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The degradation of linuron in sandy soil

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Abstract. The degradation of linuron occurs both in aerobic and anaerobic sandy soil with a slight lag when the conditions change from aerobic to anaerobic or from anaerobic to aerobic. Liming was found to stimulate the degradation rate of linuron so clearly that liming can be recommended for acceleration of linuron degradation as a normal agricultural treatment, particularly in sandy soils.

Index words: Liming, degradation acceleration, herbicide, ^{14}C-linuron, flow-through system.

Introduction

Linuron (3,4-dichlorophenyl-1-methyl-1-methoxyurea) has been used in many countries as a pre-emergency or post-emergency herbicide in the cultivation carrot and some other plants.

The disappearance of linuron from soil occurs mainly by microbial cometabolic degradation (GLAD et al. 1981; WALKER & ZIMDAHL 1981; STEPP et al. 1985; WANG et al. 1985).

The mobility of linuron is very low because of its high tendency to adsorb with soil particles and organic compounds as determined by the adsorption constants of GLAD et al. (1980) and WALKER (1987). Most linuron residues can be found in the soil layer of 0—6 cm (WALKER 1987). Thus ZAHNOW and RIGGLEMAN (1980) did not find linuron in the mud or water of a North American bay despite the great amounts of linuron used on the fields near this bay and its tributaries. In one case (FRANK et al. 1987), linuron was found in farm well water, but in this case it was assumed that linuron was in the water because of spills while mixing and loading the spray equipments near the wells.

Linuron forms complex compounds with humic acids (SENESI 1981) as well as some of its potential degradation products (SAXENA & BARTHA 1983 and BARTHA et al. 1983).

The microbial degradation of linuron can begin either by dechlorination or by side chain degradation. STEPP et al. (1985) found the reductive dechlorination of *para*-chlorine to occur in anaerobic pond sediment. The

side chain degradations (demethylation, demethoxylation and hydrolysis of amide bound) have been known for a long time (BÖRNER, 1965), and at least in aerobic soil they may be more important. When ^{14}C-labelled linuron degraded in soil, the amount of ^{14}C-carbonyl-labelled demethylated and demethoxylated degradation products in soil was only 5 % that of the undegraded ^{14}C-carbonyl-labelled linuron (WALKER 1976), but the formation of ^{14}carbon dioxide was a good indicator of the total degradation of linuron. Thus it can be assumed that hydrolysis of the amide bound following by decarboxylation is the most important degradation way of linuron, the main metabolite being 3,4-dichloroaniline.

Linuron has been found to degrade in some soils quite rapidly (KLEMPSON-JONES & HANCE 1979; WALKER 1976 and 1987) or in some other soils very slowly (GLAD et al., 1980; WALKER & ZIMDAHL 1981). The degradation rate depends on temperature, soil moisture and pH. The degradation rate was higher at 22°C than at 10°C and the rate was higher when the moisture was neither too high nor too low (KLEMPSON-JONES & HANCE 1979). A pH-value above pH 6 seems to be more favourable than lower pH-values (HANCE 1979). The very slow degradation of linuron has in some cases damaged the next yields (EAGLE 1981; HEINONEN TANSKI et al. 1986), or the soil residue levels can be critically high if the weather is unfavourable (MUNDELL & OLAFSSON 1982).

Thus, there is a great need for methods to accelerate the degradation of linuron in practical agriculture. This need may be greatest in the Nordic climate after cold and short summers, such as summer 1987, or after very dry or very rainy summers. The cometabolic degradation could be accelerated by addition to soil substrates, which increase the microbial activity of soil. In practice, such compounds could be organic or inorganic fertilizers or lime. DOYLE et al. (1978) found that dairy manure and sewage sludge increased the degradation rate of linuron. Liming may generally increase microbial activity in easily acidified Finnish soils. Therefore it was selected for this experiment as a possible accelerator for the degradation of linuron.

Materials and methods

Soil: Carrot was cultivated in sandy soil in Laukaa, Central Finland (62° 28′ N and 25° 56′ E), weeds were controlled annually for seven years by two sprayings of 1.8 kg/ha, and then for four years by one spraying of 1.8 kg/ha linuron (as Afalon). The plots were then limed with dolomitic lime (0, 5 or 10 t/ha) in May before the last seeding and linuron application. Soil samples were taken in autumn five months after the liming, when harvesting the eleventh carrot yield. The organic matter of soil was 2.6 % and mechanical analysis gave the following percentages: medium coarse sand 3.0 %, fine sand 35 %, very fine sand 25 %, silt 26 %, and clay 11 %. This soil had earlier contained up to 0.4—0.5 mg/kg linuron one year after the last linuron application (HEINONEN-TANSKI et al. 1986). The other properties of autumn samples are presented in Table 1.

Laboratory tests: Soil samples were air-dried at room temperature and added to a flow-through system bottles (GOSWAMI & KOCH 1976). ^{14}C-carbonyl linuron (Hungarian Academy of Sciences, Institute of Isotopes, Budapest) and unlabelled linuron (Hoechst) were applied to 1 mg/kg. The field capacity of the soil was adjusted to 60 % with tap water

Table 1. The chemical analyses of the soils five months after liming (unlimed control, limed with 5 t/ha and 10 t/ha).

	Unlimed	Limed 5 t/ha	Limed 10 t/ha
pH_{KCl}	6.2	6.7	6.7
Conductivity µS 10^2/cm	0.45	0.54	0.81
Ca mg/l	875	1 175	1 975
K mg/l	105	100	95
Mg mg/l	120	150	210

and the temperature was set at 15°C. The soils were watered when the field capacity had decreased 30—40 %, which is too low for optimal microbial activity and linuron degradation. Radioactive carbon dioxide was trapped with ethanolamine and measured with a scintillation counter (LIGNELL et al. 1984). The trapping capacity was tested with $Na^{14}CO_3$ and HCl, and it was better than 95 %. The flow-through gas was synthetic air (80 % N_2 and 20 % O_2) until the 164th day, then nitrogen until the 234th day, and air again until the end of the experiment on the 252th day.

After the flow-through system experiment, the soil (1.25 g) was extracted three times with water to separate the water-soluble metabolites. After the water extraction, linuron and related aromatics in the soil were extracted for 8 hours in a Soxhlet apparatus with acetone. The humins were then separated from the soil by extraction with 0.5 N NaOH solution, first overnight and then twice for 2 hours, and by centrifugation for 30 min at 10 000 rpm. The humins were found in vacuum-dried precipitant. The supernatant was acidified with concentrated HCl to pH 1.0 and centrifuged again as above. The HCl-supernatant contains then fulvic acids and HCl-precipitant humic acids. The separation was based on the method described by HÄNNINEN et al. (1981). The radioactivities of soil extractions were measured by using 1.5 ml of sample solution or water and 10 ml of scintillator cocktail (University Pharmacy, Helsinki YA-gel). The total radioactivity of the soil was combusted in a sample oxidizer, trapped and counted as described by LIGNELL et al. (1984).

Results

The cumulative evolution of $^{14}CO_2$ from ^{14}C-linuron during the incubation is shown in Fig. 1. In limed plots the degradation of linuron was clearly accelerated. This acceleration was statistically significantly higher in the two limed plots as compared to the unlimed plots, both in the first sampling (limed 5 t/ha) or after one week (limed 10 t/ha).

The degradation rate was practically the same in both soils limed with either 5 or

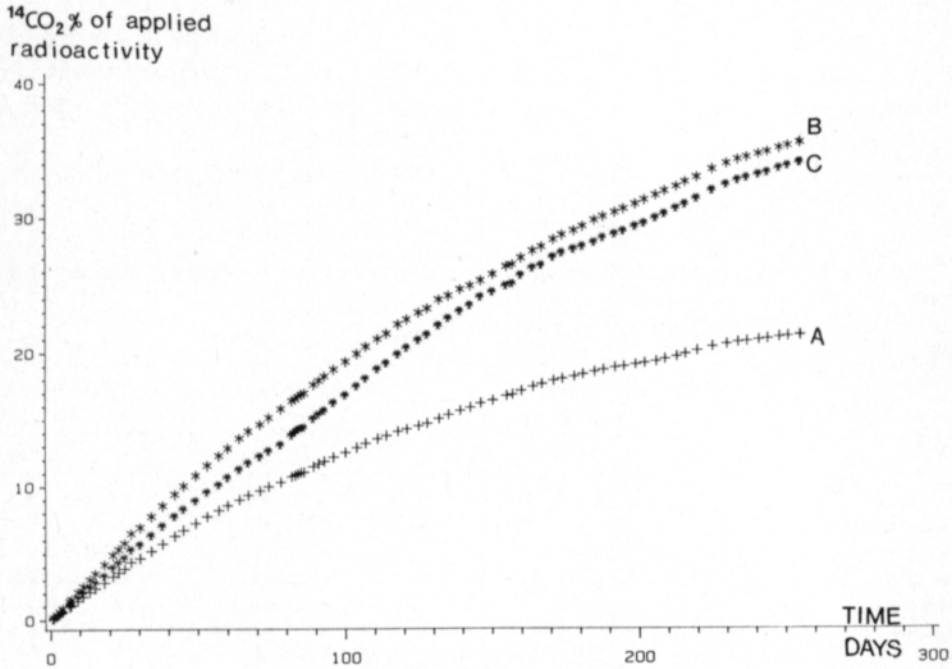

Fig. 1. The evolution of $^{14}CO_2$ in flow-through systems. A = unlimed, B = limed 5 t/ha and C = limed 10 t/ha.

10 tn/ha, and there was no statistically significant difference.

The initial degradation rate was highest, but after 1—2 weeks the degradation rate was more stable. The main rates per day are presented in Table 2. When air was substituted for nitrogen, the degradation rate first decreased, but it increased again gradually without ever reaching the degradation rates before incubation with nitrogen as the flow-through gas. Again, when nitrogen was substituted for air, the degradation rates first decreased and then increased.

The distribution of ^{14}C-activity between CO_2 and different soil fractions after 252 days' of incubation is shown in Table 3.

Discussion

In this experiment, the degradation of linuron was much slower than presented by HANCE (1979), MAIER-BODE and HÄRTEL (1981) and WALKER (1987). The half-life would be more than eight months, calculated from the formation of $^{14}CO_2$. At the same time, half or almost half of the radioactivity added as linuron was still found in soil, most of it in acetone extract (and possible partly in water, too) in the form of linuron.

The binding of linuron or its metabolites to humus was less than 15 % of the linuron added. The possible binding of 3,4-dichloroaniline, an important metabolite of linuron known to bind to humus (BARTHA et al. 1983) is not included in this figure because this aniline derivate would not be radioactive.

The changes from aerobic to anaerobic and from anaerobic to aerobic initially caused a microbial lag, which might be more important in natural soils with dry and rainy periods.

Lime accelerates the degradation of linuron so clearly that liming could be recommended in acid soils, for instance, after spills or accidental overdoses of linuron or if linuron has been used for many years in the same plot, or perhaps after unfavourable growing seasons (cold, short, very rainy or very dry), like summer 1987 in Northern Europe. After such growing seasons, it would be worth performing liming earlier, which is a normal and regular operation in Nordic agricultural soils lacking calcium buffer.

Organic fertilizers, such as manure or

Table 2. The degradation rate per day in unlimed and limed soils (5 t/ha and 10 t/ha) using a flow-through gas air or nitrogen.

Flow-through gas phase	Degradation rate of linuron % / day of initially added in soils.		
	Unlimed	Limed 5 t/ha	Limed 10 t/ha
Air before N_2	0.10	0.17	0.16
31 days with N_2	0.05	0.11	0.10
Air after N_2	0.03	0.06	0.06

Table 3. The distribution percentage of ^{14}C-activity in unlimed and limed soils after 252 days. (Mean ± standard deviation).

Fraction	Unlimed	Limed 5 t/ha	Limed 10 t/ha
$^{14}CO_2$	21.0 ± 2.0	35.1 ± 3.3	33.7 ± 5.1
In soil	54.7 ± 11.1	37.0 ± 7.4	40.9 ± 13.4
Recovery	75.7 ± 12.0	72.1 ± 8.4	76.6 ± 14.3
In soil:			
Water soluble compounds (maybe partly linuron)	9.1 ± 2.0	4.3 ± 1.5	6.6 ± 2.9
Acetone extract (linuron ect.)	20.7 ± 7.7	20.5 ± 4.4	23.0 ± 5.1
Fulvic acids	6.8 ± 6.1	6.6 ± 2.3	5.3 ± 1.5
Humic acids	0.3 ± 0.1	0.6 ± 0.3	0.3 ± 0.1
Humins	7.6 ± 5.8	5.4 ± 3.6	2.5 ± 1.2
Sum in soil found	44.5 ± 11.6	37.4 ± 6.3	37.7 ± 6.2

sludge which DOYLE et al. (1978) found to accelerate the degradation of linuron, would also be worth trying.

The results presented in Table 3 show the fate of only 75—80 % of linuron. A leakage in the flow-through system would easily explain this lack but it is not a probable explanation because the parallel results were too close to each other. There is always some leakage during the sampling of $^{14}CO_2$ results, which occurred 85 times during this experiment, each time taking approximately 30 secs. In addition to the weighing and changing of gas bottles, watering also caused some leakage. Watering was done approximately 10 times, each time taking 10—15 minutes. As the entire experiment took 252 days, these errors may have some importance. It is also possible that the original application of linuron solution in 100 µl had an error of up to 10—15 %.

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SELOSTUS

Linuronin hajoaminen hietamaassa

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Linuronia on käytetty meillä lähinnä porkkanan viljelyssä herbisidinä joko ennen tai jälkeen taimettumisen. Karuissa maissa sekä epäedullisissa sääoloissa (liian kuivaa, liian sateista tai liian lyhyt tai liian kylmä kasvukausi) linuron ei ehdi hajota riittävän täydellisesti ja jäämävaara maan pintakerroksissa on olemassa. Jäämäriski lisääntyy myös, jos samaa maata käsitellään toistuvasti tai linuronia käytetään ylisuurina annoksina. Pahimmillaan linuronjäämät ovat alentaneet seuraavan samassa lohkossa viljeltävän kasvin kasvua ja satoa, mistä on olemassa kirjallisuudessa esimerkkejä.

Tässä työssä on tutkittu keinoja nopeuttaa linuronin hajoamista maassa. Linuron on lisätty ^{14}C-leimattuna suomalaiseen karkeaan ja melko happamaan hietamaahan.

Osa maista oli kalkittu (5 tn tai 10 tn/ha) edellisenä keväänä, viisi kuukautta ennen maanäytteiden ottoa. Maan alkuperäinen pH oli pH 6,2 ja kalkituksen jälkeen se oli pH 6,7 kummassakin kalkitussa maassa. Seurattiin $^{14}CO_2$:n vapautumista 15°C:ssa 252 päivän ajan. Kalkitus lisäsi erittäin selvästi linuronin hajoamista. Tässä kokeessa ei voitu havaita eroja eri kalkkimäärien välillä.

Linuronin hajoaminen jatkui sekä aerobisissa että anaerobisissa olosuhteissa; tosin kun olosuhteita muutettiin aerobista anaerobisiksi ja päinvastoin, hajoamisnopeus aina aluksi hidastui, millä seikalla on varmasti merkitystä kesinä, joina runsassateiset ja kuivat jaksot vuorottelevat.

Tämän kokeen perusteella linuronin puoliintumisaika olisi tutkitussa maassa noin 8 kk, mikä on selvästi pidempi kuin kirjallisuudessa tavallisesti esitetyt 2—4 kk.

Kokeen perusteella voidaan olettaa, että maan normaali ylläpitokalkitus nopeuttaa merkittävästi linuronin hajoamista ja tätä kalkitusta kannattaisi käyttää hyväksi jopa aikaistettuna, jos on syytä epäillä, että maahan on jäänyt liian korkeita linuronjäämiä.