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The effects of added fertilizer and carbon source on the persistence of carbaryl in two types of soil[1] /

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Compendio

El efecto de la adición de fertilizantes y una fuente de carbono en la persistencia de carbaril fue estudiada en dos tipos de suelos usando la técnica de centelleo líquido.

En los dos suelos, la adición de fertilizantes (NPK), tuvo un pequeño efecto en la degradación de carbaril.

En contraste, la adición de sacarosa con o sin fertilizante incrementa grandemente la degradación de carbaril en el suelo Latosol Rojo-Amarillo pobre en materia orgánica pero tuvo un pequeño efecto en la degradación en el suelo Gley Húmico, rico en materia orgánica.

Introduction

Carbaryl is perhaps the most widely used member of the group of N-methyl carbamate insecticides for the control of pests in Brazil. Although not used as a soil insecticide much carbaryl may reach the soil because it has been employed in great quantities as a substitute for DDT, a substance which poses considerable residue problems (3).

As more areas of Brazil are brought into cultivation, pesticides are applied to an increasingly wide range of soils and if residue and other hazards are to be avoided, it is necessary to know how pesticides behave in these soils. With cultivation, the soils will be modified by the use of fertilizers and the incorporation of plant materials, which will influence the soil flora and fauna and which in turn may be expected to modify the persistence and behaviour of pesticides.

This paper describes the initial tests in a programme to investigate changes in populations of soil microorganisms which may be induced by the addition of fertilizers and carbon sources. This work, comparing the separate and combined effects of fertilizer and sucrose on the degradation of carbaryl in two soils, forms part of a systematic investigation by radiometric techniques of the fate and behaviour of pesticides in soils under Brazilian conditions.

Materials

Soils

Two types of soil collected in the grounds of the Biological Institute were used in the experiments. One of them, the Humic Gley soil, is characterised by being rich in organic matter and the other, the Yellow Red Latossol, by being poor in organic matter. A full description of the two soils is given in Table 1. Before use, both soils were air-dried and passed through a 2-mm sieve to remove stones and other large pieces of materials.

Radiolabelled pesticide

^{14}C-carbaryl (1-naphthyl N-methyl ^{14}C-carbamate) was obtained from the Radiochemical Centre,

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Table 1. Soil properties

Characteristics		Humic Gley	Yellow Red Latossol
		% composition	
Physical*	Clay	57	77
	Silt	12	9
	Fine sand	19	10
	Coarse sand	12	4
Chemical**	Total Fe_2O_3	4.30	8.90
	Free Fe_2O_3	1.70	1.90
	Organic carbon	2.52	0.21
	Organic matter	4.33	0.36
	Total nitrogen	0.24	0.07
	Carbon/Nitrogen ratio	10.50	3.00
	pH (Water)	5.70	6.40
	pH (KCl)	4.85	4.90
Texture		Clay	Heavy Clay

* Determined by the Agronomical Institute, Soil Division, Pedology Section; Campinas, São Paulo

** Determined by the School of Agriculture "Luiz de Queiroz", Soil, Geology, and Fertilizer Department; Piracicaba, São Paulo

Amersham, England, in benzene solution. The radiochemical purity was 99% and the specific activity 57 mC i/mmol.

For tests, an aqueous solution of technical-grade carbaryl was prepared containing 2 μg/ml unlabelled carbaryl to which labelled carbaryl was added to give solutions containing 23,370 dpm/ml.

Fertilizer (NPK)

Commercial fertilizer was dissolved in water to give a solution containing 1.1 mg/ml $(NH_4)_2SO_4$, 1.6 mg/ml $Ca(H_2PO_4)_2$, and 0.27 mg/ml KCl. Portions of this solution (2.3 ml) were added to soil samples (10 g) giving soil concentrations of 250 mg/kg, 375 mg/kg and 62 mg/kg equivalent to the rates of application of 200 kg/ha, 300 kg/ha and 50 kg/ha respectively, used in São Paulo for beans, assuming incorporation to a depth of 20 cm (5).

Methods

Soil treatments

Ten gram samples of the soils were weighed into 250-ml glass-stoppered bottles. Then, either 2.3 ml of water or aqueous sucrose solution (3.5 mg/ml) or fertilizer solution, with or without the addition of sucrose (3.5 mg/ml), were added to each bottle.

The soils were kept for a week at ambient temperature to allow the development of microorganisms and then 1.0 ml of the radiolabelled aqueous carbaryl solution was added. This raised samples of Humic Gley soil to 2/3 field moisture capacity but a further 1.0 ml of water was added to achieve this moisture content for the Yellow Red Latossol. At intervals, duplicate samples of each treatment were analysed.

Analytical procedures
Extraction

Each 10 g of soil was extracted by shaking with 20 ml dichloromethane for 2 hours. The mixture was allowed to separate and the solvent decanted. The remaining soil was extracted twice more with further 20 ml portions of dichloromethane, the extracts combined and the volume adjusted to 50 ml in a volumetric flask by evaporation in a gentle air stream. 5.0 ml of the extract was evaporated to dryness in a scintillation vial and 10 ml of scintillator liquid added.

Thin layer chromatography

A further 5.0 ml aliquot of the soil extract was dried over anhydrous sodium sulphate before concentrating to 1.0 ml for examination by thin layer chromatography on silica gel with fluorescent indicator using hexane-acetone 4:1 as solvent. The plates were divided into sections and the silica gel scraped into vials for liquid scintillation counting. Most of the radioactivity had the same R_f (0.38) as reference samples of authentic unlabelled carbaryl which were located by the quenching of fluorescence under UV light.

Wet combustion of soil

After extraction, the radiocarbon remaining in the soil was determined by wet combustion to $^{14}CO_2$, the procedure used being essentially that of Smith et al. (6).

The $^{14}CO_2$ from 2.0 g samples of Yellow Red Latossol and 1.0 g of Humic Gley soil was absorbed in 2.0 ml monoethanolamine dissolved in 20 ml scintillation cocktail containing 5.5 g/l PPO in toluene (2 parts by volume) and ethyleneglycol monomethylether (1 part).

Determination of radioactivity

The radioactivity in the evaporated extracts was determined using 10 ml scintillator cocktail composed of 200 mg POPOP, 4 g PPO, 500 ml Triton X and 500 ml xylene or toluene per litre of mixture. Radioactivity measurements were made in a Nuclear Chicago Mark I model liquid scintillation spectrometer. Samples were counted for at least 10 minutes. Results were corrected for background activity and quench, which was estimated using an external standard and the channel ratio method.

Results and discussion

The decrease with passage of time in the amount of radioactivity which could be extracted from the Humic Gley soil and the Yellow Red Latossol after the various treatments is shown in Figure 1. Thin layer chromatography of the extracts showed that over 95% of the radioactivity extracted had the same R_f as carbaryl so that in these tests the radioactivity extracted may be regarded as unchanged carbaryl.

Carbaryl is sorbed more strongly on the Humic Gley soil, rich in organic matter, than in the Yellow Red Latossol which contains little organic matter (2).

Although concentrations of carbaryl available in the soil water would thus be lower in the Humic Gley soil, when no additions but carbaryl are made to the soils, carbaryl is degraded faster in this soil. This is perhaps to be expected since generally organic matter is associated with microbial activity (1, 4).

The addition of fertilizer (NPK) has little effect on the degradation of carbaryl in either soil. In contrast, the addition of sucrose greatly increases degradation of carbaryl in the Yellow Red Latossol poor in organic matter whilst having little effect on degradation in the other soil. Presumably, much microbial activity is to be expected in soil rich in organic matter so that the addition of sucrose has little effect but when indigenous carbon sources are scarce, as in the Yellow Red Latossol, then a readily available carbon source has a larger effect on microbial activity. However, the effects of the addition of sucrose persist only for a short time, 4 weeks after addition, degradation having almost ceased in the Yellow Red Latossol. Where the degradation of carbaryl is stimulated (Yellow Red Latossol) by addition of sucrose, fertilizer added at the same time diminishes degradation of carbaryl. This is possibly the result of competition for the added carbon source (sucrose) stimulated by the fertilizer diminishing the growth achieved by carbaryl-degrading organisms.

Additional evidence for this hypothesis is provided by combusting the soils to determine the ^{14}C remaining after extraction (Table 2). In the Humic Gley soil, rich in organic matter, the residual radiocarbon is generally small and is increased only slightly by the separate or joint addition of sucrose and fertilizer. In contrast, although the amount of ^{14}C remaining after extraction of the Yellow Red Latossol without added sucrose is only about half that remaining in the Humic Gley soil, addition of sucrose alone increases this about 7 fold. Fertilizer alone has little effect but in conjunction with sucrose it increases the amount of unextracted ^{14}C about 10 times, although slightly less carbaryl seems to be degraded. Presumably addition of sucrose stimulates microbial activity in Yellow Red Latossol and some of the ^{14}C from the carbaryl is used as a carbon source, the addition of NPK increasing the utilisation of the radiolabelled carbon although the fertilizer slightly diminishes the rate of degradation of carbaryl.

These results suggest that the biological degradation of carbaryl may be increased by addition of carbon or energy sources to soils poor in organic matter, and improved cultivation resulting in increases in organic matter in such soils may initially decrease the persistence of carbaryl. It remains to be seen whether this is a general phenomenon and whether other, less readily available carbon sources such as cellulose or other plant components, will also stimulate carbaryl-degrading organisms.

Although carbaryl in unlikely to cause a major residue problem in soils because it is readily degraded and is not used as a soil insecticide these investigations provide evidence that the persistence of pesticides may be modified by soil treatments likely to affect soil microbial activity. Thus modifying soil fertility may provide possibilities for avoiding unwanted pesticide residues in addition to increasing crop yields.

FIGURE 1 : DECLINE OF CARBARYL EXTRACTED FROM TWO SOILS AFTER ADDITION OF SUCROSE AND NPK

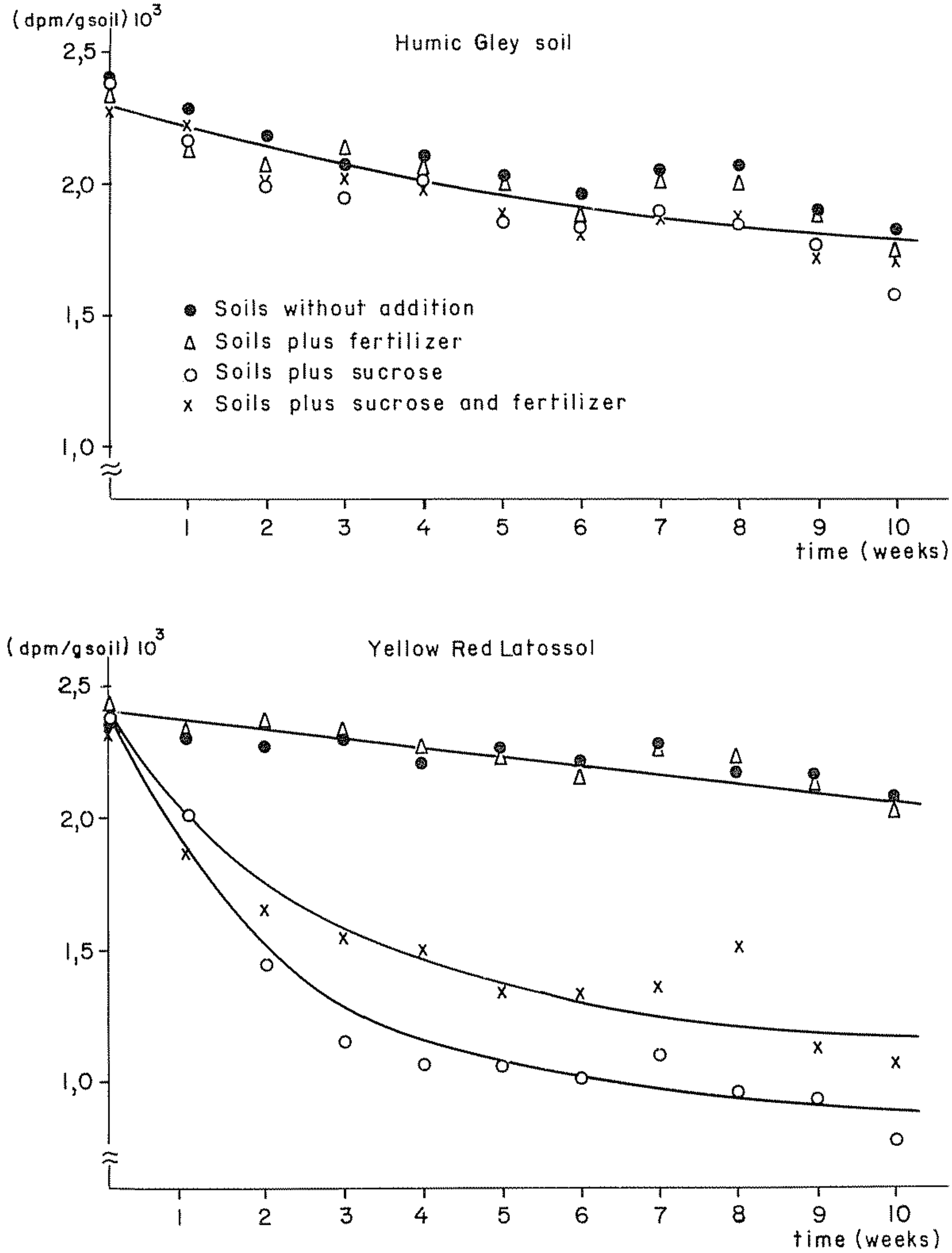

Fig. 1. Decline of carbaryl extracted from two soils after addition of sucrose and NPK.

Table 2. Effects of additions of fertilizer and sucrose on distribution of radiocarbon extracted and remaining in 2 soils 8 weeks after application of ^{14}C-carbaryl (23,370 dpm/ml).

Soil addition	^{14}C recovered as % of applied					
	Humic Gley			Yellow Red Latossol		
	Extracted[a]	Combusted	Total	Extracted[a]	Combusted	Total
None	92	9.8	101.8	94	5.0	99
Sucrose	79	13	92	42	33	75
Fertilizer	86	17	103	95	4.3	99.3
Sucrose + Fertilizer	80	11	91	48	54	102

(a) Examination of the extracts by thin layer chromatography showed that at least 95% of the extracted ^{14}C was carbaryl.

Resumo

Os efeitos da adição de fertilizantes e fonte de carbono sobre a persistência do carbaril foi investigado em dois tipos de solos, usando cintilometria em líquido.

Nos dois solos, a adição de fertilizantes (NPK) tem pouco efeito sobre a velocidade de degradação do carbaril.

Em contraste, a adição de sacarose, com ou sem fertilizante, aumenta acentuadamente a degradação do carbaril no Latossolo Vermelho-Amarelo pobre em matéria orgânica, mas tem pouco efeito sobre a degradação no solo Gley Humico rico em matéria orgânica.

Summary

The effects of added fertilizer and a carbon source on the persistence of carbaryl was investigated in two types of soils, using liquid scintillation counting. In both soils, the addition of fertilizer (NPK) had little effect on the rate of degradation of carbaryl. In contrast, the addition of sucrose, with or without fertilizer increases degradation of carbaryl in a Yellow Red Latossol poor in organic matter, but has little effect on degradation in a Humic Gley soil rich in organic matter.

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