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Effects of Organic Fertilizer Treatments and Old Humus on Thiofanox and Aldicarb Soil Metabolisms in Sugar Beets

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Abstract. Cow manure, pig slurry, or a mixture of both were applied on field plots of a sugar beet trial, 1 month before sowing and an insecticide thiofanox soil treatment. During the first 2 months crop period, the S-+SO-+SO_2-thiofanox soil half-lives were about 43 days in the organic fertilizer treated plots and 24 days in the organic fertilizer untreated control plots. In another sugar beet trial, soil was treated at sowing with the insecticide aldicarb, and the field was divided into two parts. The first part had been treated with cow manure in the autumn preceding sugar beet sowing; its organic matter concentration was 2.4%; that cow manure treatment had been repeated every 3 years for 18 years. In the second part, the soil contained a high concentration of old soil organic matter, humus (4.3%); this corresponded to a meadow ploughed 18 years ago; since then, no organic fertilizer had been applied. During the first 2 months crop period, the S-+SO-+SO_2-aldicarb soil half-lives in the first and second part of the field were 63 and 29 days, respectively. The results show that the recent soil organic matter slows down insecticide soil metabolisms, and increases their protection efficiencies. However, the old soil organic matter, humus, had no significant effect on biodegradation, in spite of its high soil concentration.

The efficiencies of soil insecticides and herbicides may be quite different from one field to the other of the same soil type, on which crops are grown simultaneously. These differences normally are minimized at the prescribed doses of insecticides and herbicides, which include an excess for safe crop protection. These prescribed doses however sometimes are insufficient. It has been reported that the soil metabolism of the herbicides butylate and EPTC (*S*-ethyl dipropylthiocarbamate) was accelerated in soils where the same herbicides had been repeatedly applied for many years (Harvey 1987); this corresponded to lower herbicide protection efficiencies. Soil metabolism of the insecticide carbofuran also was accelerated in soils where the same insecticide had been applied repeatedly, resulting in lower insecticide protection efficiencies (Suett 1987). Searching for phytotechnic parameters that cancel accelerated insecticide soil metabolisms, we studied the influences of the organic fertilizers and of the soil organic matter on this soil metabolism (Honnay 1989).

It was previously observed that repeated applications in the past of organic fertilizers—made every 3 years at the beginning of the crop rotation cycle—slow down aldicarb soil metabolism in the sugar beet (Rouchaud *et al.* 1993a). Was this effect mostly due to the latest organic fertilizer treatments or to the old soil organic matter, humus, accumulated for 30 years? The soil organic matter due to the organic fertilizer treatments is permanently mineralized to CO_2. Has the remaining old soil organic matter—humus—still some influence on the insecticide soil metabolism?

In order to answer to these questions, in the present work, we studied the effects of the organic fertilizers applied recently, on the soil metabolism of the insecticide thiofanox (3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime) in sugar beet. Cow manure, pig slurry, or mixture of both of them was applied 1 month before sowing. There were control plots not treated with organic fertilizers.

In another sugar beet trial made simultaneously, we studied the effect of the very old soil organic matter—humus—on the insecticide aldicarb (2-methyl-2-(methylthio)propanal *O*-[(methylamino)carbonyl]oxime) soil metabolism. The field was divided into two parts. In the first, the soil organic matter concentration was 2.4%; cow manure had been applied repeatedly every 3 years for 18 years, in the autumn preceding the first crop (sugar beet) of the crop rotation cycle. In the second part, the old soil organic matter concentration was 4.3%; it was due to a meadow which had been ploughed 18 years ago; since then, no organic fertilizers at all had been applied onto that field.

Materials and Methods

Sugar Beets with Recent Organic Fertilizer Treatments and with Thiofanox Application

A sugar beet crop trial with thiofanox insecticide treatment at sowing was made in 1992 at Lubbeek, Belgium [clay 10%, silt 65%, sand

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25%, silt loam, pH(KCl) 7.00, organic matter 2.16%], Belgium. On March 2, 1992, each plot of the field was treated with one of the organic fertilizers cow manure (40 tons ha^{-1}), or pig slurry (40 tons ha^{-1}), or with the mixture of both (20 + 20 tons h^{-1}). There were control plots not treated with organic fertilizers. The field was tilled at 20–25 cm depth, sugar beet (cv. Monohil) was sown on 8-4-1992, and 1 kg thiofanox ha^{-1} was applied in the sowing furrow (22 222 m of line ha^{-1}) using the granulates of Dacamox® 10G (10 g% thiofanox, Rhône-Poulenc Agro). There were four replicate plots for each organic fertilizer treatment. At intervals during the trial (Table 1), samples were taken separately (and analyzed once separately) in the sowing line (3–4 cm broad) from the 0–15 cm soil layer of each of the four replicate plots, for each of the three organic fertilizer treatments and control. In addition, at two times (May 18 and July 30, 1992) single samples were taken separately (and analyzed once separately) from the 15–25 cm soil layer in the sowing line of each of the four replicate plots. For each soil sample, 15 cores (2.5 cm diameter) were taken from each replicate plot at random points; the cores from each replicate plot were bulked together and then stored at −25°C until analyzed. At harvest, an aliquot of sugar beet root (about 20 kg) and foliage (about 15 kg) was taken at random in each organic fertilizer treatment object, sampling being made in the four replicate plots, but bulking together the samples from each replicate. The roots and foliage were separately cut into small pieces which were mixed, and an aliquot of each of them was separately stored at −25°C until analyzed. Four replicate analyses were made on each of the root and foliage from each of the organic fertilizer treatments.

Sugar Beet Crop with Aldicarb Treatment

A sugar beet crop trial with aldicarb insecticide treatment at sowing was made in 1992 at Remicourt, Belgium, (clay 12%, silt 79%, sand 9%, silt), in the same way as at Lubbeek, except the following. The field was divided in two parts. In the first one, the soil organic matter concentration was 2.4%; for 18 years, cow manure (40 tons ha^{-1}) was applied every 3 years in the autumn preceding the sowing in April of the sugar beet crop, which is the first crop of the crop rotation cycle; the latest cow manure treatment thus had been made in November 1991, *i.e.*, 6 months before aldicarb treatment. The second part of the field had a high soil organic matter concentration (4.3%); it corresponded to a meadow which had been ploughed 18 years ago; no organic fertilizer at all had been applied since then. In both field parts, the soil pH(KCl) was 6.9. Sugar beet was sown on April 11, 1992, and 1 kg aldicarb ha^{-1} was applied in the sowing furrow using granulates of Temik® 10G (10 g% aldicarb, Rhône-Poulenc Agro). In addition to the 0–15 cm surface soil layer samplings (Table 2), at two times (May 31 and July 13, 1992) samples were taken in the 15–25 cm soil layer in the sowing line.

Thin-Layer (TLC) and Gas-Liquid (GLC) Chromatographies. Infrared (IR), Nuclear Magnetic Resonance (NMR), and Mass (MS) Spectrometries

Thin-layer chromatography (TLC) was carried out with silica gel 60F254 20 × 20cm, 0.2 mm thick plates. The sample solution was applied as a band. Standards were applied on another part of the TLC plate, next to the band of the sample solution. This made possible the accurate separation on the TLC plate of the insecticide soil residues out of the soil contaminants. This was done by the removal of and the extraction of the silica gel of the insecticide TLC band. The insecticide Rf was not constant from one TLC plate to the other, but the insecticide standard accurately indicated the insecticide band on each TLC plate. When the extract was not sufficiently clean for GLC and MS analyses, the TLC was repeated.

S-Thiofanox, SO-thiofanox, and SO_2-thiofanox extracted from soil and plants were analyzed by GLC as SO_2-thiofanox after oxidation with peracetic acid. Similarly, S-aldicarb, SO-aldicarb, and SO_2-aldicarb extracted from soil and plant were analyzed by GLC as SO_2-aldicarb after oxidation with peracetic acid (Rouchaud *et al.* 1993a). Flame photometry detection was operated in the sulfur mode. Injection at 225°C, detection at 180°C. Glass column 1.80 m × 2 mm i.d., 5% Carbowax 20M on Gas Chrom Q 80-100 mesh, nitrogen as carrier gas at 40 ml min^{-1}. With column oven at 115°C, retention time of SO_2-thiofanox was 3.7 min; at 130°C, it was 1.9 min. With column oven at 140°C, retention time of SO_2-aldicarb was 2.6 min. Frequently, the SO_2-derivatives of thiofanox and aldicarb extracted from soil were further analyzed by MS.

IR spectra were recorded with KBr disks (cm^{-1}). ^1H NMR spectra were recorded in $CDCl_3$ at 200 MHz with tetramethylsilane as internal standard: δ, ppm. MS were recorded at 70 eV in the electron impact mode; m/e, relative abundance, %. Frequently the SO_2-derivatives of thiofanox and aldicarb extracted from soil and analyzed by GLC, were further analyzed by MS.

Standards for Analysis

S-Thiofanox (Thiofanox): Dacamox® 5G (400 g; 5 g% thiofanox, Rhône-Poulenc Agro) was extracted repeatedly by stirring with acetone (4 × 500 ml) at room temperature. The pooled acetone extracts were evaporated to an oil in a vacuum rotary evaporator. Dichloromethane (300 ml) was added, the mixture was washed four times with water (4 × 300 ml), the dichloromethane solution was dried (Na_2SO_4), and concentrated to dryness. One half of the oily product was applied onto a silica gel (30 g) chromatography column, which was eluted with ethyl acetate. The second half of the oil was purified similarly on a second chromatography column. The ethyl acetate solutions were gathered, and evaporated to dryness. The solid was recrystallized in dichloromethane + hexane ½ vol/vol, giving thiofanox (16 g) whose purity was greater than 99% as shown by TLC and GLC.

IR: 3381(NH), 2967, 1717(CO), 1499, 1414, 1237, 1107, 1082, 951, 912, 887, 764, 671.

^1H NMR: 1.24(s, 9H, $C(CH_3)_3$); 2.26(s, 3H, SCH_3); 2.91(d, 3H, $NHCH_3$); 3.44 (s, 2H, SCH_2); 6.29(br, 1H, NH).

MS: 218(M^+, 18); 173(M-CHS, 95); 172(M-CH_2S, 95); 161(M-$C(CH_3)_3$, M-CH_3NCO, 79); 144(M-$OCONHCH_3$, 84); 143(M-$OCONHCH_3$-H, 78); 128(173-$NH(CH_3)_2$, 173-CH_3NO, 81).

3,3-Dimethyl-1-(methylsulfonyl)-2-butanone *O*-[(methylamino) carbonyl]oxime, SO_2-Thiofanox: To a stirred solution of S-thiofanox (5 g, 23 mmole) in ethylacetate (25 ml) at 0°C was added dropwise a solution of peracetic acid (17 g, 72 mmol; 32 g% peracetic acid from Aldrich) in ethylacetate (25 ml). The mixture was stirred overnight at room temperature, and washed with 0.5 M Na_2CO_3 in water. The ethyl acetate solution was dried with Na_2SO_4 and concentrated; hexane was added, and the solid was filtered, giving SO_2-thiofanox (4.9 g, 20 mmol, 87%) whose purity was greater than 99% as shown by TLC and GLC.

IR: 3422(NH), 2973, 1738(CO), 1512, 1416, 1318, 1235, 1148, 1080, 953, 909.

^1H NMR: 1.26(s, 9H, $C(CH_3)_3$); 2.93(d, 3H, $NH(CH_3)$); 3.26(s, 3H, CH_3SO_2); 4.30(s, 2H, SO_2CH_2); 6.25(br, 1H, NH).

MS: 250(M^+, 39); 192(M-$CONHCH_3$, 88); 177(M-$OCONHCH_3$ +H, 77); 175(M-$OCONHCH_3$-H, 71); 159(175-O, 43); 150(192-$C(CH_3)_2$, 78); 134(150-O, 100); 119($CH_3SO_2CH_2CN$, 88).

The synthesis procedures for S- and SO_2-aldicarb have been described (Rouchaud *et al.* 1993a).

Soil and Sugar Beet Analyses

The soil concentrations of the sum of S-+SO-+SO_2-thiofanox and of S-+SO-+SO_2-aldicarb were measured by means of the same proce-

Table 1. Concentrations and half-lives of total toxic residues of S-+SO-+SO_2-thiofanox in sugar beet field at Lubbeek Belgium in 1992. Cow manure, pig slurry, or a mixture of cow manure + pig slurry was applied 1 month before sugar beet planting

Date[a]	Days after thiofanox treatment	Cumulative rainfall (mm)	Organic fertilizer: Control (no organic fertilizer)	Cow manure	Pig slurry	Cow manure + pig slurry
			S-+SO-+SO_2-Thiofanox concentrations (as equivalents of thiofanox; mg kg^{-1} dry soil) in the 0–15 cm soil surface layer in the sowing line[b]			
8-4	0	0	4.2	4.2	4.2	4.2
21-4	13	23	3.02 ± 0.15	3.78 ± 0.19	3.44 ± 0.17	3.52 ± 0.18
2-5	24	63	1.99 ± 0.10	3.08 ± 0.15	2.70 ± 0.14	3.12 ± 0.16
18-5	40	79	1.36 ± 0.07	2.23 ± 0.11	2.00 ± 0.10	2.04 ± 0.10
31-5	53	96	0.95 ± 0.05	1.95 ± 0.10	1.72 ± 0.09	1.81 ± 0.09
14-6	67	157	0.28 ± 0.01	0.79 ± 0.04	0.47 ± 0.02	0.61 ± 0.03
29-6	82	183	0.10 ± 0.01	0.11 ± 0.01	0.08 ± 0.01	0.13 ± 0.01
30-7	113	251	nd	nd	nd	nd
Corr. coeff.[c]			−0.9959	−0.9853	−0.9916	−0.9821
y intercept[c]			1.434	1.479	1.437	1.471
Slope (day^{-1})[c]			−0.02842	−0.01555	−0.01753	−0.01704
Soil half-lives (days)[c]			24 ± 1	45 ± 2	40 ± 2	41 ± 2

[a] Sampling date, day-month, year 1992. On 8-4-1992, sugar beet sowing and in furrow treatment with 1 kg thiofanox ha^{-1}

[b] Means of four replicates ± s.d. nd = None detected. On 8-4-1992, thiofanox concentration is a calculated value

[c] For the first 53 days crop period, linear regression ln y = kt + b of the naperian logarithms of the total insecticide S-+SO-+SO_2-thiofanox soil concentrations (y, mg kg^{-1} dry soil, as equivalents of S-thiofanox), in the 0–15 cm surface layer in the sowing line, against time t (days) following thiofanox treatment: correlation coefficient, y intercept, and slope (day^{-1}). The total S-+SO-+SO_2-thiofanox soil half-lives with their 95% confidence intervals were obtained using the SAS logical CMS SAS 5.18 (1984, 1986, SAS Institute Inc., Cary, NC 27512)

dure. Soil (100 g) was refluxed for 10 min with stirring in acetone/water (8/2 vol/vol, 200 ml). The mixture was filtered, and the extraction repeated. The filtrates were combined, water (100 ml) was added, and the acetone removed in a vacuum rotary evaporator (30°C). NaCl (15 g) was added to the aqueous solution, which was then extracted with dichloromethane (200 + 150 ml). The dichloromethane solution was dried (Na_2SO_4), concentrated to 50 ml in a rotary evaporator (30°C), peracetic acid was added (8 ml; 32 g% from Aldrich), the mixture was stirred at room temperature for 30 min, dichloromethane (100 ml) and solid $NaHCO_3$ (11.2 g) were added; the mixture was stirred for 15 min, water (50 ml) was added, the mixture was stirred for 2 min, the dichloromethane solution was separated, dried (Na_2SO_4), concentrated to 40 ml in a rotary evaporator (30°C), and then concentrated further to 0.5 ml under a slow stream of nitrogen (20°C). The concentrate was applied to a TLC plate, together with the standards of SO_2-thiofanox or SO_2-aldicarb. For SO_2-thiofanox analysis, TLC elution with 1/1 vol/vol acetone/hexane gave a band containing SO_2-thiofanox at Rf = 0.72. For SO_2-aldicarb analysis, TLC with ½ vol/vol dioxane/benzene gave a band containing SO_2-aldicarb at Rf = 0.54. The band was scraped off, the silica gel was extracted with ethyl acetate (40 ml), the extract was concentrated to 0.5 ml under a slow stream of nitrogen (20°C), and analyzed for SO_2-thiofanox or SO_2-aldicarb by means of GLC and, in several cases, by MS.

At the 0.1 mg of S-+SO-+SO_2-thiofanox kg^{-1} level in soil, the recovery of the total soil concentration as SO_2-thiofanox was 84–95%. The corresponding value for S-+SO-+SO_2-aldicarb was 82–94%. The analytical limit of sensitivity for SO_2-thiofanox and SO_2-aldicarb was 0.01 mg kg^{-1} dry soil.

Sugar beet root and foliage were analyzed in the same manner as the soil. However, the samples were first cut into small pieces, and extracted at 20°C in a laboratory blender. At the 0.1 mg kg^{-1} fresh weight level, the recoveries of the sum of S-+SO-+SO_2-thiofanox and of S-+SO-+SO_2-aldicarb were similar to those in the soil. The limits of detection of SO_2-thiofanox and SO_2-aldicarb in the sugar beet root and leaves were 0.01 mg kg^{-1} fresh weight.

Results

In all the organic fertilizers treated and untreated plots in the trial at Lubbeek, and in both field parts in the trial at Remicourt, the soil concentrations of the sum of S-+SO-+SO_2-thiofanox and of S-+SO-+SO_2-aldicarb in the 15–25 cm soil layer always were lower than 10% of concentrations in the 0–15 cm surface soil layer. No residues of S-+SO-+SO_2-thiofanox and of S-+SO-+SO_2-aldicarb were detected in the roots and the leaves of sugar beet at harvest, the limit of sensitivity for each of the sums of these compounds being 0.01 mg kg^{-1} fresh weight of roots or leaves.

In all field plots of both trials at Lubbeek and Remicourt, during the first 2 months of the sugar beet crops, the rates of disappearance of the total S-+SO-+SO_2-thiofanox or of S-+SO-+SO_2-aldicarb (the total insecticide carbamate residues) soil concentrations were proportional to the total S-+SO-+SO_2-thiofanox or S-+SO-+SO_2-aldicarb soil concentrations (apparent first order kinetics) (Tables 1 and 2). After the first 2 months crop period, the rates increased greatly and became greater than the ones indicated by first order kinetics. After the third to fourth crop months, no more residue of S-+SO-+SO_2-thiofanox and of S-+SO-+SO_2-aldicarb could be detected in the soil, the limit of sensitivity being 0.01 mg of S-+SO-+SO_2-thiofanox and of S-+SO-+SO_2-aldicarb kg^{-1} dry soil.

In the trial at Lubbeek, during the first 2 months period which followed sowing and thiofanox treatment, the soil half-life of the sum of S-+SO-+SO_2-thiofanox—in the 0–15 cm surface soil layer in the sowing line—was 24 days in the control plots not treated with organic fertilizers (Table 1). In the plots treated 1 month before sowing and thiofanox treatment with cow manure, pig slurry, or a mixture of both of them, the S-+SO-

Table 2. Concentrations and half-lives of total toxic residues of S-+SO-+SO_2-aldicarb in sugar beet field at Remicourt Belgium. In the first part, the organic matter concentration in soil was normal (2.4%) and corresponded to recent and repeated organic fertilizer treatments. In the second part, the old soil organic matter concentration was high (4.3%), due to a meadow ploughed 18 years ago, no organic fertilizers having been applied since then

			Field part:	
			Normal concentration or recent soil organic matter	High concentration of old soil organic matter
Date[a]	Days after aldicarb treatment	Cumulative rainfall (mm)	S-+SO-+SO_2-Aldicarb concentrations (as equivalents of aldicarb: mg kg^{-1} dry soil) in the 0–15 cm soil surface layer in the sowing line[b]	
11-4	0	0	4.20	4.20
24-4	13	25	3.97 ± 0.20	3.35 ± 0.16
2-5	21	59	3.50 ± 0.17	2.83 ± 0.14
18-5	37	82	3.00 ± 0.15	1.91 ± 0.10
31-5	50	98	2.47 ± 0.12	1.28 ± 0.06
14-6	64	184	0.64 ± 0.03	0.20 ± 0.01
28-6	78	251	0.03 ± 0.01	0.04 ± 0.01
13-7	93	301	nd	nd
Corr. coeff.[c]			−0.9742	−0.9917
y Intercept[c]			1.479	1.495
Slope, $days^{-1}$[c]			−0.01092	−0.02389
Soil half-lives, days[c]			63 ± 3	29 ± 2

[a,b,c] As in Table 1, except the following:

[a] On 11-4-1992, sugar beet sowing and in furrow treatment with 1 kg aldicarb ha^{-1}

[b] On 11-4-1992, aldicarb concentration is a calculated value

[c] For the first 50 days crop period, linear regression ln y = kt + b of the naperian logarithms of the total insecticide S-+SO-+SO_2-aldicarb soil concentrations (y, mg kg^{-1} dry soil, as equivalents of S-aldicarb in the 0–15 cm surface soil layer in the sowing line) against time t (days) following aldicarb treatment

+SO_2-thiofanox soil half-lives were about 43 days. To the greater soil concentrations of S-+SO-+SO_2-thiofanox insecticide compounds in the organic fertilizers treated plots corresponded a greater insecticide protection efficiency of the sugar beet foliage against green-flies, relative to the organic fertilizers untreated control plots.

In the trial at Remicourt, during the first 2 months crop period which followed sowing and aldicarb treatment, the S-+SO-+SO_2-aldicarb soil half-life was 63 days in the field part which had been repeatedly treated with cow manure. In the second field part at Remicourt containing high soil concentrations of old humus (no recent organic fertilizer treatment), during the first 2 months crop period, the S-+SO-+SO_2-aldicarb soil half-life was 29 days (Table 2).

Discussion

In the trial at Lubbeek, the organic fertilizers had been applied 1 month before sowing and thiofanox treatment. In the trial at Remicourt, in the cow manure treated part of the field (which had a soil organic matter concentration of 2.4%), the organic fertilizer had been applied 6 months before sowing and aldicarb treatment. Moreover, this cow manure treatment had been repeated in the past every 3 years for 18 years. Such a situation was already studied in a trial made at Gembloux, which has been described (Rouchaud *et al.* 1993a). What is new in this trial at Remicourt is that the second reference part of the field contained a high (4.3%) soil organic matter concentration. This was due to a meadow ploughed 18 years earlier. No organic fertilizer at all had been applied since then. The results show that the old soil organic matter (humus) had no influence on the rate of aldicarb soil biodegradation. This occurred in spite of the fact that its soil concentration was about two times greater than the soil organic matter concentration in the other part of the field. These results thus show that only the recent organic fertilizer treatments slow down the rate of the insecticide soil metabolism. One to two years after the latest organic fertilizer treatment, this effect should disappear. On the other hand, the very old soil organic matter—humus—had no significant influence on the rate of insecticide soil metabolism.

It is well known that green manure (Geller and Nikolaenko 1972), cow manure (Zagorcha and Lupashku, 1977), and pig slurry (in spite of the heavy elements it contains: Cu, Zn, . . .) (Zakharov *et al.* 1977) greatly increase the soil microbial activity after their soil incorporation. Insecticides and herbicides are soil metabolized mainly by the soil microbial activity. Before the trials, the increase of the rate of pesticide soil metabolism thus was expected after the application of the organic fertilizers. However, the observed slowing down effect of the pesticide soil metabolism—due to the recently applied organic fertilizers—suggested that this effect was not primarily related to the soil microbial activity. We suggested that it was due to the pesticides adsorption onto the soil organic matter, whose soil concentration was increased by the organic fertilizer treatment (Rouchaud *et al.* 1992a, 1993a, 1993b). In cauliflower crops, positive correlations indeed were found between the recent organic fertilizer treatments, the density of chelating functions in the soil organic matter, and the slowing down of the insecticides soil metabolism (Rouchaud *et al.* 1992b). We extend to the present trials the hypothesis of insecticides adsorption to the soil organic matter.

It is known that the soil organic matter—due to an organic fertilizer treatment—is permanently mineralized into CO_2 by the soil microbial activity; about 50, 75, and 85% of the soil organic matter due to this treatment is mineralized into CO_2 after 1, 2, and 3 years, respectively. The decrease of the soil organic matter concentration, with the time which follows the organic fertilizer treatment, should reduce the effect of the organic fertilizer treatment onto the rate of insecticide soil metabolism. In the second part of the field at Remicourt, the old soil organic matter (humus) concentration, however, was very high (4.3%), and its lack of effect on the rate of aldicarb soil metabolism may be due to the chemical structure of the humus, relative to the chemical structure of the recent soil organic matter (2.4% in the soil of the first field part).

The results show that the recent soil organic matter should contain the chemical functions capable of chelating the insecticides. It is known that during the first 5 months period of the humification process of the young soil organic matter, the percentages of ketone, carboxyl, phenolic, and aromatic chemical functions progressively increase (Inbar *et al.* 1989). These chemical functions indeed are the ones which are able to chelate and adsorb the insecticides in soil. However, it is known that the long-term aging of the soil organic matter not only results in its mineralization into CO_2, but also—for the soil organic matter remaining in the soil—in the progressive loss of its oxygen-containing chemical functions (carbonization-coalification of the soil organic matter) (Stevenson 1982). This defunctionalization of the soil organic matter, to which correspond the increase of the carbon content and the decrease of the oxygen one, should explain the reduced chelation and adsorption powers of the old humus towards the insecticides in soil.

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