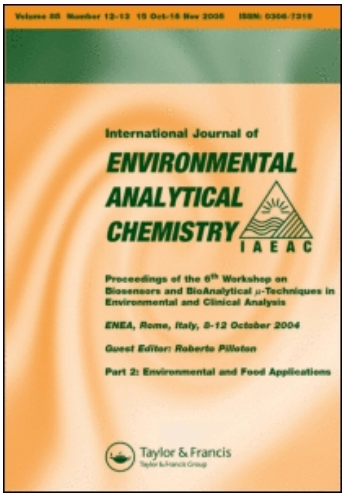

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Degradation of Pesticides in Subsurface Soils, Unsaturated Zone—a Review Of Methods and Results

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DEGRADATION OF PESTICIDES IN SUBSURFACE SOILS, UNSATURATED ZONE - A REVIEW OF METHODS AND RESULTS

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Methods and results from degradation studies in subsoils, unsaturated zone, were reviewed for mecoprop, 2,4-D, atrazine, alachlor, aldicarb, carbofuran, linuron, oxamyl, methomyl, MCPA, dichlorprop, monochlorprop, dichlorphenol, TCA, parathion, metribuzin, metolachlor and fenamiphos.

Most of the investigations were laboratory studies where small soil samples were sieved and pesticides were added in concentrations from 0.5–5 $\mu g \cdot g^{-1}$. A few of the studies mentioned the importance of working with undisturbed samples; another few studies used isotope-labelled pesticides which made it possible to work with concentrations as low as 0.02 $\mu g \cdot g^{-1}$.

Subsoil samples were characterized according to factors as microbial activity, soil temperature, water content, oxygen content, concentration of pesticide, pretreatment of the soil and soil type, factors considered to have influence on degradation of pesticides. Chemical hydrolysis was considered to be the most dominant pathway in the degradation of aldicarb in subsoil in one of the published papers; all other investigations considered the degradation of pesticides in subsoil to be primarily microbiological. Only a few of the investigations measured the biomass or biological activity of the subsoil samples.

KEY WORDS: Subsurface soil, unsaturated zone, pesticides, degradation, methods, review.

INTRODUCTION

During the last decade pesticides have been detected in ground water and drain water in many European countries as well as in North America.[1,2] Nygaard[3] presented the results from a monitoring of Danish ground water quality, 1989–1991, covering analysis of dichlorprop, mecoprop, MCPA, dinoseb, atrazine and simazine. Pesticides were detected in 36 out of 528 wells. In half of the 36 samples the concentration exceeded 0.1 $\mu g \cdot l^{-1}$. It is not known whether detection of pesticides in ground water at concentrations above the residue limit (0.1 $\mu g \cdot l^{-1}$) are caused by point source pollution or the use of these chemicals in agriculture.

Until recently most of the published degradation studies focused on soil from the upper layer. Persistence criteria for registration of pesticides normally refer to half-lives of pesticides in different soil types and at different application rates,—but not in soil from the subsurface. Nevertheless, the finding of pesticides in ground water has increased the

importance of elucidating degradation rates of these compounds in the subsurface environment. Moreover, information about the kinetics of pesticide biodegradation in subsoils is required for the development and validation of mathematical models used to predict the fate of pesticides in the environment.

The present study reviews the methodology and results in published pesticide degradation studies in subsoils, mainly from the unsaturated zone (the zone above the water table): Alachlor[4,5], aldicarb[6–10], aldicarb sulphoxide[7,9,11,12], aldoxycarb[6,7,9,12,13], atrazine[14–18], carbofuran[19], 2,4-D[18,19], dichlorphenol[20], dichlorprop + monochlorprop[20], fenamiphos[21], linuron[22], MCPA[23], mecoprop[24], methomyl[25], metolachlor[14], metribuzin[5,22,26], oxamyl[12], parathion[20], TCA[20]. Based on the reviewed papers, general recommendations for a methodology for degradation studies are given.

DEGRADATION MECHANISMS IN SUBSOIL

General

Several factors are responsible for the dissipation of pesticide residues from soil, factors such as surface run-off, volatilization, plant uptake, transport through soil and degradation. Pesticides in soil are degraded by photochemical, chemical and microbiological processes. The photochemical degradation (induced by sunlight) is only occurring in surface soil.

Degradation of a pesticide is a series of stepwise processes leading to various end products. If the pesticide is totally mineralized, CO_2 is formed. A part of the pesticide-carbon is built into humus and soil microorganisms. Stable degradation products can be produced, too, and may end up as residues bound in the organic fraction of the soil. Figure 1 illustrates the degradation of a pesticide. Degradation of pesticides in subsoil follows a microbial or chemical pathway or a combination of both.[27]

Microbial degradation

The important role of microorganisms in the degradation of pesticide residues in soil was described by Torstensson[28]. Helweg[29] reviewed degradation studies in soil of 230 pesticides. Microbial degradation was reported in 80 cases and chemical degradation only in 13 cases. Microbial decomposition of pesticides can occur by metabolism or by cometabolism.

The number of microorganisms found in subsoil often is up to 100 times smaller than in soil from the upper layer (Table 1). In Danish subsurface soil Eiland[30] found up to 10^9 bacteria per gram soil at a depth of 1 meter and 10^7 at 5–6 meter depth.

Table 1 Microorganisms in soil determined by direct counting

	Bacteria (mill/g)	Fungi (meter/g)
Plough layer	500–1000	200–2000
Below root zone	1–10	only few

Sinclair and Lee[17] compared degradation rates of atrazine in active (non-sterile) and sterile (autoclaved) subsoil samples. The reason for the lack of degradation in the active soil was said to be due to the small bacterial population.

The addition of nutrients increased the transformation of alachlor, which indicated that the degradation was microbiological and cometabolic.[4] No relation was found between degradation rate (determined during 161 days) and microbial number determined by plate counting on PTYG medium. Viable cell counts often give lower and more variable results than total cell counts.[31]

Degradation of atrazine occurred more rapidly at the surface than at deeper levels. This was explained by the lower number of microorganisms and the lower temperature at lower depths.[18] The reason why the lower number of microorganisms measured at lower depths did not affect the aerobic degradation rate of 2,4-D was not explained.

The faster dissipation rate in the field than in the laboratory of metribuzin[5] was suggested to be due to the treatment of the laboratory sample—a possible decrease in microbial activity during the drying period and a lack of natural cracks and channels in the dried and sieved soil.

The mineralization of carbofuran and the microbial biomass content decreased with depth except in one zone where both were higher.[19] The microbial population present in these subsurface soils seemed to be ineffective in the degradation of 2,4-D.[19]

Chemical degradation

Chemical degradation does not appear to have much importance in the total degradation of pesticides in subsoil. In some cases chemical hydrolysis as one of the degradation steps is mentioned. The degradation rate of aldicarb[8] did not change significantly with depth, and, taking into account that the amount of microorganisms in deeper soil layers normally diminishes, Jones[8] concluded that chemical hydrolysis was an important degradation pathway for aldicarb in subsoil. Microbiological activity was not determined.

Degradation of aldicarb decreased with increasing depth, but total carbamate residues were not influenced by depth. Aerobic degradation of aldicarb in upper soil layers was caused by microbial oxidation and in deep subsurface samples by chemical hydrolysis.[9]

For sterilized (autoclaved) unsaturated subsoil half-life for aldicarb sulphoxide, aldoxycarb and oxamyl increased 3–4 times compared to unsterilized soil. The fact that there was a conversion of pesticides in sterilized soil showed that at least the first stage of degradation was not purely microbiological.[12]

ESTIMATION OF DEGRADATION RATES (DEGRADATION KINETICS)

Pesticides like the phenoxyherbicides (MCPA, mecoprop and 2,4-D) are known to be decomposed metabolically[32] while most other pesticides are decomposed through a cometabolic process.[33] Cases can be seen, where different processes are followed during the step-wise degradation of a pesticide.

Table 2 Summary of degradation rates of pesticides in subsoil from the unsaturated zone (below 30 cm) calculated on basis of residues of parent compound.

Compound	*Soil type*	*% OC*	*Conc* $\mu g \cdot g^{-1}$	*Temp*	*Method*	*Half-life* $T_{1/2}$	*Ref*
Alachlor	loamy sand	0.08–0.14	1.5	20°C	lab.study of composited samp, aerobic incub.	22–285 days	4
Alachlor	loamy sand	0.08–0.14	1.5	20°C	lab.study of composited samp, anaerobic incub.	53–148 days	4
Alachlor	coarse sand	0.04–0.24	appl♠/ 1–4	23°C	field, enclosed samples/lab, dried and sieved soil	34–39 days	5
Aldicarb	sand-clay loam	0.0–2.0	appl	nat°	field, normal application	0.5–2 months	6
Aldicarb	sand	< 0.02 –0.16	appl	nat	field, normal application	11–23 days	7
Aldicarb			appl	nat	field, normal application	0.5–3 months	8
Aldicarb/ sulphox/ Aldoxycarb	sandy	0.01–0.16	4	23°C	lab, moist soil, aerobic incub.	61–178 days	9
Aldicarb/ sulphox/ Aldoxycarb	sandy	0.01–0.16	4	23°C	lab, moist soil, anaerobic incub.	52–105 days	9
Aldoxycarb	sand-clay loam	0.0–2.0	metabo lite	nat	field, metabolite	0.5–2 months	6
Aldoxycarb	sand	< 0.02 –0.16	metabo lite	nat	field, metabolite	69 days	7
Aldoxycarb	silt	0.7	5	15°C	lab, moisture content of soil adjusted	46 days	13
Aldoxycarb	sand	0.5	5	15°C	lab, moisture content of soil adjusted	slow degr.	13
Aldoxycarb	sand	0.8	3	10°C	lab, moisture content of soil adjusted	82 days	12
Aldoxycarb	loamy fine sand	1.2	3	10°C	lab, moisture content of soil adjusted	116 days	12
Aldoxycarb	fine sand	0.4	3	10°C	lab, moisture content of soil adjusted	1100 days	12
Aldicarb sulphoxide	sand	< 0.02 –0.16	metabo lite	nat	field metabolite	69 days	7
Aldicarb sulphoxide	silt	0.7	5	15°C	lab, moisture content of soil adjusted	53 days	11
Aldicarb sulphoxide	sand	0.5	5	15°C	lab, moisture content of soil adjusted	very slow degr.	11
Aldicarb sulphoxide	sand	0.8	3	10°C	lab, moisture content of soil adjusted	84 days	12
Aldicarb sulphoxide	loamy fine sand	1.2	3	10°C	lab, air-dried soil	194 days	12

Table 2 *continued*

Compound	*Soil type*	*% OC*	*Conc* $\mu g \cdot g^{-1}$	*Temp*	*Method*	*Half-life* $T_{1/2}$	*Ref*
Aldicarb sulphoxide	fine sand	0.4	3	10°C	lab, air-dried soil	410 days	12
Atrazine	silty clay/ sandy loam	0.1–1.3	0.5–2	nat	field, enclosed samples	meas. phytotoxicity	18
2,4-D	silty clay/ sandy loam	0.1–1.3	0.5–2	nat	field, enclosed samples	meas. phytotoxicity	18
Fenamiphos	sandy-clay loam	0.16–0.40	appl	nat	field, normal application	7–10 days	21
Linuron		0.6–1.2	2	10°C	lab, 6–30% adjusted moisture	17–39 weeks	22
Linuron		0.6–1.2	2	22°C	lab, 6–30% adjusted moisture	3–8.8 weeks	22
Linuron		0.8	2	10°C	lab, 6–30% adjusted moisture	12–20 weeks	22
Linuron		0.8	2	22°C	lab, 6–30% adjusted moisture	7.2–9.5 weeks	22
Mecoprop	sandy soil	0.2–0.5	0.05	10°C	lab, undisturbed soil cores	34–70 days♦	24
Methomyl	loamy-fine sand	0.1–0.9	appl	nat	field, normal application	0.5–1.6 months	25
Metribuzin	coarse sand	0.04–0.24	appl/ 1–4	23°C	field, enclosed samples/lab, soil dried and sieved	27–69 days	5
Metribuzin		0.6–1.2	2	10°C	lab, 10–60% moisture adjusted	11 weeks	22
Metribuzin		0.6–1.2	2	22°C	lab, 10–60% moisture adjusted	6.5 weeks	22
Metribuzin		0.8	2	10°C	lab, 10–60% moisture adjusted	2 weeks	22
Metribuzin		0.8	2	22°C	lab, 10–60°C moisture adjusted	8.8 weeks	22
Metribuzin		48.3	2	10°C	lab, 10–60% moisture adjusted	43 weeks	22
Metribuzin		48.3	2	22°C	lab, 10–60% moisture adjusted	9.4 weeks	22
Oxamyl	sand	0.8	3	10°C	lab, air-dried soil	26 days	12
Oxamyl	loamy fine sand	1.2	3	10°C	lab, air-dried soil	92 days	12
Oxamyl	fine sand	0.4	3	10°C	lab, air-dried soil	415 days	12

♠ applied as in normal agricultural practice
° natural circumstances
♦ half-life of mecoprop based on correlation between evolution of CO_2 and residues of mecoprop

Generally first-order reaction kinetics are presumed for the degradation process, sometimes even for pesticides which are decomposed by metabolic degradation. In a first-order reaction

$$dc/dt = -k \cdot c(t)$$

If ln c(t) is plotted versus time, the degradation curve turns out to be a straight line with slope $-k$.[34]

Degradation of aldoxycarb in silty subsoil[13], aldicarb sulphoxide in silty and sandy subsoil[11], aldoxycarb, aldicarb sulphoxide and oxamyl in sandy subsoil[12] and alachlor in subsoil both under aerobic and anerobic conditions was reported to follow a first-order reaction. Stenström[35] checked the equation for first-order kinetics against experimental data on degradation of herbicides. The first-order rate constant proved to be dependent on initial concentration. Applying an empirical equation $c = c_0 - k \cdot t^{1/2}$ to the degradation experiments, a high correlation was found between the rate constant k and biological activity. This could be valid for subsoils, too. The order of reaction for linuron and metribuzin degradation in subsoil varied from 1.36 to 6.26.[22] Metribuzin degradation in subsoil was a half-order process.[26]

Some authors calculated degradation half-lives assuming first-order kinetics.[5–10,21,25] In some cases, where field studies with normal application of the pesticide were carried out, the reported half-lives should be seen as dissipation rates, since surface losses via pathways such as volatilization and plant uptake would influence the concentrations found.[5,6,7,21,25]

Having analyzed the changes of concentration of parent pesticide with time, half-life can be calculated as $T_{1/2} = \ln 2/k$, assuming first-order kinetics. Reported half-lives in different soil types, at different temperature, concentration and OC content and with different methods are summarized in Table 2.

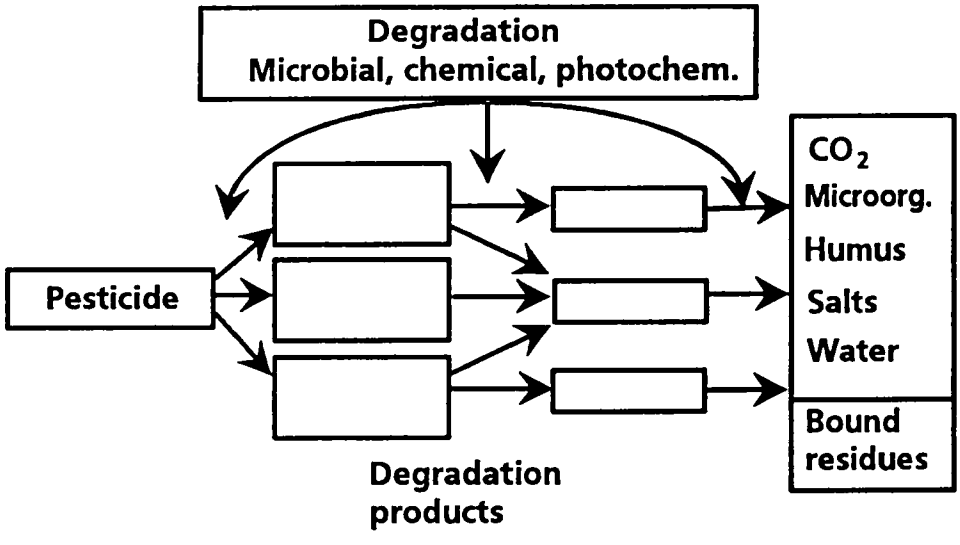

Figure 1 Diagram showing degradation of pesticides.[27]

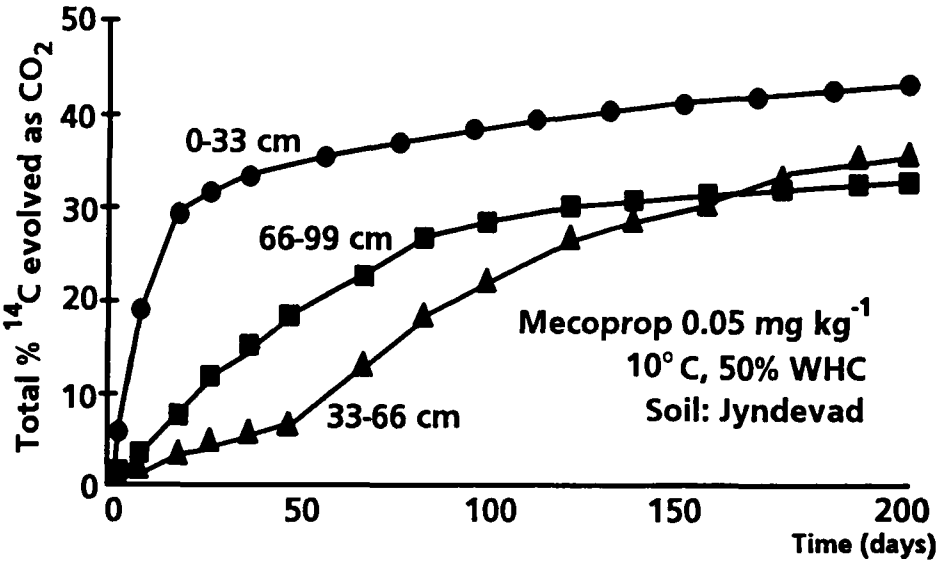

Figure 2 Degradation of ^{14}C-mecoprop (0.05 $\mu g \cdot g^{-1}$) in a soil profile.[24]

Other authors made degradation experiments following the evolution of $^{14}CO_2$ from ^{14}C-labelled pesticide. As seen in Figure 1., only part of the pesticide turns into CO_2. For that reason the evolution of $^{14}CO_2$ cannot be used to calculate half-lives. A typical pattern for the evolution of $^{14}CO_2$ from a pesticide is seen in Figure 2. When the rate of evolution of $^{14}CO_2$ decreases, the remaining ^{14}C has been built into stable organic compounds in the soil. Further evolution of $^{14}CO_2$ (the "flat" part of the curve) is a result of turn-over of biomass and other organic residues of the soil. Reported results from studies where the degradation was measured through evolution of $^{14}CO_2$ are summarized in Table 3.

Helweg[24] found a correlation between the amount of evolved $^{14}CO_2$ and the corresponding amounts of decomposed ^{14}C-mecoprop. Only on the basis of such a correlation, $^{14}CO_2$ evolution can be used to calculate half-lives.

FACTORS INFLUENCING DEGRADATION RATES

In almost all the reviewed papers a decrease in degradation rate with increasing depth was seen. The factors that were mentioned to be of importance for the degradation rate of a pesticide in subsoil were: microbial activity, soil temperature, water content, oxygen content, concentration of pesticide, repeated treatment of the soil and soil type. Reported degradation rates for pesticides in subsoil at varying conditions are summarized in Tables 2 and 3.

Table 3 Summary of degradation rates of pesticides in subsoil from the unsaturated zone (below 30 cm). Degradation rates reported as number of days for evolution of a certain amount of CO_2 from ^{14}C-labelled pesticide.

Compound	*Soil type*	*% OC*	*Conc* $\mu g \cdot g^{-1}$	*Temp*	*Method*	*Degr. rate*	*Ref*
Aldicarb	sand	0.02	5	23°C	lab, moist soil, aerobic incub.	15.8% in 63 days	10
Aldicarb	sand	0.52	5	23°C	lab, moist soil, aerobic incub.	16.9% in 63 days	10
Aldicarb	sandy loam	0.15	5	23°C	lab, moist soil, aerobic incub.	26.7% in 63 days	10
Aldicarb	loamy sand	0.18	5	23°C	lab, moist soil, aerobic incub.	16.9% in 63 days	10
Aldicarb	sand	0.02	5	23°C	lab, moist soil, anaerobic incub.	4.8% in 63 days	10
Aldicarb	sand	0.52	5	23°C	lab, moist soil, anaerobic incub.	12.6% in 63 days	10
Aldicarb	sandy loam	0.15	5	23°C	lab, moist soil, anaerobic incub.	17.2% in 63 days	10
Aldicarb	loamy sand	0.18	5	23°C	lab, moist soil, anaerobic incub.	12.9% in 63 days	10
Atrazine	sand/silt/clay	0.05–0.37	10	12°C	lab, moist soil, saturating with ground water	no degr.	14
Atrazine	coarse sandy	0.1	2	10°C	lab, moist soil, soil formerly treated with manure	21% in 500 days	15
Atrazine	clay	0.1	2	10°C	lab, moist soil	0.4% in 500 days	15
Atrazine	coarse sandy	0.1	0.02	10°C	lab, moist soil, soil formerly treated with manure	11–14% in 535 days	15
Atrazine	clay	0.1	0.02	10°C	lab, moist soil	11–14% in 535 days	15
Atrazine	coarse sandy	0.1	0.1	10°C	lab, moist soil, soil formerly treated with manure	11–14% in 535 days	15
Atrazine	clay	0.1	0.1	10°C	lab, moist soil	11–14% in 535 days	15
Atrazine	coarse sand		0.02	10°C	lab, undisturbed soil cores, N_2-atmosphere	5–22% in 626 days	16
Atrazine	coarse sand		0.1	10°C	lab, undisturbed soil cores, N_2-atmosphere	5–33% in 626 days	16
Atrazine	clayey sandy soil	0.01–0.03	0.1	22°C	lab, moist soil, aerobic incub.	no degr.	17
Atrazine	clayey sandy soil	0.01–0.03	0.1	22°C	lab, moist soil, anaerobic incub.	slow degr.	17
carbofuran		0.00–0.25	0.033		lab, moist soil	23–45% in 12 weeks	19
2,4-D		0-00–0.25	0.033		lab, moist soil	< 10–58% in 12 weeks	19

Table 3 *continued*

Compound	*Soil type*	*% OC*	*Conc* $\mu g \cdot g^{-1}$	*Temp*	*Method*	*Degr.rate*	*Ref*
Dichlorphenol	sand	0.05	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	11–15% in 359 days	20
Dichlorphenol	moraine sand	1	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	10% in 359 days	20
Dichlorphenol	sand	0.05	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	5–10% in 359 days	20
Dichlorphenol	moraine sand	1	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	1–2% in 359 days	20
Dichlorprop + monochlorprop	sand	0.05	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	10–16% in 447 days	20
Dichlorprop + monochlorprop	moraine sand	1	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	12–15% in 447 days	20
Dichlorprop- + monochlorprop	sand	0.05	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	12–17% in 447 days	20
Dichlorprop + monochlorprop	moraine sand	1	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	2% in 447 days	20
MCPA	clayey sandy soil	0.1	5	10°C	lab, undisturbed soil cores, MCPA formerly used	40% in 80 days	23
MCPA	sand	0.1	5	10°C	lab, undisturbed soil cores, MCPA formerly used	20% in 240 days	23
MCPA	clayey sandy soil	0.1	5	10°C	lab. undisturbed soil cores	3% in 80 days	23
MCPA	sand	0.1	5	10°C	lab, undisturbed soil cores	13% in 240 days	23
Mecoprop	sandy soil	0.2–0.5	0.05	10°C	lab, undisturbed soil cores	36% in 227 days	24
Metolachlor	sand/silt/clay	0.05–0.37	10–20	12°C	lab, moist soil, saturating with ground water	no degr.	14
Metribuzin	silty clay loam		0.1–1	25°C	lab, moist soil	5% in 91 days	26
Parathion	sand	0.05	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	3–6% in 419 days	20
Parathion	moraine sand	1	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	7–14% in 419 days	20

Table 3 *continued*

Compound	*Soil type*	*% OC*	*Conc* $\mu g \cdot g^{-1}$	*Temp*	*Method*	*Degr.rate*	*Ref*
Parathion	sand	0.05	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	12–14% in 438 days	20
Parathion	moraine sand	1	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	16–20% in 438 days	20
TCA	sand	0.05	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	35–40% in 833 days	20
TCA	moraine sand	0.1	0.05	10°C	lab, undisturbed soil cores, N_2-atmosphere	22% in 833 days	20
TCA	sand	0.05	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	8–31% in 833 days	20
TCA	moraine sand	0.1	5	10°C	lab, undisturbed soil cores, N_2-atmosphere	2–3% in 833 days	20

♠ applied as in normal agricultural practice
° natural circumstances

Microbial activity

As mentioned above, the degradation of a pesticide in soil is considered to be merely microbial.[4,17,19,23,26] However, no direct correlation between degradation rate and microbial activity could be shown. The microbial activity depends on number of microorganisms present, soil temperature, moisture, presence of oxygen and composition of soil (pH, OC content and nutrients).

Soil temperature

Degradation rate of aldicarb increased with higher temperature.[8] Degradation of atrazine occurred more rapidly at the surface than at deeper levels.[18] This was explained by the lower number of microorganisms *and* the lower temperature at lower depths.

Water content

Moisture is essential for microbial activity and for pesticide transport. In dry soils microbial activity diminishes, and in water saturated soils anaerobic conditions may prevail, which will impede the activity of all aerobic and microaerophilic bacteria. The content of water will generally not be a limiting factor for degradation in subsoil from the unsaturated zone, since downward and upward movement of water will prevent the soil from drying out.

High soil moisture content was one of the factors that tended to increase the degradation rate of aldicarb.[8] Ou *et al.*[10] showed an increasing degradation rate of aldicarb with increasing water content in subsoil in one case, in the other there was no significant difference. Konopka and Turco[14] showed no degradation of atrazine and metolachlor in water saturated soil from

the unsaturated zone. Kempson-Jones and Hance[22] found shorter half-lives of linuron and metribuzin at higher temperature and moisture levels in subsoil.

Oxygen content

The unsaturated zone is normally aerobic and the oxygen content in the soil atmosphere is often close to oxygen content in atmospheric air.

Sinclair and Lee[17] found that atrazine was slowly degraded in anaerobic subsoil. With aerobic incubation no degradation was seen. The degradation of 2,4-D was slower under anaerobic conditions, but for atrazine no difference was seen.[18] Alachlor had a half-life of 22–285 days under aerobic conditions and 53–148 days under anaerobic comditons.[4] Ou *et al.*[9] found an aerobic half-life for total carbamate residues (aldicarb, aldicarb sulphoxide and aldoxycarb) of 61–178 days and an anaerobic half-life of 52–105 days. In loamy sand and sandy loam the aerobic degradation was significantly more rapid than the anaerobic. No significant difference was shown in sandy samples.[10]

Concentration of pesticide

Few investigations were made comparing degradation rates in subsoil of pesticides at varying concentrations.

The degradation rate of dichlorprop and dichlorphenol was significantly slower at 5 $\mu g \cdot g^{-1}$ than at 0.05 $\mu g \cdot g^{-1}$ in moraine sand.[20] For parathion and TCA no significant difference at varying concentrations was shown.[20]

Extrapolating degradation rate results from laboratory studies at high concentrations to nature, where the pesticides often are found at very low concentrations, can lead to erroneous conclusions of the fate of these compounds.[36]

Repeated treatments

Treatment of soil with pesticides can result in a build up of microorganisms capable of degrading the pesticide.

Zeuthen *et al.*[23] reported a significantly higher degradation rate of MCPA in subsoil taken 1 m below a barley field treated with phenoxyacids for 10 years than in subsoil taken below an uncropped field. Also the number of MCPA degraders determined by a ^{14}C-MPN method was significantly higher in subsoil below the field where MCPA had been used.

Soil type (OC content, pH)

Overall microbial activity often depends upon pH and upon content of organic material in the soil. These parameters may also influence adsorption of the pesticide and chemical hydrolysis. Smelt *et al.*[11, 12, 13] found slower degradation rates of aldoxycarb, aldicarb

sulphoxide and oxamyl in sandy subsoil than in silty subsoil. The low pH of the sandy subsoil could be the reason for this. At high concentrations (5 $\mu g \cdot g^{-1}$) Helweg[20] found a significant lower degradation rate of dichlorprop + monochlorprop in moraine sand (1% OC) than in sand (0.05% OC).

METHODS

Environmental factors that influence degradation rates of pesticides are all closely interrelated and it is difficult to investigate only one factor at a time. Moreover, it is difficult to compare degradation rates from different published studies because of the variation between employed methods.

Comparing degradation rates for example for atrazine (Table 3) in different studies, it is seen that these vary from a degradation to CO_2 of 21% in 500 days to no degradation at all. These differences could—to some extent—be the result of differences between employed methods.

One important methodological difference is the way of reporting degradation rates. In Table 2 half-lives are calculated assuming first-order kinetics on basis of residues of parent compound. In Table 3 degradation rates are reported as number of days for the evolution of a certain percentage of CO_2. Another important difference is, whether the investigation is made in the field or in the laboratory.

Field studies

In field studies performed after normal agricultural application of the pesticide it is difficult to distinguish between degradation and transport. Dissipation rates may include both degradation, movement, volatilization and plant uptake.

Hornsby *et al.*[7] discussed the contrast between sampling protocols designed to maximize the possibility of finding the applied pesticide and protocols designed to obtain "representative soil samples". With the sampling design used, they computed reliable "field-average concentrations".

Lavy *et al.*[18] eliminated leaching as a dissipation factor in their degradation study of 2,4-D and atrazine. Sieved soil samples with added pesticide (from 0.5 to 2 $\mu g \cdot g^{-1}$ to match the soil adsorption capacity) were buried in jars in the soil profile for up to 41 months in order to incubate the samples as closely as possible to natural conditions.

Jones *et al.*[5] carried out a comparative study of dissipation by depth of alachlor and metribuzin both in the field and in the laboratory. Statistical comparison was made when possible. The field study was made with soil columns enclosed in steel tubes and with injection of the pesticide to eliminate leaching as a dissipation factor. At the lowest depth, metribuzin dissipated significantly faster in the field than in the laboratory. This was most likely due to the treatment of the laboratory sample—a possible decrease in microbial activity during the drying period and a lack of natural cracks and channels in the dried and sieved soil.

In most field studies, considerable variability is found in pesticide residue concentrations in soil samples. Jones *et al.*[6] found a CV % (rel.std.dev) of replicate samples of 86–223% in their aldicarb study. Minton *et al.*[21] reported a CV % as high as 400% in field degradation studies of fenamiphos. Jones[8] collected and analyzed 3100 soil samples for one published field degradation study to be able to assess the effect of spatial variability on the measurements.

Laboratory studies

Few unsaturated zone field studies have been undertaken and/or published because of the high number of soil samples needed to reduce the influence of variability on the results and the expense associated with the collection and analysis of such a high number of samples. Most of the published data on degradation of pesticides in subsoils were generated in laboratories.

Most of the laboratory studies with subsoil samples were made with dried and sieved samples where pesticide was added and the samples then given a water content close to field capacity. Helweg[24] worked with undisturbed subsoil core samples injecting the pesticide and adjusting the water content. Jones *et al.*[5] used undisturbed subsoil cores in their field studies comparing the results with laboratory studies with dried and sieved samples. In most of the studies the concentrations of added pesticide ranged from 0.5–5 $\mu g \cdot g^{-1}$, corresponding to concentrations in the plough layer after normal field application; in a few studies[15,16] where ^{14}C-labelled pesticides were used, it was possible to work with concentrations as low as 0.02 $\mu g \cdot g^{-1}$.

Helweg[24] determined the degradation rate of ^{14}C-ring-labelled mecoprop. In subsurface soil the CV % of four replicates was 30–38%.

Helweg[27] described in detail a system for laboratory studies of undisturbed soil samples using ^{14}C-labelled compounds.

DISCUSSION AND RECOMMENDATIONS

The complex structure of soil, the close interrelationship between factors that influence degradation, and the difficulties in maintaining the environment of the microorganisms natural during the investigations make subsoil degradation studies complicated. The interrelation between factors that influence on degradation was described by Anderson.[37] The factors were a) The structure of the pesticide, b) The availability of the pesticide to enzymes or microbial cells (mobility of pesticide in soil, amount of water in soil, total amount of pesticide present in the soil), c) The quantities of enzymes or cells that can degrade the pesticide d) The activity of these enzymes or cells (depending on soil temperature, soil moisture composition of soil atmosphere, nutrients available and soil pH).[37]

Field studies such as the ones by Lavy *et al.*[18] and Jones *et al.*[5] where leaching, volatilization and plant uptake as dissipation factors are eliminated or laboratory studies are the easiest type of degradation studies. The modern use of simulation models to predict the

environmental fate of pesticides and to evaluate the threat of these pesticides to ground-water also need precise, reliable data sets for—among many factors—degradation rates at all levels of the unsaturated zone.

Laboratory studies such as those described by Helweg[16, 24, 27] and Zeuthen *et al.*[23] are to be recommended for subsoil degradation studies because they leave the soil samples undisturbed. Drying and sieving of subsoil affect the microbial activity. Variations between replicates of undisturbed soil samples are expected to be higher than in dried and sieved samples because of the greater heterogeneity of the undisturbed soil. This must be taken into account, working with a sufficient number of replicates, calculating standard deviations and making statistical comparisons of the results. Furthermore it is important to ensure that the subsurface samples are not contaminated with surface soil. The influence of microorganisms on degradation can be determined by incubation of sterilized soil samples. Saltzman and Mingelgrin[38] showed that sterilization with KN_3, ethylene oxide and by autoclaving resulted in changes in the soil properties which affected the degradation capacity of reinoculated soil. Sterilization by irradiation is a possible alternative. However, sterilization cannot assure us, that degradation is not carried out by microbial extracelluar enzymes, produced before the sterilization.

A disadvantage in laboratory studies could be a possible lack of nutrients in the enclosed soil samples as the incubation proceeds.

If only residues of parent compound are measured, one cannot be sure that no toxic residues are formed. In the studies of aldicarb[6,9,12] and fenamiphos[21] the toxic metabolites were known and measured, too. If only CO_2-evolution is measured, half-life cannot be calculated and it is difficult to know, when there is nothing left of the parent compound. Both residues of parent compound and CO_2-evolution should be measured.

Laboratory degradation studies should be performed at concentrations as close to the naturally occurring residue concentrations as possible. It is suggested that subsoil degradation studies include characterization not only of the physical composition of the soil, but especially investigations of the relation between degradation rate and microbial biomass and activity as described by Anderson.[37,39,40]

It is clearly to be recommended that standardized laboratory studies on degradation of pesticides are performed,—but it is absolutely necessary to validate results in field experiments. Results obtained in studies where the above methodological recommendations were followed, will be published in the near future.

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