

Soil Persistence of Atrazine, Metolachlor, and Metribuzin as Influenced by Temperature, Soil Moisture, and Soil Characteristics

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1.0 Rationale and Objectives

The herbicides atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), metolachlor (2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidine) and metribuzin (4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one) are extensively used in Canada for control of a wide variety of broadleaf and grassy weeds. All three herbicides are relatively mobile and have been detected in various public and domestic surface and ground water resources at concentrations greater than drinking water guidelines (Trotter et al., 1990; Pauli et al., 1990; Kent et al., 1991). Consequently, in an attempt to improve management practices that will minimize contamination of our water resources, there has been considerable effort placed on studying and predicting the environmental fate of herbicides under various agricultural conditions.

Government and other research institutions are now developing new and cost effective methodologies for determining pollution potential of pesticides. Screening models, management models, and expert systems provide estimates of the suitability of pesticides for various sites. Another approach, the use of computer simulation models, is gaining wider acceptance for advisory purposes. Simulation models predict transport and fate of pesticides according to principles of specific processes expressed quantitatively. Often the processes are not well understood and/or have not been extensively validated experimentally (Jury and Ghodrati, 1989; Wagenet and Hutson, 1990). Also, detailed parameters are required to describe the processes at specific sites and under various environmental conditions.

The processes of degradation and nonlabile residue (bound residue) formation determine, to a large extent, the persistence of pesticides in soils. Walker (1976) found that the first-order rate law when fit to simazine and prometryne degradation data produced correlation coefficients significant at $P=0.001$, and thus assumed first order kinetics. A simulation model, which Walker developed, satisfactorily estimated the persistence of these herbicides under field conditions. In subsequent years the modified version of this model adequately predicted field persistence of several pesticides from laboratory derived first order rate constants (Walker, 1978; Walker and Zimdahl, 1981; Smith and Walker, 1989; Walker et al., 1992). Wagenet and Hutson (1990), in their simulations with LEACHP (Wagenet and Hutson, 1989), found that pesticide persistence was very sensitive to the first order decay rate.

Hamaker and Goring (1976) suggested a model in which the pesticide was assigned to an 'unavailable' and a 'labile' compartment. First order rate constants were assumed for decomposition, for movement to unavailable sites and for release to labile pesticide. Very few models simulate formation and release of nonlabile (bound) residues. One reason for this is the lack of detailed data available in the literature. Most decay rates of pesticides are determined solely by solvent extractions with no radioactively labelled parent compounds. Thus the decay

rate constants in literature often include both decay and bound residue formation as a lump sum (dissipation). Racke and Lichtenstein (1985), and Khan and Behki (1990) have found that bound residue formation can be a reversible process and thus it is not accurate to include it in the dissipation process.

For various pesticides, it has been shown that dissipation rate may vary greatly, not only with soil type but with temperature and soil water content (Walker, 1976; Gillian and Hance, 1979; Ou et al., 1982; Walker and Brown, 1985; Walker et al., 1992; Obrador et al., 1993). In many instances, however, the effects of temperature and moisture on the kinetics of disappearance of pesticides are not well enough understood to be described quantitatively by temperature and moisture functions in simulation models. Also, information is currently lacking on the spatial and temporal behaviour of decay rate (Wagenet and Hutson, 1990).

The main objectives for this study were as follows:

- i)** Determine the kinetics of dissipation and bound residue formation of widely used pesticides in the Great Lakes area, as influenced by soil moisture, temperature and soil structure.
- ii)** Test laboratory derived dissipation and bound residue formation data by comparing it to dissipation kinetics under field conditions.
- iii)** Provide decay rates and hydrologic transport parameters for soils in the Great Lakes Basin as input for simulation models. Also, modify the pesticide fate and transport model, LEACHP, to provide improved measures of pesticide dissipation kinetics.

2.0 Methodology

To achieve the objectives a series of experiments were carried out:

- i)** A study was performed in the laboratory to determine the effect of soil structure on dissipation and bound residue formation. Incubations were carried out in intact soil cores, packed soil cores and in flasks.
- ii)** To determine the kinetics of dissipation and bound residue formation, laboratory flask experiments were performed at various temperatures and soil moisture contents.
- iii)** Field lysimeters were used to determine field dissipation and bound residue formation kinetics, as well as leaching of herbicides and release of aged residues.
- iv)** Long intact soil core experiments were carried out to determine water and herbicide transport parameters for use in the LEACHP simulation model.

2.1 Effect of soil structure on herbicide dissipation and bound residue formation

Three different incubation systems were chosen to assess the effects of soil structure on pesticide dissipation; intact cores provided the full range of macro (interped), meso (interaggregate), and micro (intergranular) structure; packed cores provided a range of meso- and micro- structure; and flasks provided only microstructure. All incubations were carried out at 25°C and 70% of saturated water content.

2.1.1 Soils

All flask and soil core experiments were performed with 3 soils. Soil properties, determined according to Sheldrick (1984), and are shown in Table 1.

The sandy loam soil was continuously cropped with soybeans and had not received atrazine, metolachlor, or metribuzin for at least 3 years. The loam soil was cropped with alfalfa and had not been sprayed with any pesticides for at least 9 years. The clay loam soil was in fallow and had not been sprayed for 2 years.

2.1.2 Soil core incubations

Design of the soil core apparatus is shown in Fig. 1. All materials were resistant to atrazine and metolachlor adsorption (Topp and Smith, 1992). Average soil water content in the cores was measured using the time domain reflectometry (TDR) method as described by Topp (1993). Soil water content was held constant by a hanging water column (Haines) apparatus similar in concept to that described by Topp and Zebchuk (1979). The constant head buret allowed water to flow into or out of the core as required in order to maintain the set tension (60 cm).

Table 1. Physical and chemical properties of soils.

Soil	Location	pH	CEC (Meq/ 100g)	OC (%)	Sand -----	Silt (%)	Clay -----
Sandy loam	Alliston	6.3	7.14	1.16	72.2	20.5	7.3
Loam	Ottawa	5.0	8.73	1.90	37.5	48.8	13.7
Clay loam	Harrow	5.1	20.6	1.43	25.4	35.2	39.4

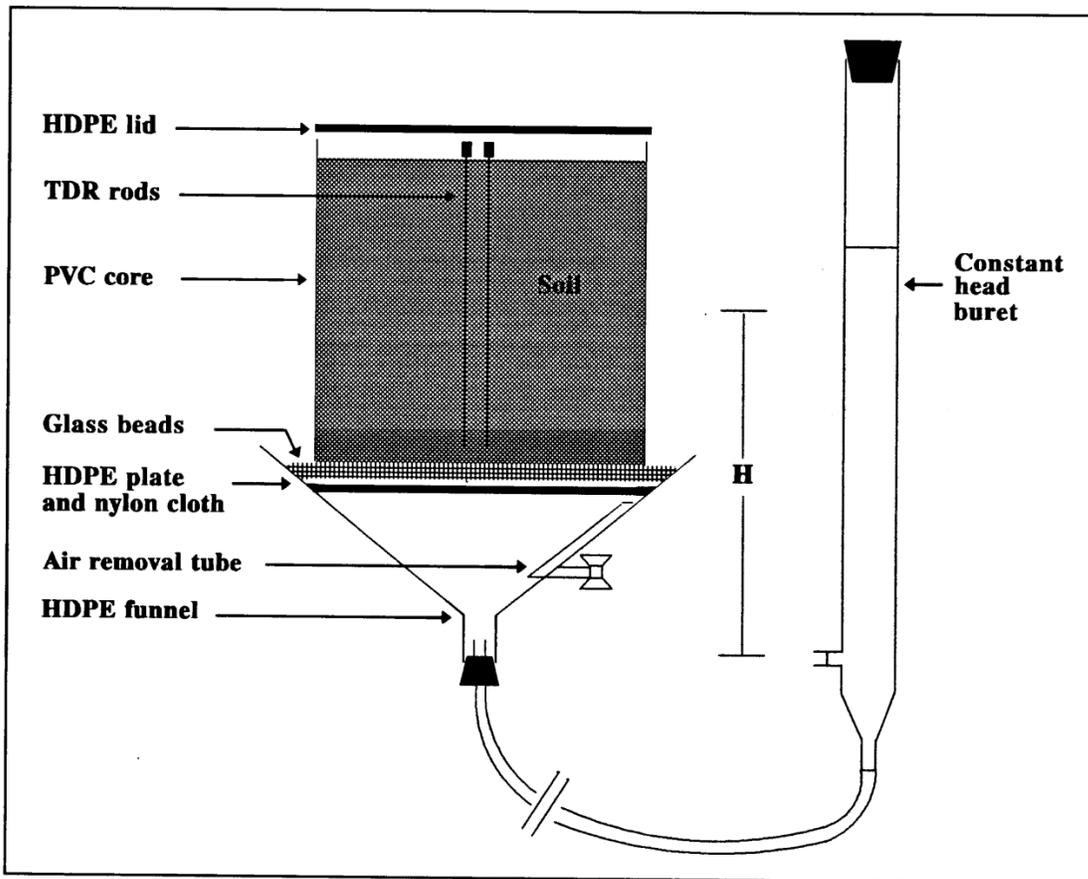


Figure 1 Haines apparatus for the control of soil moisture content in soil cores.

Commercial grade atrazine and metolachlor were applied to the surface of the cores at a rate of 3 kg ha⁻¹. Water (0.5 cm) was applied 1 hour after pesticide application and at weekly intervals with a capillary applicator. Cores were sampled to a depth of 20 cm with a soil sampler of 0.375 cm diameter. The hole left by the sampler was plugged with a snug-fitting glass rod to prevent preferential entry of air or water. For each soil texture, six intact soil cores were incubated, four of which received non-radioactive herbicide, and two of which received radioactive atrazine (20 uCi per core). In addition, six repacked cores of the loam soil were prepared and similarly incubated.

Packed cores were prepared with soil taken from intact cores. The soil was removed, air dried, and sieved to a maximum particle size of 2 mm. The soil was then replaced into the PVC pipe in 2 cm layers, sequentially adjusting the bulk density to 1.43 g cm⁻³ with a hydraulic press, until a depth of 20 cm was achieved (Sheldrick, 1984).

2.1.3 Flask incubations

Fresh soil was air dried and passed through a 2 mm sieve. A methanol stock solution (0.4 ml) containing 1020 mg L⁻¹ of atrazine, metolachlor and metribuzin and 0.5 µCi of either radio-labelled atrazine or radio-labelled metolachlor was added to the soil by syringe, the solvent was allowed to evaporate, and the soil was thoroughly mixed. Enough water was pipetted into each jar to provide the desired gravimetric water content. The initial concentration of each herbicide was 4.3 µg g⁻¹ (similar to the top 5 cm depth for field recommended rates) and the radioactive content was 11 000 dpm g⁻¹ for either atrazine or metolachlor. The desired soil water content was kept constant by weighing the flasks and adding water at 3 day intervals. Flasks were loosely capped and incubated at the desired temperature for 63 days. Samples corresponding to 10 g dry weight were periodically taken from each flask. They were extracted and analyzed as described below. Four replicate flasks were incubated for each soil type.

2.2 Kinetics of dissipation and bound residue formation as influenced by temperature and soil moisture

Flask experiments, incubated as described above, were carried out at 15, 25, and 35 °C at 70% of saturated water content and under air dried, 20, 30, 70, and 100% of saturated water content at 25 °C.

In sterile flask incubations with γ-irradiated soils (1.8 Mrad of radioactivity from a ⁶⁰Co source) all equipment including flasks, caps, spatulas and weighing boats were sterilized with an autoclave before use and were kept sterile throughout the experiment. Sterile experiments were performed at 15, 25, and 35 °C at 70% of saturated water content.

2.3 Kinetics of field dissipation and bound residue formation, as well as leaching of herbicides and release of aged residues

Twenty four intact PVC cores of 20.1 cm inside diameter and 20 cm length were extracted from the Ap horizon of a Dalhousie clay soil according to procedures described by Smith et al. (1992). Half of the cores were collected from two tilled plots and the other half from two no-till plots. A pair of cores were taken at three locations within each plot, making a total of three sites/plot (six cores per plot) for a total of 12 sites. Soil properties at the 12 sites are shown in Table 2. Sites 1,2,3,7,8, and 9 were in tilled plots. In the previous four years the 14 ha field was continuously cropped in corn and sprayed with atrazine and metolachlor. The field was adjacent to a control field (no herbicides applied for several years) from which the loam soil in Table 1 was collected.

Table 2. Soil properties at twelve lysimeter sites.

Site	pH	Clay (%)	Cation Exchange Capacity (mEq/100g)	Carbon (%)
1	5.12	17.8	6.87	1.47
2	5.21	5.29	4.24	1.96
3	5.31	4.47	4.01	1.63
4	5.25	13.4	5.50	1.26
5	5.36	20.3	9.45	2.05
6	4.82	13.5	4.92	2.05
7	4.89	20.8	8.38	1.71
8	4.84	24.3	9.23	1.73
9	5.12	11.41	4.77	1.73
10	4.58	20.39	6.32	2.02
11	5.51	22.07	10.31	1.61
12	4.59	20.59	5.71	1.94

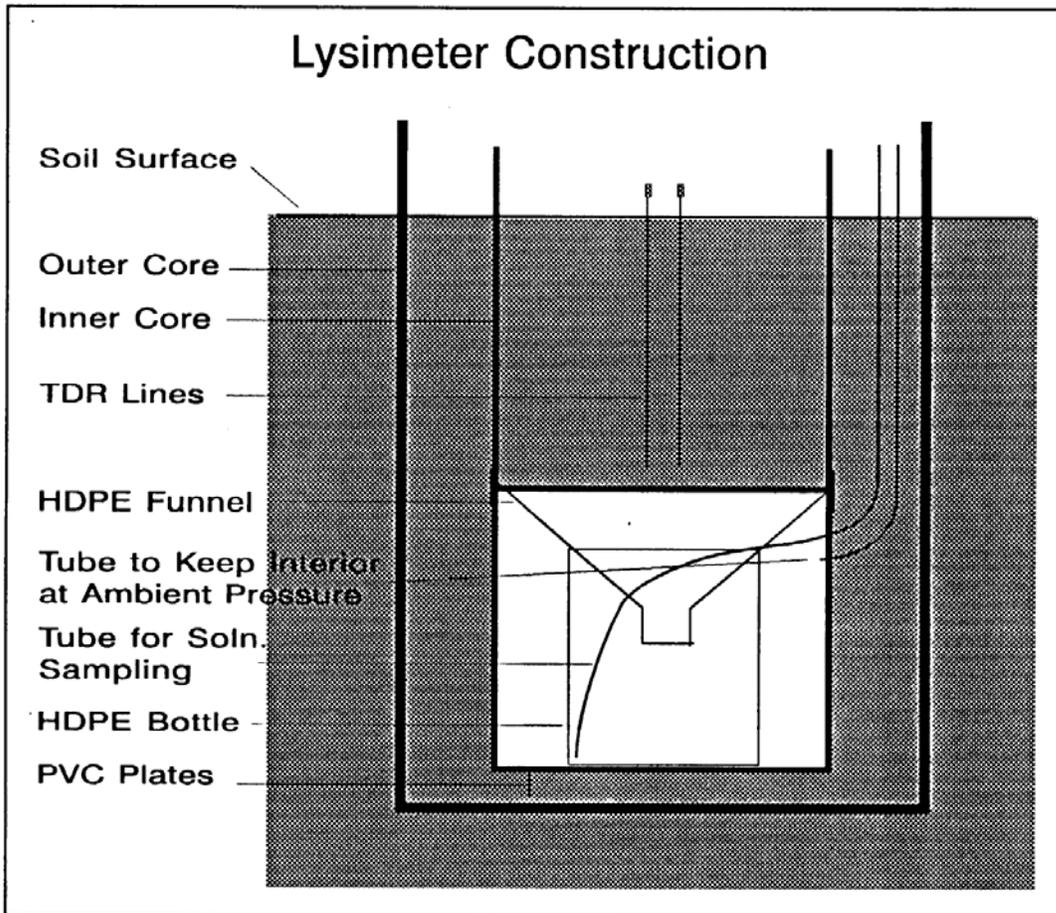


Figure 2 Design of field lysimeters

A cross section of the lysimeter design is shown in Fig. 2. To safeguard against contamination of the field with ^{14}C labelled herbicide, the lysimeters were placed within a second larger (30 cm diameter) core which protruded 15 cm above the soil surface. Soil water content was measured using TDR probes installed both in the intact lysimeters (inner core) and in the field beside each set of lysimeters. Thermocouples were installed just outside the outer core at 1, 5, 10, 20 and 30 cm depths. Herbicides were applied in a 10 ml water suspension at a rate of 1.25 kg ha⁻¹ and 20 μCi of radioactivity. Atrazine was applied to one lysimeter at each site, while metolachlor was applied to the other.

At the end of each rainfall event leachate was collected from below the lysimeters through teflon tubing with a hand held vacuum pump. Also, eight lysimeters, two in each plot (one with atrazine and one with metolachlor), were subsampled in triplicate with a core sampler eight times during the four month cropping season. All 24 lysimeters were sectioned at the end of the experiment and sampled at five depths.

To determine the rate of release of bound atrazine residues from aged atrazine treated soil, six cores were extracted at one location in an adjacent field (control field), where no herbicide had been applied in the last 10 years. The soil was a loam whose properties are given in Table 1. The aged atrazine treated soil was produced prior to experimentation by applying ^{14}C atrazine, at a rate of $1.8 \mu\text{Ci g}^{-1}$, to 3 different soils (Table 1) and incubating them in flasks for one year. One hundred grams of each of the treated soils was mixed with 300 g of unspiked soil and half of the mixture (200 g) was placed on each of two replicate lysimeters (i.e. 2 cores with sandy loam soil, 2 with loam soil, and 2 with clay loam soil).

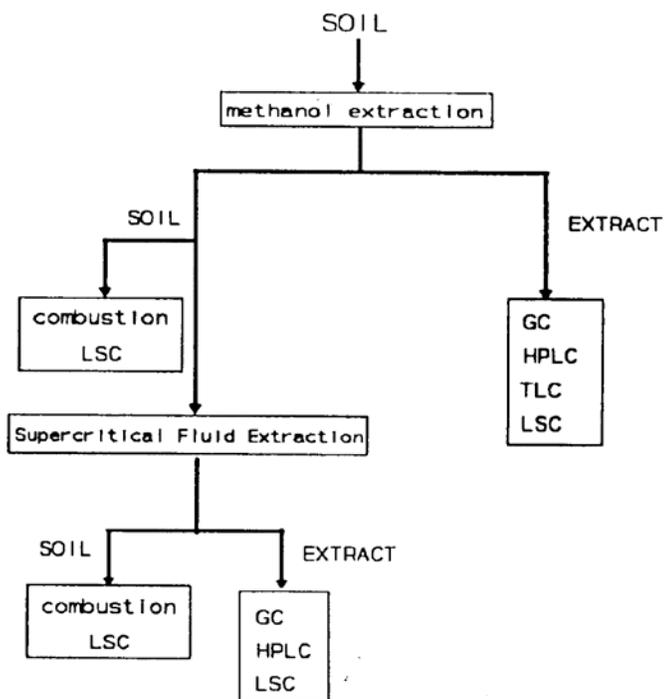


Figure 3 Scheme for fractionation and analysis of extractable and bound (non-extractable) herbicide residues

2.4 Leaching of atrazine and chloride through long intact soil columns

Leaching of chloride and atrazine through 65 cm long by 20 cm diameter intact PVC soil columns was carried out to determine water flow and chemical transport parameters for testing the pesticide transport model LEACHP. Duplicate intact soil columns were taken from the loam control field mentioned above (Table 1). At six depths (in 10 cm increments starting 10 cm below the soil surface) the columns were instrumented with, two soil water solution samplers for measuring chloride and atrazine break through curves (BTC), a horizontal TDR probe (Topp, 1993) for measuring soil water content, and a tensiometer for measuring soil water pressure head. Leachate was collected from below the columns under both positive and negative pressure head conditions. Water at constant flux rates of 2.2 and 54 cm day⁻¹ was applied to the surface of the columns with a peristaltic pump. Potassium chloride and atrazine were applied, in a pulse, at rates of 5.1 g/column and 9.56 mg/column, respectively. Soil solution was collected periodically through the solution samplers with a hand held vacuum pump.

2.5 Analysis of herbicide residues

Analysis of soil samples was carried out according to the flowchart in Fig. 3. Soil was extracted with methanol according to Smith et al. (1992). The three herbicides, as well as deisopropylatrazine and deethylatrazine, were quantified simultaneously by gas chromatography (GC). Total radioactivity in the extracts was determined with a liquid scintillation counter. Extracts were also analyzed by reverse phase high pressure liquid chromatography (HPLC) with a UV and a radioactive detector coupled in series. Operating instructions were identical to those described by Topp et al. (1994). The radioactivity (bound residues) remaining in the methanol-extracted soil was determined by combustion, trapping the ¹⁴CO₂ in Carbo-Sorb, and quantifying by liquid scintillation counting (LSC). The chemical identity of the nonextractable residues was established by subjecting methanol-extracted soil to supercritical fluid extraction (SFE) and analyzing extracts by GC, HPLC, or thin layer chromatography (TLC).

Water samples were extracted with dichloromethane as described by Smith et al. (1992). The extracts were analyzed for herbicides and metabolites by GC and were analyzed for total radioactivity by LSC.

2.6 Calculations and computer modelling

The rate of decrease in concentration (dissipation) of extractable herbicides was determined by GC analysis of extracts. The following rate model proposed by Hamaker (1966) was used to fit the data:

$$\frac{dC}{dt} = -kC \quad (1)$$

$$C = (C_o^{(1-n)} + (n-1)kt)^{\frac{1}{(1-n)}} \quad (2)$$

or

where C is concentration ($\mu\text{g ml}^{-1}$), C_o ($\mu\text{g ml}^{-1}$) is concentration at time = 0 days, t is time (days), k is kinetic rate coefficient (days^{-1}), and n is order of reaction. The constants n and k were determined as the slope and intercept, respectively from a linear regression of the natural log of dC/dt vs the natural log of C.

When n = 1, Eq. 1 reduces to a first order equation and C can be expressed as:

$$C = C_o e^{-kt} \quad (3)$$

For the above equation, linear regressions of the natural log of concentration vs time can be used to determine the first order rate constants (k).

Non-extractable ^{14}C residue formation was calculated by combusting extracted soil samples followed by LSC. Mineralization / volatilization of ^{14}C atrazine and metolachlor was determined by adding extractable and non-extractable ^{14}C (^{14}C recovery) and subtracting from the amount of radioactivity applied.

To characterize temperature and moisture effects three temperature functions and one moisture function were examined. The Arrhenius equation is based on the theory that reactants must attain certain minimum activation energy (E_a) for product formation. It is expressed as follows:

$$E_a = \frac{\log\left(\frac{H_1}{H_2}\right)(2.303R)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \quad (4)$$

where H_1 (day^{-1}) is a first order half life at temperature T_1 ($^{\circ}\text{K}$), H_2 (day^{-1}) is a half life at temperature T_2 ($^{\circ}\text{K}$), and R ($\text{J mol}^{-1} \text{K}^{-1}$) is the ideal gas constant.

The Q10 function is the ratio of rates measured at temperatures differing by 10 $^{\circ}\text{C}$. Like the Arrhenius function, it has a thermodynamic basis but is often said to be more easily understood. The equation is as follows:

$$Q_{10} = e^{\ln\left(\frac{H_1}{H_2}\right)\left(\frac{10}{T_2 - T_1}\right)} \quad (5)$$

The Arrhenius and Q10 functions can not describe the decrease in decay rates as temperatures exceed biological optima. An empirical function can be used to describe this phenomena:

$$k = e^{(A + BT + CT^2)} \quad (6)$$

where k is the first order decay rate and A, B, and C are empirical constants derived from data. This quadratic temperature function accommodates diminishing responses to temperature by fitting a specific data set, but has no thermodynamic basis on which to estimate parameters for other soil types.

In his work on modelling the persistence of alachlor Walker et al. (1992) successfully made use of the following moisture relationship:

$$H = AM^{-B} \quad (7)$$

where M is the moisture content of the soil, and A and B are empirical constants determined as the intercept and slope of the regression of log H vs log M.

3.0 Study Findings

3.1 Comparison of atrazine and metolachlor dissipation in soils incubated in undisturbed cores, repacked cores, and flasks

The rates of atrazine or of metolachlor dissipation in soils incubated in flasks or in intact cores were indistinguishable ($p < 0.05$). The rate of net accumulation of extractable transformation products of atrazine and the rate of bound residue formation in soils incubated in flasks were also similar to those from intact cores. However, the rate of dissipation of metolachlor, the rate of accumulation of atrazine transformation products, and the rate of formation of bound atrazine residues were all significantly slower in repacked cores of the loam soil. These results indicate that, under controlled laboratory conditions, atrazine and metolachlor dissipation occurred at the same rate in intact cores and in flask incubations, even though the flask soil had been disrupted by previous air-drying and sieving.

3.2 Kinetics and pathways of herbicide dissipation and bound residue formation as influenced by temperature and soil moisture

Atrazine dissipated according to first order kinetics whereas the apparent metribuzin and metolachlor reaction orders varied with temperature and soil type. There was a general trend for higher reaction orders, sometimes greater than two, at lower temperatures. Gillian et al. (1979) had similar observations for linuron and metribuzin dissipation. A concise mathematical description of reaction order kinetics for these herbicides as a function of temperature, moisture and soil properties would be difficult to establish due to the complexity of soil systems. Rate of dissipation for a specific herbicide may be a function of several reactions occurring simultaneously or subsequently. Because of the variation involved, and the fact that most of the data fit first order kinetics reasonably well, Tables 3 and 4 only present first order half lives.

Temperature and moisture had pronounced effects on the half lives of all three herbicides, especially on atrazine (Table 3). The hydrolysis reaction of atrazine with clay in the clay loam soil followed by subsequent mineralization / volatilization probably caused it to dissipate faster than in the other two soils. At 25 and 35°C and 70 and 100% of saturated moisture content, mineralization / volatilization of ^{14}C atrazine residues in the nonsterile clay loam soil was greater than 50% by the end of the incubations. Less than 9% of mineralization / volatilization occurred in the sterile experiments, indicating that microbial activity was required for substantial mineralization of atrazine. Unlike for atrazine, metolachlor and metribuzin were more persistent in the clay loam soil than in the other soils.

Table 3. Half lives (d) and Q10 of herbicide dissipation for three temperatures, with incubations carried out at 70% of saturated soil water content.

SOIL	Temperature (°C)				Temperature (°C)				Temperature (°C)			
	15	25	35	Q10	15	25	35	Q10	15	25	35	Q10
Nonsterile												
Sandy loam	112a*	32.3a	22.6a	2.3	52.1a	28.0a	20.2a	1.63	43.4a	25.4a	21.1	1.43
Loam	104a	39.9b	15.9b	2.65	100b	55.0b	40.5b	1.60	87.8b	38.7b	26.3b	1.87
Clay loam	85.3b	24.9c	13.4c	2.61	134b	56.8b	40.5b	1.87	92.2b	32.9b	24.1b	2.00
Sterile												
Sandy loam	153a	69.4a	33.7a	2.19	208a	87.7a	51.2a	2.07	159a	73.0a	38.3a	2.09
Loam	120b	46.0b	18.1b	2.57	130b	98.8b	635b	0.45	111b	68.0a	48.1b	1.54
Clay loam	72.5c	30.9c	12.1c	2.66	256a	101b	557b	0.47	293c	130b	45.7b	2.61

* mean separators, significant at the 0.05 level, were determined across soil type using the least significant difference test

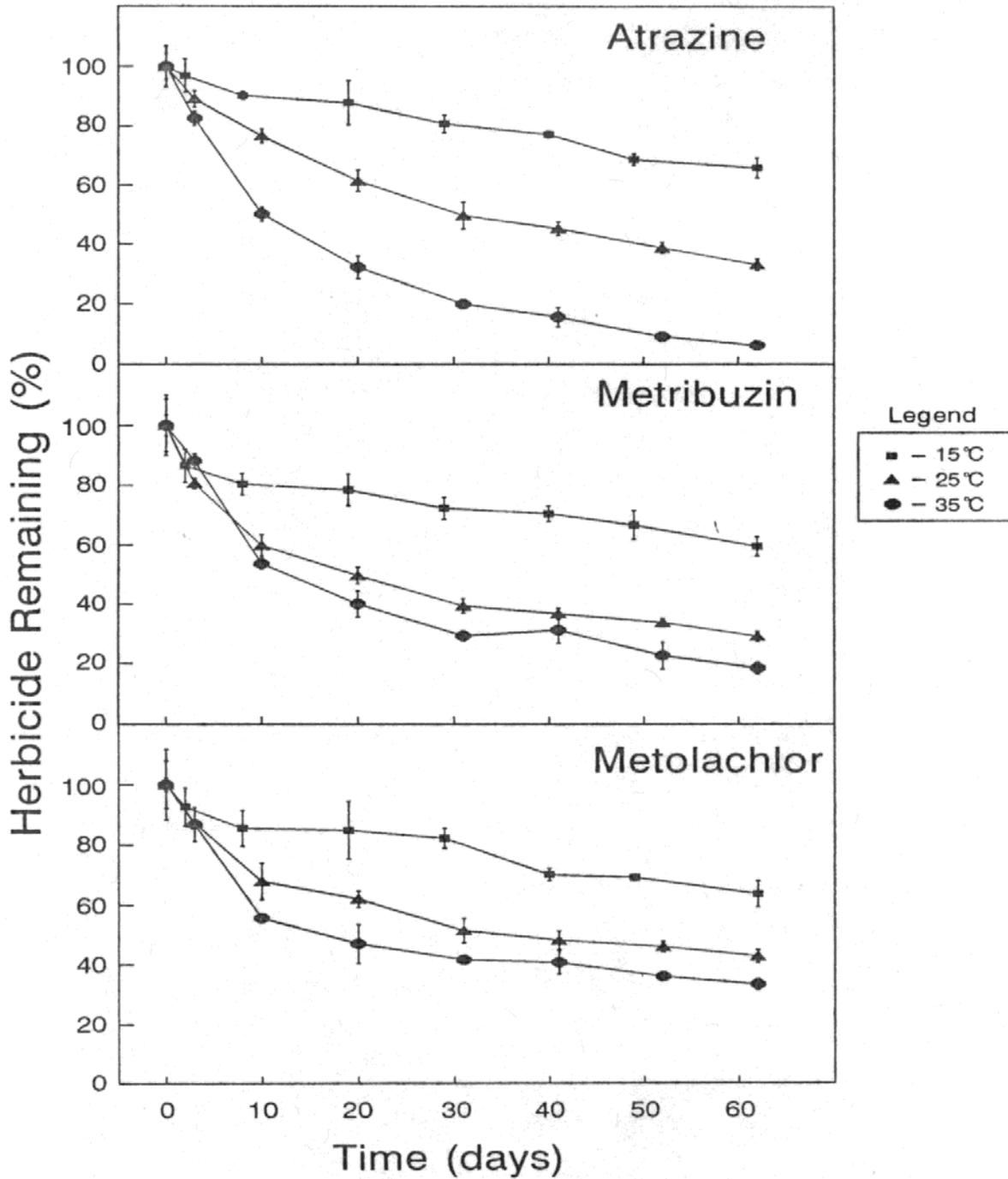


Figure 4 Dissipation of herbicides as influenced by temperature in the loam soil

The Q10 function measures dissipation response to temperature. It was used in this study because it fit the data well, and was already included in some pesticide transport models (LEACHP, Wagenet and Hutson, 1989; PESTFADE, Clemente and Prasher, 1992). Q10 values (average for three soils) of 2.52, 1.77, and 1.70 for atrazine, metolachlor, and metribuzin, respectively, indicated that the response of herbicide dissipation to temperature was large and more pronounced for atrazine. Also, for the three herbicides Q10 was typically greater in soils with higher clay content. For the loam soil, dissipation curves for atrazine, metribuzin and metolachlor at 15, 25, and 35 °C are shown on Fig. 4. For atrazine there was a much larger difference in dissipation rates at 25 and 35°C than for metribuzin and metolachlor, indicating that biological and/or chemical degradation of metribuzin and metolachlor may have nearly reached its optimum at 25°C.

The Q10 for atrazine dissipation was similar between the sterile and nonsterile incubations. Metribuzin, and particularly metolachlor dissipation kinetics were, however, very different. In the sterile incubations metolachlor showed irregular behaviour in that it dissipated slower at 35°C than at 15 and 25°C in both the loam and clay loam soils. It is possible that enzymatic activity that degraded metolachlor at 15 and 25°C was heat-killed at 35°C.

Soil moisture had a considerable influence on atrazine, metribuzin, and metolachlor dissipation in all three soils (Table 4). The influence on atrazine dissipation was greatest in the clay loam soil. In the loam soil, metribuzin, for some unknown reason dissipated rapidly under air dried conditions. Metribuzin has a low vapour pressure (<1.3 mPa at 20°C) thus it is not likely to have volatilized from the soil in such large quantities. Since metribuzin was not radioactively labelled it was not possible to determine its pathway of dissipation. For the rest of the moisture treatments, dissipation of metribuzin in the loam soil behaved in a similar manner as in the other soils.

Walker (1978), in his dissipation model, used Eq. 7 to accurately predict half lives of various pesticides. In Table 4 the empirical constants A and B were determined from the log-log regression of half life and water content in the range from 20 to 100% of saturation. In this moisture range Eq. 7 produced a good fit to our data. Under air dried conditions dissipation occurred much slower, probably by different processes. Equation 7 was incorporated into the decay subroutine in LEACHP. If water content came within 1% of air dried conditions a provision was made to employ half lives under air dried conditions.

3.2.1 Metabolites of atrazine

To determine the amount and identity of atrazine metabolites, HPLC-radioactivity detector analysis of methanol extracts from the three soils was done at the end of the incubations. Results at 25°C are shown on Table 5. In the nonsterile systems more dealkylated products were formed in soils with higher sand contents. Nair and Schnoor (1992) found that atrazine degraded

much slower under anaerobic than aerobic conditions. More aeration in the soils with greater sand content likely encouraged microbial activity.

Under sterile conditions no dealkylated atrazine metabolites were detected in the loam and clay soils at 25 and 35°C and few were detected in the remainder of the incubations. The degradation of atrazine follows three main pathways: hydrolysis at the number two carbon, N-dealkylation of side chains, and ring cleavage (Kaufman and Kearney, 1970). The first is a form of chemical degradation and the latter two are caused in soil by microbial degradation. Supporting this hypothesis, there was little dealkylation and mineralization of atrazine occurring in the sterile systems, where there was limited or no microbial activity. The small amount of dealkylated degradation that occurred could have been a result of enzymatic activity. Winkleman and Klaine (1991a, 1991b) commented that γ -irradiation would not destroy enzymes which could still catalyze transformation reactions. The accumulation of hydroxyatrazine in the loam and clay loam soils was probably caused by chemical degradation. However, more hydroxyatrazine was formed in the sandy loam under nonsterile conditions than sterile conditions indicating that some form of microbial activity could have been responsible for its formation.

Table 4. Half lives (d) and A and B constants for dissipation at various soil water contents and a temperature of 25°C.

Soil	Water content (percent of saturation)					A	B
	air dry	20	30	70	100		
Atrazine							
Sandy loam	151.0a *	62.7a	46.0a	32.3a	40.3a	109.3	0.301
Loam	131.3b	49.3a	48.8a	39.9b	30.9b	96.1	0.276
Clay loam	327.8c	53.0a	43.9a	24.9c	19.6c	240.2	0.639
Metolachlor							
Sandy loam	368.9a	82.4a	53.5a	28.0a	36.4a	250	0.561
Loam	390.4a	247.5b	138.3b	55.0b	39.4a	3129	1.166
Clay laom	343.6a	218.9b	198.3c	56.8b	52.6b	2369	1.027
Metribuzin							
Sandy loam	318.6a	71.5a	52.8a	25.4a	36.0a	201.9	0.512
Loam	68.1b	73.5a	67.8b	38.7b	36.3a	233.8	0.506
Clay	273.7a	113.4b	79.7b	32.9b	45.2a	454.3	0.668

* mean separators, significant at the 0.05 level, were determined across soil type using the least significant difference test

Table 5. Formation of Extractable Atrazine Transformation Products at 25 °C.

	Recoverable radioactivity (%)					
	Sandy loam	Nonsterile			Sterile	
		Loam loam	Clay loam	Sandy loam	Loam loam	Clay loam
Atrazine	71	73	78	91	79	71
Deethylatrazine	10	2	1	3	0	0
Deisopropylatrazine	4	1	1	1	0	0
Hydroxyatrazine	15	5	20	5	21	29
Unknown	0	19	0	0	0	0

3.2.2 Mineralization and bound residue formation

The rate of bound atrazine and metolachlor residue formation was typically faster at higher temperature and soil moisture contents (Tables 6 and 7). Under air dried conditions, however, bound residues were still formed. Bound ¹⁴C atrazine residue accumulation at the end of the air dried incubations was 15.9, 27.0, and 6.8% in the sandy loam, loam, and clay loam soils, respectively. The long term fate of bound residues is unclear, but atrazine residues have been reported to persist in a mineral soil for at least 9 years (Capriel et al., 1985).

In the clay loam soil (Table 6) accumulation of bound residues was not as responsive to temperature as in the other soils due to loss of ¹⁴C from the system via mineralization or loss of a volatile derivative of atrazine at 25 and 35°C. Recovery of ¹⁴C was 94.6, 42.7, and 47.0% at 15, 25 and 35 °C, respectively. Such a large amount of mineralization / volatilization of atrazine from soils is seldom reported, especially under laboratory conditions. In a review of the literature, Esser (1977) found that experiments with ¹⁴C ring-labelled atrazine generally resulted in only a few percent of the applied radioactivity evolving over a period of about four months. For the sandy loam and loam experiments over 85% of the applied radioactivity was recovered at the end of the experiments. Recovery of ¹⁴C ring-labelled metolachlor was greater than 87% in all incubations.

3.3 Persistence and leaching of atrazine and metolachlor in field lysimeters.

Recovery of ^{14}C labelled atrazine and metolachlor residues in effluent collected below the lysimeters during the growing season is shown in Fig. 5. More atrazine and metolachlor reached 20 cm in the no-till than in tilled soil but in both cases, little leaching occurred. The main difference between till and no-till occurred just after herbicide application on June 14. At this time, the soil was very moist and the herbicides had little time to adsorb and diffuse into the soil matrix. Atrazine and metolachlor probably moved down macropores that were more likely to have been present in the no-till soil. From July to October, when evaporation was high, the soil seldom reached field capacity and thus water flow below the 20 cm depth was small. In the tilled soil greater leaching correlated with greater clay content ($r^2 > 0.65$).

Over the entire 1993 growing season the average half life of atrazine and metolachlor in the field was 26.7 and 40.5 days, respectively. In contrast, the half lives of aged atrazine and metochlor (no herbicide applied in the present year; applied in previous years) was 65.1 and 137.2 days, respectively. Rainfall events were sometimes associated with an increase in the extractable residue concentration suggesting that the longer half life of residues from previous years applications was at least partly due to strong non-equilibrium sorption or bound residue formation with the soil. The average bound residue formation in the lysimeters at the end of 4 months was 23.6% and 28.8%, for ^{14}C atrazine and metolachlor, respectively.

In the control field, small amounts of aged ^{14}C atrazine residues were released after rainfall events. After 120 days of incubation in the field 0.44, 0.34, and 0.15 % of the applied radioactivity leached below the 20 cm depth from the lysimeters onto which the sandy loam, loam, and clay loam soils were added, respectively. This was a substantial amount considering that on average only 0.42% of the ^{14}C atrazine which was newly applied in June to the 12 lysimeters in the test field leached below the 20 cm depth.

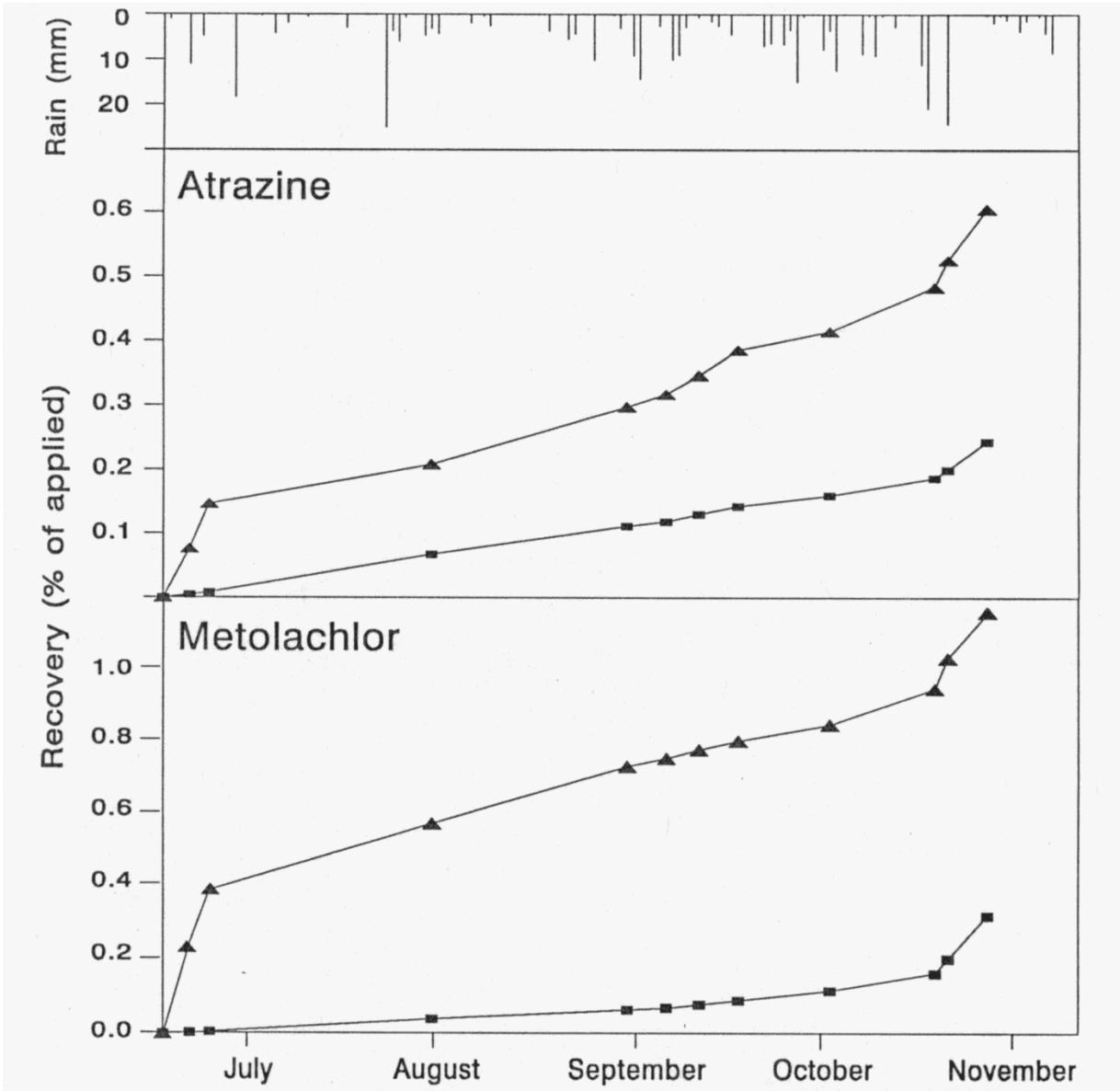


Figure 5 Recovery of ¹⁴C ring-labelled atrazine and metolachlor in lysimeter leachate from till (squares) and no-till (triangles) plots.

Table 6. Distribution of C-14 residues at various temperatures at the end of a 2 month incubation in soils at 70% of saturated water content.

ATRAZINE

Temp (°C)	Soil	Nonsterile			Sterile			
		Extract	Bound	Recovery	Extract	Bound	Recovery	
		-----			%	-----		
15	Sandy loam	71.1 ± 3.8	24.6 ± 1.7	95.7 ± 5.2	81.0 ± 2.1	15.5 ± 2.0	96.5 ± 0.5	
	Loam	72.2 ± 2.4	19.8 ± 1.7	92.0 ± 4.1	76.8 ± 0.5	23.9 ± 1.6	100.8 ± 1.5	
	Clay loam	70.4 ± 4.6	24.2 ± 2.1	94.6 ± 3.0	62.6 ± 1.8	41.9 ± 0.8	104.5 ± 1.6	
25	Sandy loam	43.9 ± 7.6	50.0 ± 3.5	94.8 ± 4.2	57.1 ± 2.4	39.8 ± 8.8	96.7 ± 14.	
	Loam	54.2 ± 1.7	40.8 ± 2.1	95.0 ± 3.3	53.6 ± 3.0	45.0 ± 2.0	97.4 ± 2.5	
	Clay loam	18.6 ± 3.1	24.2 ± 2.0	42.7 ± 3.5	36.9 ± 2.3	62.9 ± 2.5	99.5 ± 4.8	
35	Sandy loam	26.7 ± 1.8	68.9 ± 12.	95.5 ± 11.	30.0 ± 1.2	55.6 ± 6.1	85.6 ± 5.6	
	Loam	32.5 ± 0.8	52.7 ± 4.4	85.2 ± 4.7	32.4 ± 1.4	52.7 ± 7.7	85.1 ± 9.0	
	Clay loam	8.30 ± 0.6	38.7 ± 1.4	47.0 ± 1.6	27.5 ± 1.7	64.2 ± 3.0	91.7 ± 3.5	

METOLACHLOR

Temp (°C)	Soil	Nonsterile			Sterile			
		Extract	Bound	Recovery	Extract	Bound	Recovery	
		-----			%	-----		
25	Sandy loam	47.2 ± 7.3	42.5 ± 5.1	89.8 ± 4.9	76.2 ± 6.9	17.4 ± 13.	93.6 ± 13.	
	Loam	76.8 ± 1.9	23.4 ± 1.3	100.2 ± 1.8	82.6 ± 11.	12.2 ± 9.3	94.8 ± 4.1	
	Clay loam	56.4 ± 6.0	31.5 ± 5.1	87.9 ± 4.1	81.0 ± 3.0	17.7 ± 6.4	98.7 ± 3.5	
35	Sandy loam	44.1 ± 1.3	47.0 ± 3.3	91.1 ± 3.7	89.7 ± 1.7	8.50 ± 1.7	97.8 ± 2.3	
	Clay loam	50.3 ± 0.8	45.2 ± 4.4	95.5 ± 5.0	89.2 ± 5.6	8.60 ± 0.9	97.8 ± 4.9	

± represents 95% confidence interval

Table 7. Distribution of C-14 atrazine residues at various soil water contents at the end of 2 month incubations carried out at 25 °C.

Water content (% of saturation)	Soil	Extractable -----	Bound ----- % -----	Recovery -----
air dry	Sandy loam	87.9 ± 1.77	15.9 ± 2.33	103.8 ± 2.34
	Loam	76.9 ± 0.72	27.0 ± 2.77	103.9 ± 2.69
	Clay loam	97.6 ± 3.64	6.80 ± 0.91	104.5 ± 4.29
20	Sandy loam	59.4 ± 1.22	39.8 ± 4.16	99.3 ± 3.61
	Loam	55.0 ± 1.60	48.9 ± 1.65	103.9 ± 0.42
	Clay loam	58.1 ± 0.93	42.4 ± 3.80	100.5 ± 3.60
30	Sandy loam	52.0 ± 2.59	47.5 ± 0.31	99.5 ± 2.70
	Loam	60.5 ± 1.36	45.6 ± 7.09	106.1 ± 6.86
	Clay loam	50.4 ± 0.72	49.4 ± 4.28	99.8 ± 4.83
70	Sandy loam	43.9 ± 7.55	50.0 ± 3.46	94.8 ± 4.22
	Loam	54.2 ± 1.72	40.8 ± 2.14	95.0 ± 3.32
	Clay loam	18.6 ± 3.05	24.2 ± 1.97	42.7 ± 3.47
100	Sandy loam	43.3 ± 2.00	53.5 ± 4.54	96.8 ± 5.77
	Loam	36.9 ± 0.55	47.7 ± 5.03	84.6 ± 4.89
	Clay loam	15.5 ± 3.06	21.9 ± 7.44	37.4 ± 10.3

± represents 95% confidence interval

3.4 Application of LEACHP

3.4.1 Field lysimeters

The decay rate subroutine of the pesticide fate and transport model LEACHP was modified to include a revised Q10 function and the moisture function (Eq. 7). LEACHP simulations were carried out for atrazine and metolachlor in the loam soil as follows; i) temperature and moisture functions, with parameters determined from laboratory data, were employed to update dissipation rates, ii) a single rate constant was used at 20% of volumetric water content and 20°C, and iii) an average rate coefficient was taken from a literature review by Rao and Davidson (1980).

The simulated results were compared to measured field lysimeter dissipation rates. Fig. 6 and 7 show measured field data and the three LEACHP simulations for atrazine and metolachlor, respectively. Atrazine dissipation was predicted quite accurately when a variable rate constant, which was determined from laboratory data, was used. For the simulations using a constant decay rate calculated at 20% moisture and 20°C, atrazine dissipation was much slower than the measured field dissipation. A constant decay rate may be satisfactory for certain climatic conditions, however, field conditions may change drastically from season to season and from year to year. Simulations with the literature derived rate coefficient resulted in underestimation of atrazine persistence. The metolachlor literature rate produced better estimates, except later in the season. For both atrazine and metolachlor, field dissipation rates were closely predicted from laboratory data (use of the variable rate constant), however, the contribution of mineralization / volatilization was underestimated, and the contribution of bound residue formation overestimated. In the field, the average mineralization / volatilization at the end of the four month experimental period was 66.9% and 55.9% for atrazine and metolachlor, respectively. Since the herbicides were ring labelled this means that microorganisms were responsible for breaking down the aromatic ring. Although dissipation was accurately predicted the contribution of degradation and non-equilibrium sorption to the long-term fate of applied residues must be further examined.

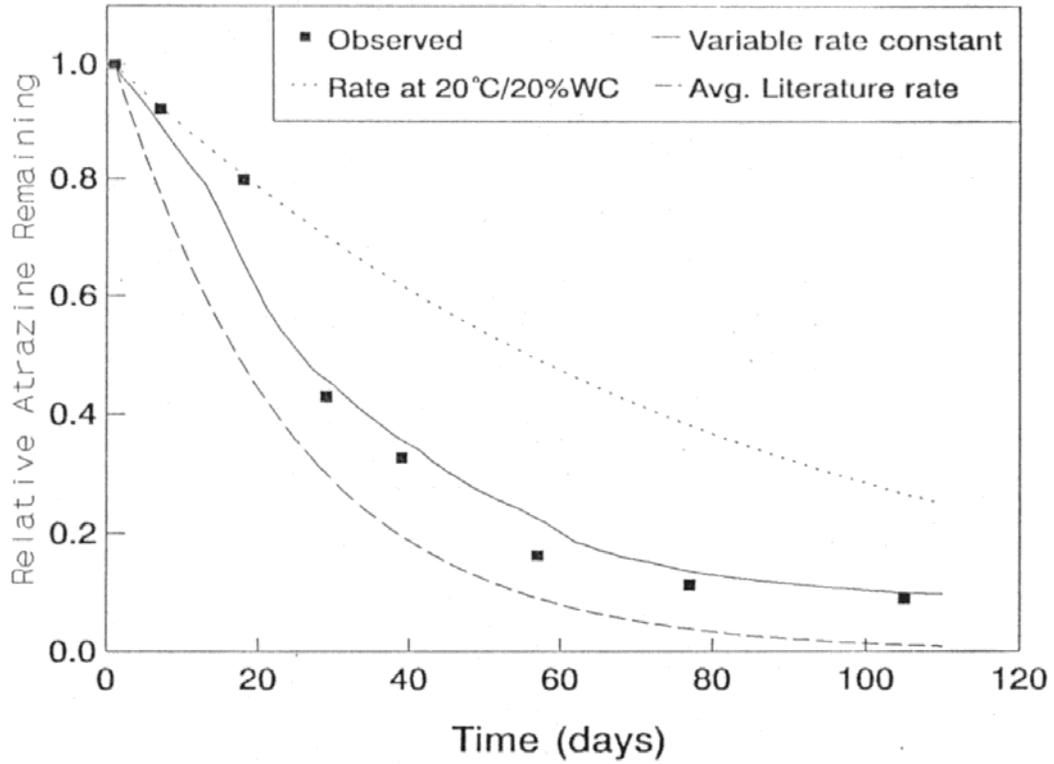


Figure 6 Predicted vs measured dissipation of atrazine in field lysimeters

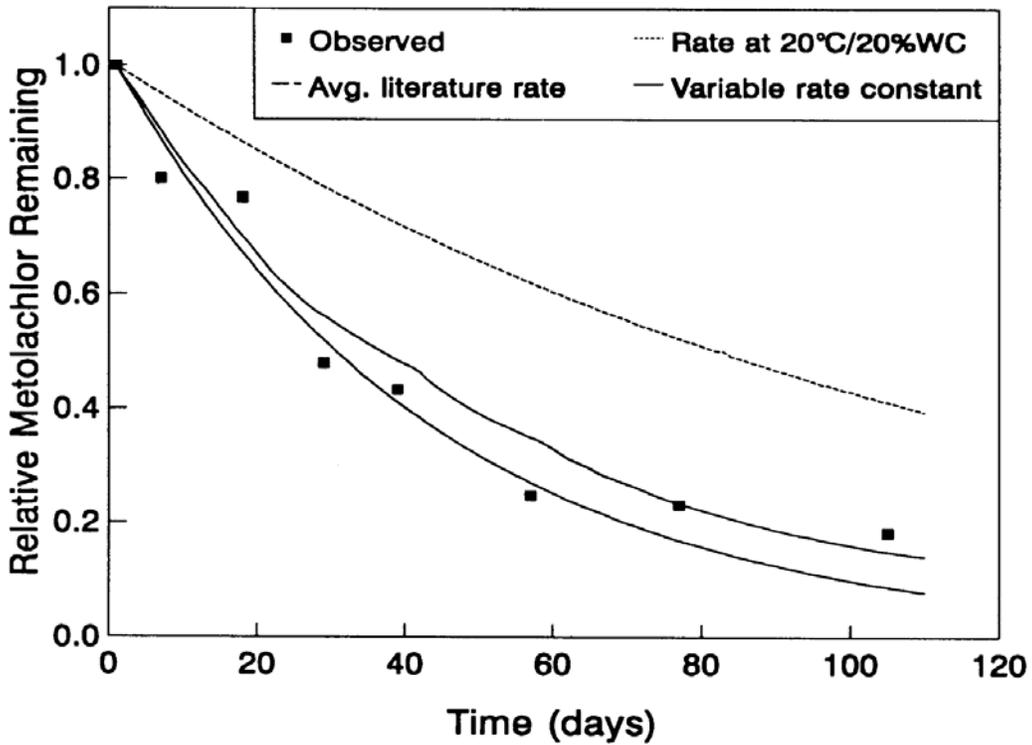


Figure 7 Predicted vs measured dissipation of metolachlor in field lysimeters

3.4.2 Indoor soil columns

Highly controlled indoor column experiments were carried out to evaluate the ability of LEACHP to simulate the leaching of chloride and atrazine. For near-saturated flow (water flux (q) of 22 mm d^{-1}), water flow and tracer transport parameters were similar between columns (Table 8). The measured chloride break through curves (BTC's) were also similar between columns. For saturated flow (water flux of 54 cm d^{-1}) transport parameters and chloride movement were dissimilar between columns and the shapes of the chloride BTCs were irregular with extreme tailing occurring. The rate of migration of the chloride peak (V_T) was found to be faster than the calculated rate of water movement (q/θ). This suggests that under saturated conditions significant bypass flow of water occurred.

For near-saturated flow LEACHP tended to slightly overpredict (column averaged relative error (RE) $\leq 10.5\%$) chloride BTCs whereas it underpredicted (column averaged RE $\geq -25.4\%$) BTCs for saturated flow (Table 9). The slight overprediction for near-saturated flow was a result of overestimation of the leading peaks from the BTCs. For saturated flow underprediction was due to underestimation of the tailing BTCs. LEACHP did not simulate the bypass flow that occurred in the soil columns.

In soil solution, LEACHP overpredicted atrazine transport for both near-saturated and saturated flow, particularly for near saturated flow. Considering that chloride concentrations were only slightly overpredicted for near-saturated flow and they were underpredicted for saturated flow the overprediction of atrazine concentration must not have been exclusively related to water flow. The overpredictions were most likely caused by the simplistic sorption routines in LEACHP. LEACHP assumes instantaneous linear adsorption and does not consider formation and release of pesticide bound (nonlabile) residues that have diffused into the soil matrix. Calibrating the model by changing the adsorption coefficient and decay rate resulted in some improvement but errors still occurred at some depths in the soil columns. Reynolds et al. (1994) provides a more detailed description of the soil column experiment.

Table 8. Water and solute transport parameters from the column experiments.

Column Number	Flux Density (mm d ⁻¹)	(q θ ⁻¹) (mm d ⁻¹)	V _T (mm d ⁻¹)	λ (cm)	θ (cm ³ cm ⁻³)	θ _T (cm ³ cm ⁻³)
1	22	60.7	61.8	8.9	0.364	0.377
2	22	62.1	62.9	8.9	0.356	0.365
1	540	1395	3061	9.0	0.388	0.351
2	540	1404	3958	38.7	0.385	0.216

V_T = average linear tracer velocity as determined from the rate of migration of the chloride BTC peak.

λ = dispersivity.

θ = volumetric water content.

θ_T = q/V_T, where q is the flux density (mm d) set by the peristaltic pump.

Table 9. Average and relative prediction errors, AE and RE respectively, for the LEACHP predictions of chloride and atrazine breakthrough curves (BTC) in the column experiments.

Column Number	Flux Density (mm d ⁻¹)	Chloride			Atrazine		
		⁺ n	*AE (mg L ⁻¹)(%)	*RE (%)	⁺ n	*AE (μg L ⁻¹)(%)	*RE (%)
1	22	99	+14.2	+10.5	124	+43.2	+206
2	22	102	+7.53	+3.88	124	+85.8	+364
1	540	70	-24.0	-25.4	63	+26.8	+36.1
2	540	28	-16.9	-21.5	30	+36.7	+26.0

⁺n includes all data points, all solution samplers, and all depths.

*AE and RE indicate average error and relative error, respectively, between predicted and measured chloride or atrazine concentrations. They are averaged over all solution samplers and all depths.

4.0 Study Conclusions

- 1) In laboratory incubations, atrazine dissipation was most rapid in clay soils whereas metolachlor and metribuzin dissipated more rapidly in sandy soils. There was a greater accumulation of toxic atrazine metabolites in soil with greater sand content.
- 2) In the field lysimeters more leaching of atrazine and metolachlor occurred in no-tilled soil but for both treatments little herbicide residues reached the 20 cm depth. In the tilled plot higher clay content correlated with greater leaching. Conventional and no-tillage practices had little effect on pesticide dissipation, bound residue formation, and mineralization.
- 3) In the field, during the four month cropping season, greater than half the atrazine was mineralized. Microbial degradation of pesticides is often influenced by treatment history. The efficacy of some soil applied herbicides such as EPTC and insecticides such as carbofuran can be compromised by the extremely active degrading microflora that develops upon repeated application. The impact of treatment history on biodegradation is difficult to predict and has yet to be incorporated into simulation models. The rate of volatile loss in our field experiments was much higher than that observed in laboratory experiments or reported in the literature. From the environmental perspective this is good news. But clearly this is an area of research which has to be further explored.
- 4) The pesticide fate and transport model LEACHP was modified to make dissipation responsive to environmental conditions. With respect to dissipation, the model worked well under field conditions. In comparison to other models LEACHP did reasonably well in predicting atrazine and chloride movement in the indoor column leaching experiments. If anything, LEACHP tended to overpredict atrazine transport which is a conservative approach to modelling.

5.0 New technologies and benefits

- 1) In this study the adsorption of atrazine or metolachlor to a variety of experimental materials was determined. We recommend that plastics used in equipment or containers coming in contact with atrazine or metolachlor be chosen accordingly. For that matter, all organic materials in experimental equipment coming in contact with pesticides should be tested for their ability to adsorb these chemicals. Otherwise the validity of the experimental results may be in question.
- 2) Experiments with intact soil core, packed soil core and flask soil incubations with atrazine and metolachlor have shown that soil structure need not necessarily be maintained in laboratory soil pesticide dissipation experiments.

- 3) Laboratory intact soil core and field lysimeters systems have been designed for determining pesticide dissipation kinetics, bound residue formation kinetics, and leaching. The field lysimeter design allows for safe experimentation with radioactively labelled compounds.
- 4) The pesticide transport models LEACHP and PESTFADE have been enhanced by introducing new chemical subroutines for degradation and pesticide sorption.
- 5) A database for half lives and bound residue formation kinetics of herbicides in the Great Lakes Basin is available.

6.0 Implications for Great Lakes Ecosystem

- 1) Degradation is the predominant means by which most pesticides are removed from the environment. Agricultural practices which promote degradation should therefore be developed and used. Such practices may include, subsurface drainage and irrigation, tillage practices, pesticide injection, and various cropping activities.
- 2) The ability of the LEACHP model to predict pesticide transport has been improved. Non-point pesticide contamination of ground water as predicted by LEACHP was generally low-level (Reynolds et al., 1994).

7.0 Technology Transfer Potential

- 1) The influence of temperature and moisture on dissipation of herbicides in soils in the Great Lakes Basin have been determined, providing improved measures of pesticide dissipation kinetics for use in computer simulation models. Temperature and soil moisture functions could be incorporated into other pesticide fate and transport models.
- 2) A data base on the kinetics of dissipation and bound residue formation has been provided for other researchers and future research.

8.0 Gaps Needing Future Research

- 1) The influence of spatial variability on pesticide behaviour needs to be further examined. On the field scale, geostatistics could be employed to determine which soil properties affect pesticide dissipation.
- 2) Agricultural practices which potentially promote degradation of pesticides in the crop rooting zone should be examined.

- 3) In this study mineralization rates of atrazine and metolachlor were much higher under field conditions than those reported in literature. Mineralization, or complete transformation of pesticides to nontoxic derivatives, provides an excellent means for decontaminating soils in agricultural fields. Mechanisms underlying the process of mineralization in this soil type should be further examined.
- 4) The release of bound (nonlabile) residues as influenced by temperature, soil moisture and soil properties, as well as wetting and drying cycles needs to be determined for use in pesticide transport models.

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10.0 Publications

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