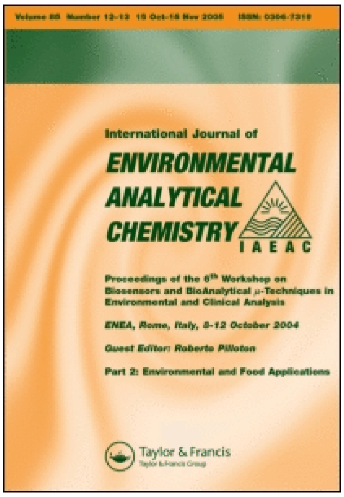

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DEGRADATION OF MECOPROP AND ISOPROTURON IN SOIL INFLUENCE OF INITIAL CONCENTRATION

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Models used to describe rates of degradation are presented and exemplified, and data from mecoprop at 0.0005 to 5000 mg kg^{-1} and isoproturon at 0.001 to 5000 mg kg^{-1} were tested in the models. Degradation was described by evolution of $^{14}CO_2$ from ^{14}C-labelled pesticides incubated in soil sampled in plough layer and in subsurface.

For mecoprop the degradation rate of 0.0005 mg kg^{-1} followed first-order models in both plough layer and in subsoil. At 5 mg kg^{-1} the degradation showed kinetics with exponential growth in both surface and subsoil. At 5000 mg kg^{-1} the degradation was very slow.

The degradation of isoproturon at all concentrations and soil types followed kinetics without growth of microorganisms. The model that gave the best fit for degradation of isoproturon was a three-half order model consisting of one first-order process and one of zero-order.

The rate of degradation for both pesticides and soil types was highest at the low concentrations, whereas at 5000 mg kg^{-1} the degradation was very low. Thus degradation appears even at concentrations near the drinking water limit whereas the degradation at very high concentration e.g. near point sources with pesticides may be very limited or absent.

Keywords: Degradation kinetics; pesticides; mecoprop; isoproturon; concentrations

INTRODUCTION

Pesticides can appear at a wide range of concentrations in soil. Typical initial mean concentrations in the top 10 cm of field soils are from 0.02 mg kg^{-1} for the low dose herbicides to about 1 mg kg^{-1}. The real concentrations in the treated soil on the other hand vary much more, and during degradation and after leaching of pesticides out of the plough layer very low concentrations will appear in

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subsurface. Very high concentrations may appear from point sources like pesticide spillage on sites used for filling of sprayers and on waste disposal sites.

All these ranges of concentrations from several thousands mg $kg^{-1}$to below 0.0001 mg kg^{-1} have to be decomposed in the soil since even concentrations of 0.0001 mg kg^{-1} are relevant for protection against ground water pollution at the EEC drinking water limit which is 0.0001 mg l^{-1}. It is possible to determine rates of degradation at this wide range of concentrations by the use of evolution of $^{14}CO_2$ from ^{14}C-labelled pesticides.

Figure 1 shows the ranges of pesticide concentrations which can be found in the environment. The high concentration may appear from pesticides disposed on waste disposal sites, total weed control and spill on filling sites. Very low concentrations of pesticides in soil may appear after deposition of pesticides on untreated areas from rainwater, low concentrations of pesticides are also found in the ground water zone and in drain water.

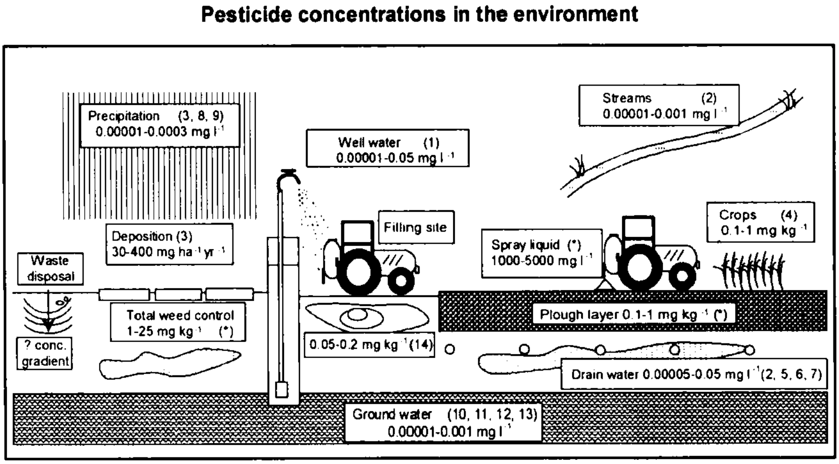


FIGURE 1 Concentration ranges of pesticides identified in the environment in Northern Europe. Numbers on the figure refer to the references. * Calculated from use rates.

Waste disposal sites

Pesticide waste may have been disposed of in large quantities during the past 40 years. Such waste appears when farmers dispose of"empty" containers, and where pesticide residues (such as pesticides destroyed by improper storage, e.g. low temperature) are disposed of. Pesticide waste may also come from effluent from production plants, broken packages etc. Until recently, there was no proper way to dispose of this waste, and most of it was either buried on farm land and near factories, disposed of on private waste disposals or was brought to municipal land fills. It is difficult to determine the abundance of these pesticide point sources, since little is known about the disposal of chemical waste in earlier days.

Finding of mecoprop and dichlorprop in US municipal landfills[15] have led to the conclusion that "the chlorinated 2-phenoxypropionic herbicides, particular mecoprop, are ubiquitous in municipal landfill leachates from US". Phenoxypropanoic acids have also been identified in leachate from Danish landfill[16].

Total weed control

The application of pesticides is very often much higher for total weed control than for normal treatment on agricultural land. Previous advise has been to use up to 10 to 20 kg a.i./ha of atrazine and simazine, 12 to 30 kg a.i./ha of monuron and diuron and 15 to 20 kg a.i./ha of chlorthiamid and dichlobenil[17]. These sites, which may be road sides, industrial areas, railways and farm yards are often covered by gravel and sand low in organic material like soil sampled in subsurface. The degradation rate on these sites will therefore be very much slower than in field soil[18]. It is not surprising, that very often found pollutants in Danish groundwater are 2,6-dichlorobenzamide (BAM), a mobile metabolite of chlorthiamid and dichlobenil, and metabolites from atrazine[19].

Filling of sprayers

Filling of sprayers and rinsing of spraying equipment will often be performed on the same site year after year. Pesticides from surplus of diluted pesticide solutions, which may contain 1000 to 5000 mg l^{-1} of pesticide, spillage of concentrated chemicals and run off from spray washing may end up here. Jørgensen et al.[14] have found concentrations of mecoprop and dichlorprop of 0.1 to 0.2 mg kg^{-1} 4 meters below such a site.

Deposition from precipitation

Cleemann et al.[8] found a deposition of γ-HCH of 70 to 170 mg per ha per year in Denmark. From Sweden, Kreuger[3] has reported deposition of 30 to 50 mg of phenoxyherbicides per ha per year and in Germany, depositions of about 400 mg ha^{-1} of lindane and up to 200 mg ha^{-1} of isoproturon have been found[9]. The depositions are highest in the spraying season[3]. A deposition of 50 to 100 mg ha^{-1} yr^{-1} may result in a concentration in the top 1 cm of soil of about 0.0003 to

0.001 mg kg^{-1}. It is important, that also these low concentrations can be decomposed.

Ground water and drain water

Findings in ground- and drainwater have shown pesticide contents between 0.00005 and 0.05 mg l^{-1} in drain water[2,5,6,7] and between 0.00001 and 0.001 mg l^{-1} in ground water[10,11,12,13]

The European Community Directive on Drinking water quality (The drinking water directive, DWD) from 1980 stated that pesticides and related products in drinking water should not exceed 0.1 $\mu g\ l^{-1}$(0.0001 mg l^{-1}) for individual pesticides and 0.5$\mu g\ l^{-1}$ for total pesticides.

Influence of concentration on degradation

Degradation kinetics has previously been shown to depend on concentrations. For pesticides which are degraded by metabolism, exponential degradation may be found showing proliferation of degrading micro-organisms. At normal field concentrations this has been shown for the herbicide mecoprop[20,21] and for MCPA[22,23].

At low concentrations however, the degradation kinetics may be of first order. This has also previously been shown for very low concentrations of phenol and p-nitrophenol[24] and for 2,4-D[25].

At very high concentrations the degradation rates may be very low. Ou et al.[26] thus found 2,4-D to be very slowly degraded at concentrations of 20000 mg kg^{-1}, either due to toxic effect on the micro-organisms or due to limited availability of supplementary nutrients. This is also found for mecoprop and indicates, that point sources may be very long lasting[20].

The purpose of the present study was to elucidate the mineralization kinetics for pesticides at different concentrations. The kinetics are exemplified by results with mecoprop and isoproturon both in plough layer and in subsurface soil.

MATERIALS AND METHODS

Pesticide degradation was determined by the evolution of $^{14}CO_2$ from ^{14}C-labelled pesticides. Mecoprop (^{14}C-ringlabelled) (Figure 2a), was incubated in a flow-through system, where 50 g soil was incubated in 100 ml Erlenmeyer flasks and moistened CO_2-free air was led through the flask and then through one absorber with glycerol and two with 1 N KOH to absorb evaporated compounds soluble in oil and $^{14}CO_2$ respectively. For the isoproturon-experiment, 50 g of soil with added ^{14}C-ringlabelled isoproturon (Figure 2b), was incubated in a 100 ml beaker which was stored in a closed 1l glass jar with a 50 ml beaker with 10 ml 1 N KOH to absorb $^{14}CO_2$.

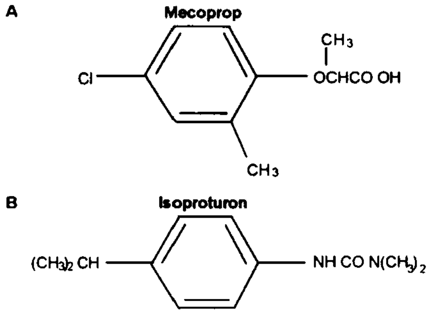


FIGURE 2 A. Structure of the herbicide mecoprop ((±)-2-(4-chloro-2-methylphenoxy)propanoic acid) and B. isoproturon (N,N-dimethyl-N'-[4-(1-methylethyl)phenyl]urea). Both are labelled with ^{14}C in the phenylring

Soil was sampled at Research Centre Flakkebjerg. The soil had not been treated with mecoprop or isoproturon for the last 2 years. Surface soil was collected at a depth of 0–30 cm and subsurface soil at 40–60 cm. After sampling, the soils were dried to about 25% of total water holding capacity (WHC) with frequent mixing to avoid extreme superficial dry-out. The dried soil was sieved to <2 mm and stored at 5°C for not more than 0.5 month before use. Table I shows the composition of the soil.

TABLE I Texture, pH (H_2O) and humus content in the soil

Depth cm	*Clay*	*Silt*	*Sand*	*Humus*	*pH*
0–30	14.3	17.7	65.2	2.9	6.1
40–60	22.9	11.1	65.7	0.3	6.5

Clay: <0.002 mm, Silt: 0.002 – 0.02 mm, Sand 0.02 – 2 mm. Humus: %C × 1.72

Accumulated amounts of evolved $^{14}CO_2$, calculated as percentage radioactivity of the total amount of added radioactivity, were described as a function of incubation time, $^{14}CO_2$ then corresponding to the amount of mineralised pesticide. A number of non-linear models were fit to the curves to evaluate the differences in the kinetics of mineralization.

Table II shows the degradation models which were tested in the present experiments.

TABLE II Models which have been tested for the best fit with the $^{14}CO_2$-evolution data

Model	*Equation*
0. order[27]	$P = k_0 t$ eq.(1) P = concentration of pesticide mineralised at time t (measured as % ^{14}C as $^{14}CO_2$) k_0 = degradation rate constant t = time in days
1. order[28,29,30]	$P = c_0(1 - e^{-kt})$ eq.(2) P = concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$) c_0 = total concentration of pesticide converted by the process to $^{14}CO_2$ k = degradation rate constant t = time in days
Two-compartment 1. order[24,31]	$P = c_1(1-e^{-k_1 t}) + c_2(1-e^{-k_2 t})$ eq.(3) P = concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$) c_1 = total concentration of pesticide converted to $^{14}CO_2$ by one first-order metabolism c_2 = total concentration of pesticide converted to $^{14}CO_2$ by another first-order metabolism k_1, k_2 = degradation rate constants for the two first-order processes t = time in days
Three half order without growth[32,24,28]	$P = c_0(1-e^{-k_1 t}) + k_0 t$ eq.(4) P = concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$) c_0 = total concentration of pesticide converted to $^{14}CO_2$ by first-order metabolism k_1 = degradation rate constant for the first-order process k_0 = degradation rate constant for the zero-order process t = time in days
Logistic growth[33,34]	$P = c_0 - \frac{c_0 + x_0}{1 + \left(\frac{x_0}{c_0}\right) e^{k_1 (c_0 + x_0) t}}$ eq.(5) P = concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$) c_0 = total concentration of pesticide converted to $^{14}CO_2$ by first-order metabolism x_0 = the amount of substrate (pesticide) required to produce the initial population density k = degradation rate constant t = time in days

Logistic growth + 0. order

$$P=c_0-\frac{c_0+x_0}{1+\left(\frac{x_0}{c_0}\right)e^{k_1(c_0+x_0)t}}+k_0 t \qquad \text{eq.(6)}$$

P = concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$)
c_0 = total concentration of pesticide converted to $^{14}CO_2$ by first-order metabolism
x_0 = the amount of substrate (pesticide) required to produce the initial population density
k = degradation rate constant
k_0 = degradation rate constant for zero order degradation
t = time in days

Logistic growth[35,36]

$$P=c_0-\frac{k_1 c_0}{(k_1+k_2 c_0)e^{k_1 t}-k_2 c_0} \qquad \text{eq.(7)}$$

P = Concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$)
c_0 = total concentration of pesticide converted to $^{14}CO_2$ by the modelled process
k_1 = rate constant
k_2= rate constant
t = time in days

Logistic growth + 0. order

$$P=c_0-\frac{k_1 c_0}{(k_1+k_2 c_0)e^{k_1 t}-k_2 c_0}+k_0 t \qquad \text{eq.(8)}$$

P = Concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$)
c_0 = total concentration of pesticide converted to $^{14}CO_2$ by the modelled process
k_1 = rate constant
k_2= rate constant
k_0 = degradation rate constant for zero order degradation
t = time in days

Exponential growth, low concentration[27]

$$P=c_0-c_0 e^{-(k/r)(e^{rt}-1)} \qquad \text{eq.(9)}$$

P = Concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$)
c_0 = total concentration of pesticide converted to $^{14}CO_2$ by the modelled process
k = degradation rate constant
r = the maximum specific growth rate
t = time

Exponential growth + 0. order, low conc.

$$P=c_0-c_0 e^{-(k/r)(e^{rt}-1)}+k_0 t \qquad \text{eq.(10)}$$

P = Concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$)
c_0 = total concentration of pesticide converted to $^{14}CO_2$ by the modelled process
k = degradation rate constant
k_0 = degradation rate constant for zero order degradation
r = the maximum specific growth rate
t = time

Exponential growth, high concentration[27]

$$P=k\frac{(e^{rt}-1)}{r} \quad \text{eq.}(11)$$

P = Concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$)
k = degradation rate constant
r = the maximum specific growth rate
t = time

Exponential growth + 0. order, high conc.

$$P=k\frac{(e^{rt}-1)}{r}+k_0 t \quad \text{eq.}(12)$$

P = Concentration of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$)
k = degradation rate constant
k_0 = degradation rate constant for zero order degradation
r = the maximum specific growth rate
t = time

The software used was Table Curve 2D[37]. The principles for the non-linear regression were previously described by Fomsgaard[38].

RESULTS AND DISCUSSIONS

General description of degradation rates

Degradation may be described by the degradation of parent compound or in some cases even "disappearance" which also may involve evaporation, leaching and sorption in the soil. To use a more sensitive measure of degradation rate, these experiments use evolution of $^{14}CO_2$ from ^{14}C-labelled pesticides. It should be taken into account, that evolution of CO_2 expresses the total mineralization, which is supposed to be "real" degradation. The degradation normally appears via a number of degradation products and finally ending up in CO_2 -evolution with some carbon from the pesticide being built into micro-organisms and in organic compounds in soil. Thus, Helweg[39] showed that when 12% ^{14}C from ^{14}C-labelled mecoprop was evolved as $^{14}CO_2$, only 50% of the applied mecoprop could be recovered in the soil.

Generally 3 different rate models are known to be useful for describing mineralization of pesticides. First-order (degradation rate dependent on concentration), zero-order (constant degradation rate) and models which involve growth of micro-organisms, either with exponential growth or with logistic growth which is limited by availability of substrate.

Figure 3 shows general diagrams for the three different degradation models, both shown by degradation of parent compound and by formation of $^{14}CO_2$.The figures are based on a relation between parent compound degradation and $^{14}CO_2$-formation of 2 to 1 e.g. when 10% of the ^{14}C-labelled parent compound is degraded, 5% of the added ^{14}C is evolved as $^{14}CO_2$.

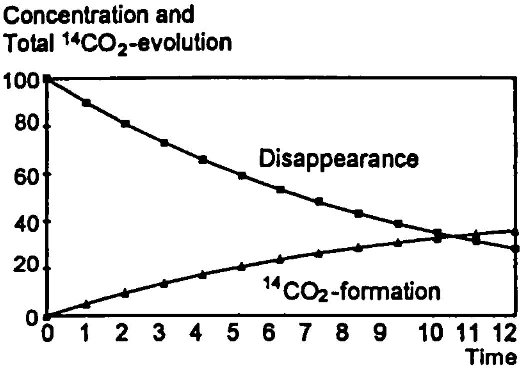
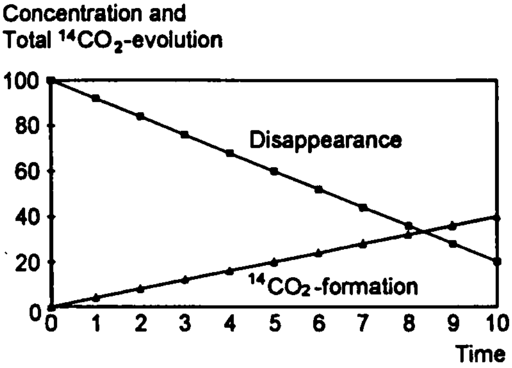


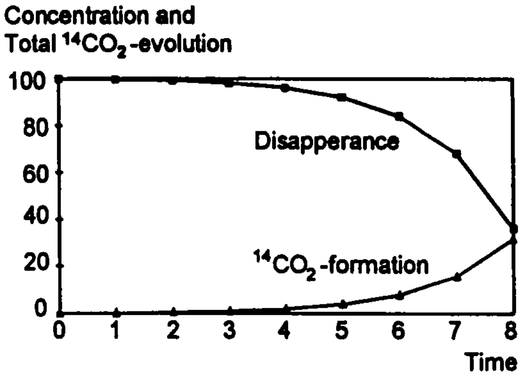
FIGURE 3 General diagramme of models for pesticide degradation.
A. first-order reaction kinetics[30]

Rate equation: $-\frac{dc}{dt}=kc$ Disappearance: $c=c_0e^{-kt}$. Formation: $P=c_0(1-e^{-kt})$.



B. Zero-order reaction kinetics[27]

Rate equation: $-\frac{dc}{dt}=k_0$ Disappearance : $c=c_0-k_0t$. Formation: $P=k_0t$.



C. Degradation with growth

Rate equation, log. growth[33]: $-\frac{dc}{dt}=k_1 c(c_0+x_0-c)$

Disappearance, log. growth[33]: $c=\frac{c_0+x_0}{1+\left(\frac{x_0}{c_0}\right)e^{k_1(c_0+x_0)t}}$

Formation, log. growth[33]: $P=c_0-\frac{c_0+x_0}{1+\left(\frac{x_0}{c_0}\right)e^{k_1(c_0+x_0)t}}$

Rate equation, exp. growth[27]: $-\frac{dc}{dt}=ke^{rt}$

Disappearance, exp. growth[27]: $c=c_0-\frac{k(e^{rt}-1)}{r}$

Formation, exp. growth[27]: $P=k\frac{(e^{rt}-1)}{r}$

Modelling results for mecoprop

The models from Table II were tested for the rate of $^{14}CO_2$-evolution from a number of concentrations of mecoprop from 0.0005 mg kg^{-1} to 5000 mg kg^{-1} and for isoproturon from 0.001 to 5000 mg kg^{-1} in plough layer and in subsurface soil.

The residual mean for the fitted equations, as presented inTable III, served as a measure of the goodness of fit. The lowest residual mean gives the best fit. When a model did not fit, no value is shown. Figure 4 shows the mineralization curves for mecoprop, a) plough layer, b) subsurface soil and Figure 5 shows the mineralization curves for isoproturon, a) plough layer, b) subsurface soil. The fit of the best model for each sample is presented as the solid line in Figures 4 and 5, whereas the dots show the actual $^{14}CO_2$ evolution data.

TABLE III Residual mean for all fitted equations. Best fit is in italics

sample	*Equations without growth of micro-organisms*				*Equations with growth of micro-organisms*								
	eq(1)	*eq(2)*	*eq(3)*	*eq(4)*	*eq(5)*	*eq(6)*	*eq(7)*	*eq(8)*	*eq(9)*	*eq(10)*	*eq(11)*	*eq(12)*	*Fig. ref.*
Mecoprop, plough layer													
0.0005 mg.kg^{-1}	-$^{*)}$	11.25	*0.3517*	0.6185	-	-	-	-	-	-	-	-	5a
5 mg kg^{-1}		80.92	-	-	-	*4.8645*	-	-	-	-	-	-	5a
50 mg kg^{-1}	-	175.93	-	-	6.5725	*2.4824*	-	-	-	-	-	-	5a
5000 mg kg^{-1}	-	-	-	-	-	-	-	-	-	-	-	-	5a
Mecoprop, subsurface													
0.0005 mg kg^{-1}	59.46	*0.9200*	-	-	-	-	-	-	-	-	-	-	5b
5 mg kg^{-1}	8.29	-	-	-	-	-	-	-	-	-	0.7938	-	5b
50 mg kg^{-1}	-	-	-	-	-	-	-	-	-	-	-	-	5b
500 mg kg^{-1}	-	-	-	-	-	-	-	-	-	-	-	-	5b
Isoproturon, plough layer													
0.001 mg kg^{-1}	0.8971	0.02651	-	*0.01209*	-	-	-	-	-	-	-	-	6a
5 mg kg^{-1}	0.4684	0.008999	-	*0.002063*	-	-	-	-	-	-	-	-	6a
50 mg kg^{-1}	0.2337	*0.08047*	-	-	-	-	-	-	-	-	-	-	6a
5000 mg kg^{-1}	0.2628	0.05187	-	*0.0005091*	-	-	-	-	-	-	-	-	6a
Isoproturon, subsurface													
0.001 mg kg^{-1}	0.01791	-	-	-	-	-	-	-	-	-	-	-	6b
5 mg kg^{-1}	0.07791	0.005642	-	*0.0000422*	-	-	-	-	-	-	-	-	6b
50 mg kg^{-1}	0.07259	0.003699	-	*0.0001177*	-	-	-	-	-	-	-	-	6b
5000 mg kg^{-1}	-	-	-	-	-	-	-	-	-	-	-	-	6b

$^{*)}$ – no useable fit

As appears from Table III, mecoprop mineralization in a concentration of 0.0005 mg kg^{-1}, both in plough layer and subsoil followed kinetics without growth.

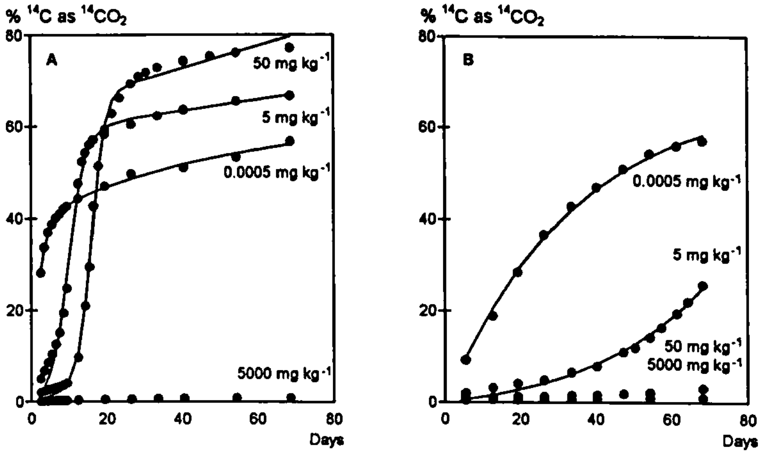


FIGURE 4 Degradation of ^{14}C-labelled mecoprop in soil at different concentrations shown by the evolution of $^{14}CO_2$. Mean of two replicates. Data taken from Reffstrup et al.[20]. Dots: data points, solid line: modelled equation. By courtesy Pesticide Science, SCI.
A. $^{14}CO_2$-evolution in soil from plough layer. 0.0005 mg kg^{-1} no-growth model; 5 mg kg^{-1} growth model; 50 mg kg^{-1} growth model; 5000 mg kg^{-1} no useable fit.
B. $^{14}CO_2$-evolution in subsoil. 0.0005 mg kg^{-1} no-growth model; 5 mg kg^{-1} growth model; 50 mg kg^{-1} no useable fit; 500 mg kg^{-1} no useable fit

The best model fit for mecoprop 0.0005 mg kg^{-1} in plough layer was given by eq. (3), a two-compartment first-order model, which consists of two simultaneously occurring first order processes. Probably one (rapid) first order process (rate constant k_1= 0.47), dominating in the beginning, expresses the mineralization of the pesticide in solution. The other (slower) first order process (the "flat" part of the curve, rate constant k_2 = 0.02), dominating from about 15 days, may express the degradation of slowly released mecoprop or degradation of organic compounds e.g. humus where part of the added ^{14}C had been built in[38]. Former studies[39] showed, that when 40% of ^{14}C-mecoprop has been converted to $^{14}CO_2$, no significant amounts of ^{14}C-mecoprop could be extracted.

Mineralization of 0.0005 mg kg^{-1} mecoprop in subsoil followed eq. (2), a simple 1. order model with a rate constant k=0.02. The rate of degradation at low concentrations of the pesticides may be limited by the rate of diffusion of the substrate to a widely distributed, but very small population of micro-organisms, which are able to metabolise the pesticides. This is even more pronounced in the subsoil, with the lower biomass. Even if the mineralization rate of mecoprop was faster in plough layer than in subsoil, a higher amount of added ^{14}C-mecoprop was converted to $^{14}CO_2$ in subsoil than in plough layer. The presence of higher amounts of humus in plough layer may favour processes where ^{14}C from mecoprop is built into humus or where mecoprop is made unavailable to degradation.

Mineralization of 5 and 50 mg kg^{-1} mecoprop in plough layer and 5 mg kg^{-1} in subsoil soil followed kinetics with growth (eq. 5 to 12).

The models were based on logistic growth of micro-organisms, where there is a limitation for growth, and on exponential growth, where there is no limitation. Two different models with logistic growth (eq. (5) and eq.(7)), one model with exponential growth and low concentration of substrate (here: pesticide) (eq. (9)) and one with exponential growth and high concentration of substrate (eq. 11) were tested.

For some of the data presented, a very slow zero-order like phase was seen at the end of the experiment. For that reason the logistic and the exponential models were combined with zero order degradation, too, to test the fit (eq. (6),(8),(10),(12)).

The residual means obtained from the fits are shown in Table III.

For both 5 and 50 mg kg^{-1} mecoprop in plough layer the mineralization followed kinetics with logistic growth combined with a zero order process (eq. (6)). Since probably no available ^{14}C-mecoprop was left after 20–30 days, these limitations made kinetics with logistic growth give the best fit.

The mineralization of 5 mg kg^{-1} mecoprop in subsurface followed kinetics with exponential growth, high conc. (eq. 11). At the end of incubation time (70 days) 28 % of the added ^{14}C-mecoprop was mineralised to $^{14}CO_2$, and probably ^{14}C-mecoprop was still left in the soil.

At the very high concentration 5000 mg kg^{-1} in plough layer and 50 and 5000 mg kg^{-1} in subsoil, as they might appear near point sources, the degradation was very slow, and no usable model fits could be found. The toxicity of the pesticide to the micro-organisms may be limiting for the degradation. The rates of degradation during the first week are only about 5 to 10% in subsoil compared to ploughlayer soil for most of the concentrations tested.

Degradation of phenoxyherbicides has previously been reported as taking place through a metabolic process, because enhanced degradation rate appeared at repeated application to microbial communities(40,41). The present results show that kinetics for mecoprop degradation highly depend on the initial concentration.

Modelling results for isoproturon

Figures 5a and b show the degradation of isoproturon 0.001, 5, 50 and 5000 mg kg^{-1} in ploughlayer and subsurface soil, respectively.

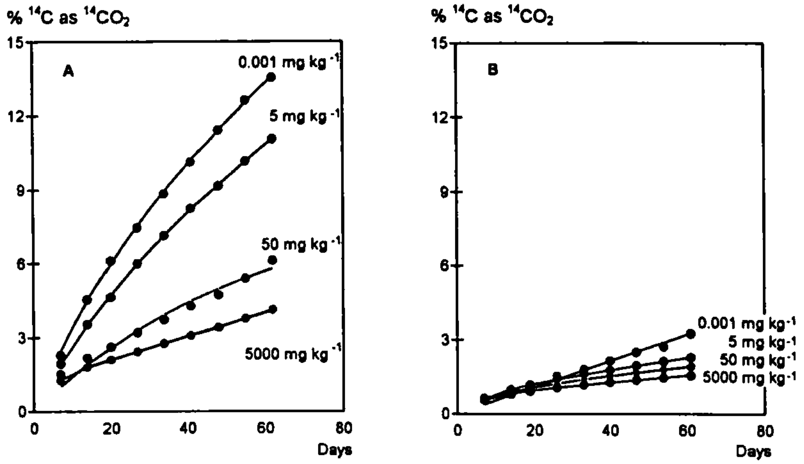


FIGURE 5. Degradation of ^{14}C-labelled isoproturon in soil at different concentrations shown by the evolution of $^{14}CO_2$. Mean of three replicates. Dots: data points, solid line: modelled equation
A. $^{14}CO_2$-evolution in soil from plough layer. All concentrations no-growth model.
B. $^{14}CO_2$-evolution in subsoil. 5000 mg kg^{-1} no useable fit. All other concentrations no growth model

For all concentrations of isoproturon both in plough layer and subsoil (except 5000 mg kg^{-1} in subsoil, where the degradation was too slow to give usable fits) the mineralization followed kinetics without growth of micro-organisms. The model that gave the best fit in most cases was eq. (4) (lowest residual mean, see Table III), a three-half order model, consisting of one first order process and a zero order process.

The explanation given by Brunner and Focht and Scow et al.[32,24] for the fit of the three-half order model to mineralization curves was, that the first order process expressed the mineralization of the chemical in solution and that the zero order process expressed the conversion of humus, where ^{14}C had been built into it may also express the degradation of slowly released isoproturon. The same concept was useful for explaining mineralization kinetics of low concentrations of pesticides, previously analysed by Fomsgaard[38]. In the present case, the kinetics composed of both a first and a zero order process occurred even if only <15 % of ^{14}C isoproturon was converted to $^{14}CO_2$, and the curve still had a steep raise. The adsorption and slow release of isoproturon could be the explanation for this. The three-half order model was also seen by Dörfler et al. (1996)[42] for the degradation of ^{14}C-DEHP in different soil samples.

Degradation rates of isoproturon are obviously slower in subsoil than in plough layer with rates about 20% of ploughlayer (Figures 5a and b). The rate of degradation in subsoil may be limited by the supply of inorganic nutrients, and the lower number of micro-organisms present in the subsoil. As seen for mecoprop the degradation rate of isoproturon is slowest at the high concentrations, though there was not seen a complete stop of the degradation at any concentration of isoproturon.

CONCLUSIONS

- The concentrations of pesticides in the environment vary from concentrated chemicals in waste disposals to trace concentrations near or below the drinking water limit.
- Trace concentrations were degraded fastest and followed first order reaction kinetics for both mecoprop and isoproturon.
- Degradation took place even at concentrations in soil near the drinking water limit.
- Degradation rate at field concentrations showed growth for mecoprop (metabolic degraded pesticide) and first order reaction kinetics for isoproturon (cometabolic degraded).
- High concentrations were degraded relatively slow. Degradation in subsurface soil was most sensitive to high concentrations.
- Degradation in surface and subsurface soil showed identical patterns but the rate in subsurface was only about 5 to 20% of the rate in surface soil.
- Under aerobic condition, trace concentrations of mecoprop and isoproturon can be degraded in both surface and subsurface soil.
- High concentrations of pesticides are degraded so slow, that point sources often will be very long lasting pollution sources.

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