

Effect of soil moisture condition on the conversion rate of oxamyl

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Summary

The rate of conversion of oxamyl in four soils under moist conditions was measured in incubation experiments at 15 °C. Half-lives of oxamyl in soils with moisture pressures of about -9.8×10^3 Pa were 13 days in a clay loam, 14 days in a loamy sand, 34 days in a peaty sand and 39 days in a humic loamy sand. With a humic loamy sand and a clay loam soil the rate of conversion was studied at six soil moisture levels. When the moisture content was lowered to values at about wilting point, a gradual decrease in conversion rate ensued. At a moisture content corresponding to soil moisture pressures far below wilting point, the conversion rate of oxamyl further decreased with the clay loam. However, with humic loamy sand the conversion rate increased sharply in the very dry range.

Introduction

Oxamyl [S-methyl N', N'-dimethyl-N(methylcarbamoyloxy)-1-thiooxamimidate] may be used for the protection of arable and horticultural crops against harmful nematodes and insects. In the Netherlands, the compound is approved for the protection of sugar-beet, potato and ornamentals. Oxamyl is applied as granules (Vydate 10G, 10 % a.i.) at sowing or planting, in dosages ranging from 0.75 to 8 kg a.i./ha. The granules are placed in the soil near the seed furrow or they are incorporated in the soil immediately after broadcast application.

The effectiveness of soil-applied pesticides like oxamyl depends on the distribution of the compound with depth in soil and on the rate of conversion to compounds with low activity. Depth of incorporation, and the further redistribution induced by rainfall have to be sufficient to protect the most important part of the root systems. Preferably, the active substance should be present for a few months in sufficient concentrations to protect the roots and the green plant parts, the latter after uptake and translocation. However, a low conversion rate would

increase the risk for leaching of such a weakly adsorbed compound to ground and surface water.

Harvey & Han (1978) incubated oxamyl in a moist silt loam soil in a soil metabolism apparatus. After 42 days, 4 % of the dosage was left as oxamyl, which corresponds to a half-life of 9 days. Upon incubation of oxamyl in a loamy sand and in a fine sand soil at 25 °C in partially covered beakers, half-lives of about 11 and 15 days, respectively, were found (Harvey & Han, 1978). Bromilow et al. (1979) investigated the rate of conversion of oxamyl after incubation in various soils at 15 °C. Under moist conditions, the half-lives of oxamyl in the six soils varied from 6 to 22 days. With two sandy loam soils, the conversion rates of oxamyl were measured at three soil moisture contents. At moisture contents of 0.10 and 0.15 kg kg⁻¹, the conversion rates were almost equal (Bromilow et al., 1979). At a moisture content of 0.05 kg kg⁻¹, the conversion rates of oxamyl were 0.56 and 0.87 times the rates for the two higher moisture contents in the corresponding soils.

The present measuring series for oxamyl was set up to study in more detail the relationship between conversion rate and soil moisture content. Conversion rate was studied at six moisture contents to get a more accurate relationship for moist soils. Further, the moisture contents were related to soil moisture pressures. A second aim of this research was to obtain conversion rates for oxamyl in important Dutch soil types. Such rates are needed to evaluate the possible reasons for failure in crop protection. Half-lives of about a week would seriously restrict the duration of crop protection at the low dosages recommended at present.

Materials and methods

Description of the soils

In February 1978 soil from top layers (0-20 cm) was collected at four locations. On the fields near Rolde and Westmaas (see Table 1) potatoes were grown in 1977 and after that winter-wheat was sown. On the fields near Creil and Emmer-compascuum sugar-beets had been cropped in 1977. None of the locations had been previously treated with oxamyl. The soils were screened when moist to remove particles larger than 2 mm and then thoroughly mixed. They were stored in layers (20 cm thick) in partly covered containers which were then kept in the dark at 10-15 °C for 55 days before starting the incubations. Characteristics of the soils are given in Table 1.

Moisture pressures down to -5×10^4 Pa were read from porous-cup tensiometers with mercury manometers. Moisture contents at lower moisture pressures (from -5×10^4 to -1.5×10^6 Pa) were measured with the membrane press method, starting with a water saturated soil slurry as described by Hofstee & Fien (1971). Moisture content at very low moisture pressure were measured by equilibrating a soil sample with an atmosphere of about 50 % relative humidity which corresponds with a soil moisture pressure of about -9.8×10^7 Pa. The soil moisture contents measured at the various pressures are given in Table 2. The relatively high moisture retention with the membrane press measurements.

SOIL MOISTURE CONDITION AND CONVERSION RATE OF OXAMYL

Table 1. Soil characteristics measured by the Laboratory for Soil and Crop Testing, Oosterbeek, the Netherlands.

Soil type Location	Humic loamy sand Rolde	Clay loam Westmaas	Loamy sand Creil	Peaty sand Emmercompascuum
Organic matter (%)	4.5	4.5	1.1	9.0
Clay (<2 μm) (%)	4	34	7	3
Silt (2-50 μm) (%)	20	41	12	7
Sand (>50 μm) (%)	71	13	76	81
CaCO ₃ (%)	0.2	7.3	3.7	0.3
pH-KCl	5.4	7.1	7.4	5.2
N (water) (mg kg ⁻¹)	100	60	40	50
N (total) (%)	0.12	0.26	0.06	0.22
P* (mg kg ⁻¹)	510	290	290	340
K (mg kg ⁻¹)	60	220	90	100
MgO (mg kg ⁻¹)	68	193	57	124
Moisture** (kg kg ⁻¹)	0.19	0.35	0.12	0.33

* Phosphorus compounds as extracted with ammonium lactate.

** Moisture content at a pressure of -9.8×10^3 Pa.

especially with the clay loam, illustrates the great effect of soil structure conditions on this retention.

Design of the incubation study

Moist soil portions, equivalent to 60 g dry soil, were weighed into 250-cm³ glass jars. The soil portions were gently air-dried for a short time until about 5 g of water had been lost. Oxamyl (200 μg; 913 nmol) in aqueous solution (5 cm³) was spread evenly with a pipette on the soil surface. By shaking and rolling the jars the oxamyl was further mixed with the soil. A calculated mass of distilled

Table 2. Soil moisture retention by the humic loamy sand and the clay loam.

Method	Humic loamy sand		Clay loam	
	pressure (Pa)	moisture content (kg kg ⁻¹)	pressure (Pa)	moisture content (kg kg ⁻¹)
Tensiometer	-3.9×10^3	0.244	-2.3×10^3	0.388
	-9.8×10^3	0.188	-2.4×10^4	0.314
	-2.4×10^4	0.137	-4.9×10^4	0.274
	-3.1×10^4	0.127		
Membrane press	-9.8×10^4	0.116	-9.8×10^4	0.338
	-3.1×10^5	0.079	-3.1×10^5	0.281
	-1.6×10^6	0.054	-1.6×10^6	0.20
In equilibrium with air of 50 % rel. humidity	-9.8×10^7	0.015	-9.8×10^7	0.036

Table 3. Conversion of oxamyl in four soils at 15 °C and the influence of moisture content with two soils.

Soil	Moisture content (kg kg ⁻¹)		Mass of oxamyl recovered (μ g) after various incubation periods (days)									
	adjusted	measured range	1	5	11	22	39	60	61	95	104	140
Humic loamy sand	0.03	0.016-0.04	177	132	99	63	36	21			7.7	
	0.055	0.042-0.055	179	156	141	129	104		84		59	40
	0.08	0.056-0.074	187	159	152	134	108		87		54	36
	0.11	0.084-0.111	188	164	151	136	99		76		45	28
	0.16	0.135-0.163	191	165	156	132	92		66		36	16
	0.22	0.19 -0.216	188	169	154	129	88		62		32	15
Clay loam	0.10	0.10 -0.106	185	166	157	139	106		78		47	25
	0.20	0.185-0.20	186	158	136	95	52	29		7.0		
	0.24	0.225-0.24	191	150	130	87	45	21		3.4		
	0.28	0.265-0.28	193	152	125	79	36	16		2.0		
	0.32	0.306-0.32	195	154	122	78	35	13		1.3		
	0.36	0.34 -0.36	197	149	122	74	33	11		0.9		
Loamy sand	0.12	0.096-0.13	186	141	109	65	28	10			1.7	
Peaty sand	0.30	0.264-0.30	194	167	148	115	83		57	27	11	

water was added to bring the moisture contents up to the desired levels as given in Table 3. The soil portions with a low moisture content were gently air-dried after the oxamyl solution had been added. In a preliminary study this procedure had shown to give no measurable loss of oxamyl.

The soil moisture contents having been adjusted, each jar was capped with aluminum foil with a hole of 80 mm² punched in it. The jars were put in loosely covered boxes with a shallow layer of water and stored in the dark in incubation cabinets at 15 \pm 1 °C. After 5, 60 and 140 days, moisture contents were measured by drying 10 g of soil from each jar at 105 °C. Water losses were not replenished. Two jars per soil type were analysed at the time intervals given in Table 3.

Extraction and clean-up

In a preliminary study it was found that extraction for oxamyl was relatively low at low soil moisture contents. Therefore, the soils were moistened with distilled water to about the moisture content at a pressure of -10^4 Pa. The entire contents of the incubation jars was extracted twice with acetone (100 and 80 cm³, respectively) for one hour on a mechanical shaker. The liquid phases were filtered off by suction, combined and the total volume was recorded (150-250 cm³). A fraction (50-100 cm³) of these filtrates was shaken in a separatory funnel with an equal volume of chloroform. After separation, the aqueous layer was extracted three times, each time with 6 cm³ of chloroform. The organic layers were dried on anhydrous sodium sulphate and collected in a 500 cm³ round bottom flask. The

volume was reduced with a rotary evaporator and the concentrate finally evaporated with a gentle stream of air on a water bath at 40 °C. The oily residue was taken up in 0.5 cm³ ethyl acetate with 2.5 % water (w/w).

The concentrated extracts were further purified on silica gel columns. Glass columns (8 cm long, 1.1 cm inner diameter) were dry-filled under vibration with about 4 g of silica gel (32-63 μm, Woelm, Eschwege, West Germany). Columns were preconditioned with 40 cm³ eluting solvent (ethyl acetate with 2.5 % (w/w) water). After introduction of the samples, the columns were eluted with 50 cm³ eluting solvent. The first 15 cm³ fraction contained oxamyl-oxime (S-methyl N'N'-dimethyl-N-hydroxy-1-thiooxamimidate). This non-toxic metabolite is not separated from the oxamyl in the gas chromatograph (Bromilow & Lord, 1976). The 15 to 50 cm³ fraction contained oxamyl. This fraction was evaporated to dryness and taken up in a known volume of pure ethyl acetate. Recovery percentage for oxamyl with this clean-up procedure was about 100 % (S = 3).

Gas chromatography

Concentrations of oxamyl were measured using the method described by Bromilow & Lord (1976). This method is based on the conversion of oxamyl in the gas chromatograph into its methoxime with a 0.1 M solution of trimethylphenylammonium hydroxide in methanol. A Pye Unicam gas chromatograph (type GCV) equipped with a flame photometric detector operating in the sulphur mode (394 nm filter) was used. The glass column (0.9 m × 2 mm i.d.) was packed with 3 % Carbowax 20 M on Chromosorb WAW-DMCS (80/100 Mesh). The glass injection port (11 cm × 4 mm i.d.) was packed with non-silanized glass wool. Operating temperatures were: injection port 210 °C, column 180 °C, detector 235 °C. The flow rates of the gases were: carrier N₂ 50; H₂ 40; air 40 cm³ min⁻¹. Retention time of the oxamyl methoxime was 1.0 min. Each sample (4 mm³ + 1 mm³ reagent) was injected twice. Every third injection was an oxamyl solution of known concentration (2-7 μg cm⁻³). Unknown concentrations were read from standard curves based on peak heights. The gas chromatographic variation could be limited to ± 5 %. Detection limit for the complete procedure was 1 μg per jar (0.5 % of the dosage).

Recovery of oxamyl from eight 50 g soil samples (two of each soil type) fortified with 200 μg compound was found to be 90 % (S = 4.3).

Results

The ranges of soil moisture content at 5, 60 and 140 days after the start of the incubation are given in Table 3. After 5 days the measured soil moisture contents almost corresponded with the adjusted values. The lowest moisture contents were measured after 140 days of incubation. A gradual but slight decrease of the soil moisture content was thus observed.

The masses of oxamyl recovered after the various times of incubation are given in Table 3. These masses are the averages of duplicate measurements. The differences between the duplicates and their mean values ranged from 0 to 10 %

Table 4. First-order rate coefficients and half-lives for the conversion of oxamyl in four soils at 15 °C.

Soil	adjusted moisture content (kg kg ⁻¹)	rate coefficient (d ⁻¹)	half-life (d)	coefficient of determination of regression line
Humic loamy sand	0.03	0.0323	21.4	0.986
	0.055	0.0101	68.3	0.990
	0.08	0.0113	61.3	0.996
	0.11	0.0134	51.7	0.996
	0.16	0.0177	39.1	0.999
	0.22	0.0183	37.8	0.999
Clay loam	0.10	0.0138	50.2	0.997
	0.20	0.0342	20.2	0.996
	0.24	0.0414	16.7	0.992
	0.28	0.0473	14.6	0.993
	0.32	0.0518	13.3	0.991
	0.36	0.0557	12.4	0.989
Loamy sand	0.12	0.0494	14.0	1.000
Peaty sand	0.30	0.0204	33.9	0.999

of that mean value, with an average of 2.3 %. When the remaining masses were about 2 % of the dose or less, the differences ranged from 8 to 30 % of their mean value with an average of 14 %.

Plots of the recovered masses of oxamyl on a log scale versus time showed approximate linear relationships in all cases. This implies that the conversion of oxamyl could be described with the first-order rate equation $dm/dt = -k \cdot m$, where k is the first-order rate coefficient, and t the time in days. With an initial mass m_0 the solution is $m/m_0 = \exp(-k \cdot t)$. Regression coefficients were calculated for the log (mass) versus time plots and the rate coefficients from: $k = -\text{regression coefficient}/\log e$. Rate coefficients and corresponding half-lives are given in Table 4.

Oxamyl was more slowly converted in the humic loamy sand and the peaty sand, than in the loamy sand and the clay loam. At comparable moisture conditions (moisture pressure about -9.8×10^3 Pa, see Table 1) the conversion rates in the first mentioned two soil types were about 0.4 times the rates in the loamy sand and the clay loam. The relationship between conversion rate coefficient for oxamyl and soil moisture condition is clearly shown by the results in Table 4. The general pattern for both the humic loamy sand and the clay loam was that the conversion rate gradually increased with increasing moisture content. The relationship tends to level off at the highest moisture contents, which was most obvious in the case of the humic loamy sand. At a moisture content of about 0.10 kg kg⁻¹, the

conversion rate of oxamyl decreased rather sharply in the clay loam as compared with the rate at 0.20 kg kg^{-1} . However, conversion rate in the humic loamy sand increased about three times when moisture content decreased from 0.055 to 0.03 kg kg^{-1} .

The approximate soil moisture pressures at a given moisture content can be read from the moisture retention data given in Table 2. The range of moisture contents in which conversion rate gradually changed was presumably in the range of moisture pressures above the so-called wilting point (above $-1.6 \times 10^6 \text{ Pa}$). Only at moisture pressures distinctly below this values, do comparatively great differences with the conversion rate in oxamyl in moist soils, seem to occur.

General discussion

The conversion rates of oxamyl in the clay loam and the loamy sand under moist conditions fall within the range of rates recorded by Bromilow et al. (1979). However, very short half-lives of about one week were not found in the present study. Starting from the half-lives of 11 and 15 days for oxamyl in two moist soils at 25°C as reported by Harvey & Han (1979), and taking the 10°C difference in temperature into account, the conversion rates in the clay loam and the loamy sand were comparatively high, whereas those in the humic loamy sand and the peaty sand soil were somewhat lower than expected.

Harvey & Han (1978) reported that the stability of oxamyl in aqueous solution is considerably less at higher pH than at pH 4.7. The pH of the humic loamy sand and the peaty sand was about 2 units lower than those of the clay loam and the loamy sand (see Table 1). The faster conversion of oxamyl in the latter two soils could be related to these higher pH values. This would support the recommendation that highly alkaline soils may require higher amounts of oxamyl to achieve satisfactory control (Du Pont, 1977).

Slowing down of the rate of conversion with decreasing soil moisture content was also found in the case of a few other insecticides (Getzin, 1968; Roberts & Stoydin, 1976; Bromilow et al., 1979). A similar influence of soil moisture content on conversion rates was found for herbicides (Usoroh & Hance, 1974; Walker, 1978). The relationship between conversion rate coefficient and moisture content seemed to be independent of soil temperature (Smith & Walker, 1977). With both insecticides and herbicides, the extent of reduction in conversion rate when lowering moisture content varied enormously. An increase in conversion in very dry soil, as measured for oxamyl in the humic loamy sand in the present study, seems to be uncommon. This phenomenon can not easily be explained; it could involve surface-catalysed conversion.

In practice much of the oxamyl dosage will be found in soil layers in which the moisture pressures are above wilting point. However, under dry weather conditions, a comparatively thin top layer of the soil may become air dry. The differences between measured and computed concentrations of oxamyl near the soil surface under dry weather conditions reported by Leistra et al. (1979) could be partly caused by unexpectedly high conversion rates in dry soil. For more

detailed information, further study is needed for the range of low to very low moisture contents.

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