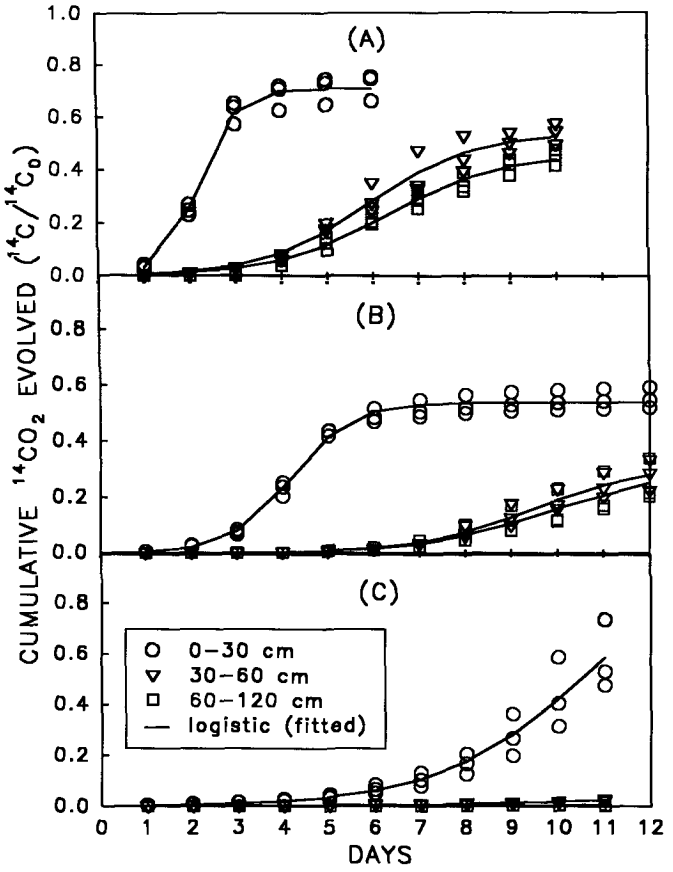

Fig. 3. Soil depth effects on 2,4-D degradation rates (expressed as cumulative $^{14}CO_2$ evolved) in Haverson silty clay loam at (*A*) 24°C, (*B*) 17°C, and (*C*) 10°C.

10°C treatments. Although first-order kinetics provided only marginal fits to the experimental data, the half-life values (Table 3) reported here show general agreement with those reported in other studies and with those commonly used in fate and transport models (Foster and McKercher, 1973; Smith, 1980; Smith and Hayden, 1981; Wagenet and Hutson, 1989).

Soil Depth Effects on 2,4-D Degradation

Figures 2 and 3 illustrate the effects of soil depth at 10, 17, and 24°C on degradation rates of 2,4-D in terms of cumulative $^{14}CO_2$ evolved for the Amsterdam and Haverson soils, respectively. An initial lag phase of minimal degradation was observed for all treatments. This initial lag phase has been observed in other studies on 2,4-D degradation (Audus, 1960) and has been characterized as a period of adaptation in which the enzymes needed for decomposition of the substrate and its metabolites are synthesized from closely related enzymes (Torstensson, 1978). The lag phase increased and the maximum degradation rate of 2,4-D decreased with depth for both soils. However, the difference in degradation rates between the 30- to 60-cm and 60- to 120-cm depths was more pronounced for the Amsterdam soil than for the Haverson soil, especially at 17 and 24°C.

Rate constants obtained using the two kinetic models described above can conveniently be used to compare soil depth treatments. Rate constants (Tables 2 and 3) decreased and calculated half-lives (first-order model) increased significantly with increasing soil depth. Degradation rate constants obtained from the logistic model (Table 2) decreased by a factor of 1.5 to 2 between the 0- to 30-cm and 60- to 120-cm depths within a given temperature treatment for the Amsterdam soil and by a factor of 2 to 3 for the Haverson soil. Rate constants obtained using a first-order model (Table 3) decreased by a factor of 3.5 to 6 and about 3.5 between the 0- to 30-cm and 60- to 120-cm depths at the two highest temperature treatments for the Amsterdam and Haverson soils, respectively, and by a factor of 106 and 155, respectively, for the 10°C treatment. The decrease in degradation rate coefficients with depth was consistent with a decrease in observed bacterial populations (Table 1). These findings agree with other studies showing a significant decrease in degradation rates of phenol, metribuzin, and alachlor in subsurface soils (Dobbins et al., 1987; Moorman and Harper, 1989; Pothuluri et al., 1990).

Temperature Effects on 2,4-D Degradation

Lag phases increased and maximum degradation rates decreased for both soils with decreasing temperature (Fig. 2 and 3). This effect is particularly apparent between the 10 and 17°C treatments for the 30- to 60-cm and 60- to 120-cm depths in both soils. A comparison of the 10 and 24°C treatments within a given soil depth shows that values of k_1 in the logistic model (Table 2) increased by a factor of 2 to 4 for the Amsterdam soil and by a factor of 3 to 4 for the Haverson soil. A similar increase in the first-order rate constants (k) with increasing temperature was observed for the 0- to 30-cm depth for both soils (Table 3). However, first-order rate constants for the 30- to 60-cm and 60- to 120-cm depths increased by a factor of 44 to 155 from 10 to 24°C. It should be noted that these reported degradation rate constants only reflect a very narrow moisture range. Walker and Zimdahl (1981) showed a significant increase in the half-life of three pesticides with decreasing soil moisture in experiments conducted at a constant temperature of 25°C. Therefore, one would expect that the interaction of different moisture contents and temperatures would significantly affect degradation rate constants.

The temperature effects reported here are consistent with other published results (Smith and Hayden, 1981; Parker and Doxtader, 1983) of the effect of temperature on persistence of 2,4-D and demonstrate the importance of accounting for temperature fluctuations in models used to predict the fate of organic chemicals in soils. Variations in first-order degradation rate constants by even a factor of 2 can result in transport predictions of the fraction of chemical leached by factors of 10 (Boesten and van der Linden, 1991). The Arrhenius equation has been used to describe the functional relationship between degradation rate constants and temperature:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad [5]$$

where A is an empirical constant (h^{-1}) dependent on the compound and nonthermal system conditions, E_a is the activation energy (J mol^{-1}), R is the gas constant (J K^{-1} mol^{-1}), and T is the temperature (K). Values of E_a calculated in other studies on 2,4-D degradation range from 52 to 111 kJ mol^{-1} between moisture tensions of 0.01 and 0.1 MPa and the temperature interval 20 to 30°C (Parker and Doxtader, 1983). Values of E_a reported for other herbicides such as napropamide (Walker, 1974) and atrazine (Padilla et al., 1988) over temperatures of approximately 10 to 30°C range from 33 to 46 kJ mol^{-1}, respectively. Calculations of E_a based on logistic model rate constants (Table 2) and Eq. [5] were obtained from a regression (n = 9) of ln k_l vs. $1/T$ for both soils. The calculated E_a values over all depth and temperature treatments were 49 ± 14 and 64 ± 20 kJ mol^{-1} (all ± values are standard errors) for the Amsterdam (r^2 = 0.63) and Haverson (r^2 = 0.58) soils, respectively. Activation energies calculated from similar regression analyses (n = 3) using first-order rate constants at the 0- to 30-cm soil depth were 43 ± 34 and 63 ± 30 kJ mol^{-1} for the Amsterdam (r^2 = 0.62) and Haverson (r^2 = 0.81) soils, respectively. These E_a values correspond to Q_{10} factors of 2 to 3 (i.e., an increase in reaction rate by a factor of 2 to 3 for a corresponding increase in temperature of 10°C), and they are consistent with values that have been employed in transport models such as LEACHM (Wagenet and Hutson, 1989).

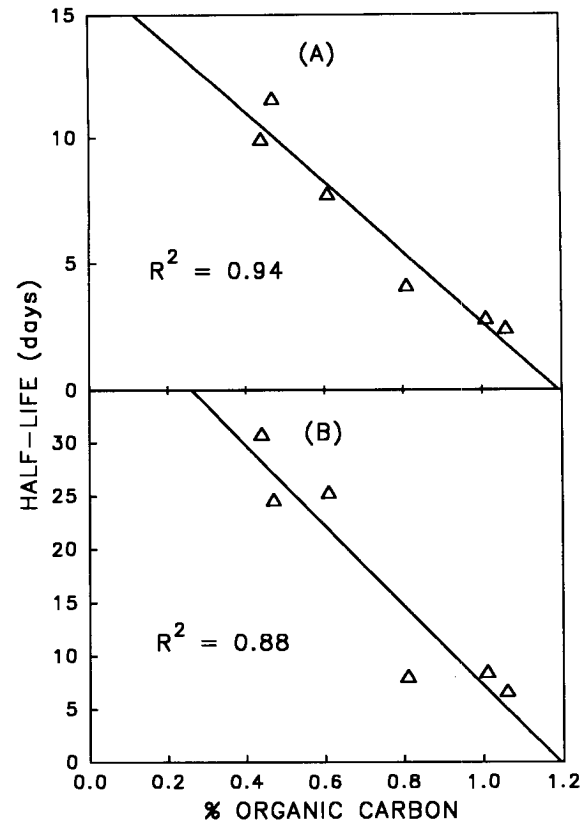

Fig. 4. Linear regression of 2,4-D half-life and % organic C for 0- to 30-, 30- to 60-, and 60- to 120-cm depths of Amsterdam and Haverson soils for (*A*) 24°C and (*B*) 17°C treatments.

Correlation of Organic Carbon with Microbial Activity

Bacterial numbers obtained using plate counts decreased with depth in both soils for both types of growth media (Table 1). A linear regression analysis was performed to determine the correlation between CFU and % organic C over all depth increments for both soils. A positive correlation between CFU and % organic C was observed for both media with regression r^2 values (n = 6) of 0.61 (2,4-D media) and 0.75 (R2A media). This is consistent with Lavy et al. (1973), showing a positive regression correlation (r^2 = 0.66) between microbial numbers and % organic matter for three soil depths in two texturally different soil types. Foster and McKercher (1973) also found 2,4-D degradation rates to be positively correlated to soil organic C and microbial plate counts. These findings suggest that changes in soil organic C as a function of soil depth may be a reasonable indicator of microbial activity and subsequent degradation rate changes as a function of soil depth.

A regression analysis (n = 6) was performed to assess the relationship between 2,4-D half-life values (Table 3) for the 17 and 24°C treatments over all depths and % soil organic C content (Table 1). Although we only collected data for two soil types, a strong negative correlation was observed between half-life values of 2,4-D and % organic C (Fig. 4). Regression r^2 values were 0.88 and 0.94 for the 17 and 24°C treatments, respectively. A positive correlation between degradation rate and organic C is a reflection of the relationship between bacterial numbers and organic C; however, this relationship may only hold for organic contaminants that are not strongly bound to soil organic matter (Hurle and Walker, 1980). Sorption of 2,4-D by most soils is low with K_{oc} values generally in the range of 0.02 m^3 kg^{-1} (Jury et al., 1987). Sorption of organic contaminants to solid phases such as organic matter may in fact result in lower degradation rates (increased half-lives) because they are not as accessible to microbial attack in the bound state (Smith and Muir, 1980; Stott et al., 1983). Consequently, based on the effects of organic C on substrate bioavailability, we would generally expect a negative correlation between degradation rates and organic C among different surface soils. However, for a given soil, changes in organic C as a function of soil depth appear to be a reasonable indicator of microbial activity. As a result, we see a positive correlation between organic C (as it changes with soil depth) and degradation rates.

Jury et al. (1987) have used an exponential function to describe changes in degradation rates as a function of soil depth. Wilson et al. (1993) used the following modified form of this expression to predict changes in degradation rates as a function of soil depth for application in coupling geographical information system (GIS) data bases with a solute fate model:

$$t_{1/2(i)} = t_{1/2(0)}\, e^{\gamma(Z - L)} \quad [6]$$

where $t_{1/2(i)}$ is the half-life (d) of the ith layer, $t_{1/2(0)}$ is the half-life in the surface layer, γ is a depth constant (m^{-1}), Z is the average depth of the ith layer (m) and L is the average depth of the surface layer (m). A depth constant of 3 m^{-1} as used by Jury et al. (1987) results in half-lives that increase by roughly 10-fold at 1 m in the soil profile (assuming a surface layer depth of 0.25 m). In the current study, half-lives at 17 to 24°C increased by factors of three- to sixfold going from the 0- to 0.3-m (surface) layer to the 0.6- to 1.2-m zone (Table 3). A depth constant of 1.5 to 2 m^{-1} more adequately describes the magnitude of half-life increases with soil depth observed in this study. Wilson et al. (1993) also noted that the same expression adequately described changes in organic C as a function of soil depth for a data base containing >60 agricultural soils in Montana, given knowledge of the surface organic C content. If one assumes that decreases in soil organic C as a function of soil depth correlate with decreases in microbial activity, then there may be some merit in using a depth function such as Eq. [5] to predict degradation rates as a function of soil depth. Certainly, the use of half-lives (or other degradation rate constants) obtained from surface soils are not adequate for describing degradation rates throughout the entire soil profile. In modeling applications performed at mapping unit or at landscape scales, the unavailability of measured data as a function of soil depth often necessitates the use of estimation routines for parameters such as organic C, and especially microbial degradation rates. From the data presented in this study, it appears that a degradation rate–depth function may be a useful tool for estimating changes in degradation rates as a function of soil depth. While this approach is convenient for modeling efforts at larger geographical scales, the applicability of such an approach needs to be tested for a larger soils data base than is presented in this study.

SUMMARY

The results of this study support the following conclusions related to soil depth and temperature effects on 2,4-D degradation:

1. Bacterial populations decreased significantly in both soils with increasing soil depth and were positively correlated to the rate of 2,4-D degradation.
2. The degradation rate of 2,4-D decreased with decreasing soil temperature from 24 to 10°C; the effect of temperature on degradation rates was adequately described by the Arrhenius equation.
3. Degradation of 2,4-D was adequately described by both a first-order kinetic model and a logistic model with the latter providing a better fit to the experimental data.
4. A positive correlation was observed between soil organic C and microbial activity as measured using bacterial plate counts. In addition, the degradation rates of 2,4-D were positively correlated with changes in soil organic C.
5. The changes in 2,4-D degradation rates associated with soil depth and temperature suggest that fate and transport models should include appropriate functions that provide a mechanism for modifying degradation rates as a function of soil depth and temperature.

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