

The sorption of carbaryl on soils determined by spectrophotometric and radiometric techniques*

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RESUMO

Determinou-se o coeficiente de sorção do carbaril em dois tipos de solos, um rico e outro pobre em matéria orgânica, utilizando-se as técnicas de espectrofotometria e de cintilometria em líquido. Os resultados segundo os dois métodos analíticos foram concordantes, de modo geral. Os solos 1 e 1A, ricos em matéria orgânica, absorvem carbaril de maneira semelhante e com mais intensidade que os solos 2 e 2A, com conteúdo menor de matéria orgânica e maior de ferro e argila. Nos solos com alto teor de matéria orgânica, a sorção do 1-naftol é aproximadamente semelhante à do carbaril, porém é maior no mais ácido dos solos minerais.

Introduction

CARBARYL, the most widely used carbamate insecticide, is applied to important crops throughout the world. Government bans and restrictions on the uses of persistent pesticides have resulted in a greater reliance on less persistent compounds such as carbaryl, and this chemical also has the advantages of being effective against a wide range of insects and of having a low mammalian toxicity. In Brazil, many insect pests attacking fruit trees, grasses, vegetables and cereals are controlled with carbaryl (1).

Recently, carbaryl was included in systematic studies of the behaviour of pesticides on soils and the sorption coefficient of carbaryl in several soils reported (3). This paper extends this work on the sorption of carbaryl by soils, and compares two analytical methods, spectrophotometry and liquid scintillation counting, for the determination of carbaryl; assay by gas chromatography (2) could not be included for comparison because the materials were not available in this laboratory.

Materials

a) Insecticide

Carbaryl (1-naphthol N-methylcarbamate) was obtained from the Biological Institute, SP, and ran as a single spot by thin layer chromatography on silica gel using benzene: acetone (95:5) as eluent, being detected by spraying the plates with 1M NaOH in ethanol followed by exposure to Br vapours for a few seconds.

¹⁴C-carbaryl, labeled in the carbonyl position with a specific activity of 57 mCi/mmol, was supplied by the Radiochemical Centre, Amersham, United Kingdom, who quoted a radiochemical purity of 99 per cent as determined by reversed-phase thin-layer chromatography on silica gel coated with silicone oil (solvent system acetone: methanol: water 10: 20: 80) and by thin layer chromatography on silica gel using two solvent systems (hexane: acetone 4:1; chloroform: ethanol 1:1).

b) Soils

Samples of four soils (1, 1A, 2, 2A) were collected from experimental plots in the grounds of the Biological Institute, SP, Brazil. All soils were prepared by air drying and passing through a 2 mm sieve, and were kindly analysed by Dr. F. Grohmann from the Agronomic Institute, Campinas, SP, following the methods described by Moniz (4), Table 1. According to the Granulometric Classification of Campinas, soils 1 and 1A are classified as loam, and soils 2 and 2A

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Table 1 —Soil characteristics (%).

Soil	1	1A	2	2A
%				
Total Fe ₂ O ₃	4.3	4.3	8.9	8.8
Free Fe ₂ O ₃	1.7	1.8	1.9	2.1
Carbon	7.5	7.5	0.5	0.5
Organic matter	13.1	13.1	0.9	0.9
Clay	36.0	35.0	64.0	62.0
Silt	15.0	16.0	12.00	12.0
Fine sand	27.0	34.0	21.0	23.0
Coarse sand	22.0	15.0	3.0	3.0
pH	4.85	5.07	4.90	5.20

as clay Free Fe₂O₃ was determined by dithionite extraction. The pH of the soils was measured in 1 M KCl using a glass electrode

c) Preparation of the solutions

1. Solutions of ¹⁴C-labelled carbaryl - Aliquots of benzene solutions containing labelled and unlabelled carbaryl were evaporated to dryness, and the compound redissolved in 200 ml water to yield solutions containing 1.25 and 20.0 μg/ml carbaryl with a specific activity of 590 dpm/ml.
2. Solutions of unlabelled carbaryl and 1-naphthol - The compounds were dissolved in water to give solutions containing 25 μg/ml.

Methods

a) Sorption of carbaryl

1. 10 ml of aqueous carbaryl solution were shaken for 24 hours with 1.0 g of soil and the mixture then left to equilibrate at room temperature for 24 hours. Each test contained four replicates, plus a control containing no carbaryl
2. The mixture was then centrifuged for 30 minutes at 3000 rpm and the amount of carbaryl in the supernatant assayed.

The distribution (K) of carbaryl between water and soils was calculated by

$$K = \frac{\text{conc in soil}}{\text{nc. in water}} = \frac{V(\alpha - c)}{w \cdot c} \text{ where:}$$

V = volume of aqueous solution (ml)

α = concentration before equilibrium (μg/ml)

c = concentration after equilibrium (μg/ml)

w = weight of soil (g)

b) Spectrophotometric assay of carbaryl

1. To a 5 ml aliquot of the aqueous supernatant was added 10 ml chloroform
2. The mixture was shaken for 2-3 minutes
3. After separation, 5 ml of the organic phase were evaporated to dryness using a gentle airstream. Extraction of carbaryl by this procedure from the aqueous supernatant was checked using the ¹⁴C-labelled compound and shown to be essentially quantitative.
4. The residue was dissolved in 5 ml water plus 0.5 ml 0.1 M Na OH solution.
5. The absorbance (of carbaryl hydrolysed to 1-naphthol) was determined at a wavelength of 330 nm, using a Perkin Elmer Coleman 46 UV-Visible Spectrophotometer, with the reference cell containing the solution obtained by the same procedure from the control in order to eliminate interference from other materials extracted from soil.

c) Radiometric assay of carbaryl

To 1.0 ml of the supernatant from soils containing ¹⁴C-labelled carbaryl were added 10 ml of scintillation cocktail (200 mg POPOP, 4 g PPO, 500 ml Triton-X and 500 ml toluence). Measurements of ¹⁴C-carbaryl were made in the Mark 1 model of a Nuclear Chicago Liquid Scintillation Spectrometer. Quench corrections were made by the channels ratio method, using an external standard. Each vial was counted for 40 min.

Results and discussion

The discovery of pesticides which could be synthesised in sufficient quantities for large scale agricultural use was soon followed by investigation aimed to make more and better use of these chemicals. It was recognised that even the most stable compounds only protected crops for limited periods of time and the use of highly toxic organophosphate insecticides immediately emphasised the risk of toxic residues on crops. These problems raised many questions which could only be answered by the development of methods of detecting and measuring small amounts of pesticides in crops and soils. Biological (toxicological) methods were first used because chemical methods either were not available or were not sufficiently sensitive to detect pesticides after field applications. However, more sensitive chemical methods were developed, at first using colour reactions alone and subsequently in conjunction with paper and thin layer chromatography. More recently,

Table 2.—Distribution coefficients (K) of carbaryl and 1-naphthol between water and soils, obtained by spectrophotometric and radio-metric techniques.

Soil	Absorbance (330 nm)		Liquid scintillation counting	
	Concentration 25 $\mu\text{g/ml}$		Concentration 1.25 $\mu\text{g/ml}$ 20 $\mu\text{g/ml}$	
	1-naphthol	Carbaryl	Carbaryl	Carbaryl
1	11.5	12.4	16.9	13.0
1A	25.8	13.0	14.1	21.0
2	4.8	0.7	0.9	0.6
2A	1.2	2.8	2.0	1.9

Each value is the mean of 4 replicates

with the development of very sensitive and specific detectors, gas chromatography has been widely applied to the detection and measurement of traces (1 $\mu\text{g/g}$ and less) of pesticides in the environment.

However, pesticides must be extracted from soils, crops and foodstuffs before they can be analysed by these methods and frequently extracts contain substances which interfere with the identification and measurement of the small amounts (from 1 μg to 1 mg per kg) of pesticide present. Such interfering co-extractives must be separated from the pesticide before the analysis can be completed or an alternative assay procedure found which is not affected by the co-extractives. In view of these difficulties in measuring pesticide residues and because each chemical has a unique combination of physical and chemical properties, it is hardly surprising that many techniques including visible, ultraviolet, infrared and mass spectrometry, spectrofluorimetry, nuclear magnetic resonance, high-performance liquid chromatography and polarography have been used when and where they are available (6).

The carbamates present special analytical problems since usually they have neither intense characteristic absorption spectra nor specific and sensitive colour reactions, and they do not gas chromatograph readily without chemical modification. Carbaryl is a typical carbamate in these respects. It is readily degraded to give naphthol and methylamine, and assays of carbaryl utilising these hydrolysis products or their derivatives in colorimetric or gas chromatography procedures, together with methods employing gas chromatography of the parent compound or derivatives thereof retaining the carbamate group, have been reviewed by Kuhr and Dorough, (2).

The reagents and equipment available in this laboratory limited our choice of methods for assay of carbaryl to measurements of UV absorption and radioisotopic assay using ^{14}C -labelled carbaryl. Both methods were used to measure the sorption of carbaryl on 4 local soils and the results are summarised in Table 2.

Two main types of soil, denoted 1 and 2 (Table 1), were used. The most obvious differences in composition were the higher organic matter content of soil 1 and the greater proportion of clay minerals and greater total Fe_2O_3 content of soil 2, although the free Fe_2O_3 contents of the two soils were similar.

The four samples of soil absorb carbaryl and naphthol to differing extents. The variation between the four replicates of each test was less than ± 4 per cent of the mean. Results obtained by the two methods of analysis are generally in good agreement, indicating that the two methods are measuring the same physical phenomenon. Significant degradation of carbaryl during the 24-hour period of the experiment is improbable (unpublished work). Sorption of carbaryl, as measured by liquid scintillation counting, is not greatly affected by the carbaryl concentration, suggesting a physical sorption process. In general, with sorption of pesticides on soils, distribution depends little on the concentration. Also, the sorption and desorption of pesticides is usually fairly rapid, and these processes are currently being investigated in these soils.

The soils 1 and 1A absorb carbaryl about equally and much more strongly than soils 2 and 2A which have lower organic matter and higher iron and clay contents, suggesting that organic matter plays an important part in the sorption of carbaryl in these soils. The sorption of non-ionised pesticides by soils is usually highly correlated with the organic matter content (5) and sorption onto soils of high organic matter content probably occurs predominantly on this soil fraction. Although the two organic soils (1 and 1A) sorb carbaryl about equally, the more alkaline mineral soil 2A (pH 5.20) sorbs carbaryl about 3 times more strongly than the other mineral soil 2 (pH 4.90). This suggests that whereas sorption of carbaryl on soil organic matter (compare soils 1 and 1A, pHs 4.85 and 5.07) is relatively unaffected by soil pH, the weaker sorption on soil minerals may be pH dependent and, being obscured by the greater sorption on organic matter, is not readily detected in highly organic soils.

On the high organic soils, 1-naphthol is sorbed to about the same extent as carbaryl, but it is more strongly sorbed than carbaryl on the more acid of the two mineral soils.

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Summary

The sorption coefficient of carbaryl in soil samples rich and poor in organic matter was determined using spectrophotometric and liquid scintillation counting techniques. Results obtained by the two methods of analysis were generally in good agreement. Soils 1 and 1A absorb carbaryl about equally and more strongly than soils 2 and 2A which have lower organic matter and higher iron and clay contents. On the high-organic soils, 1-naphthol is sorbed to about the same extent as carbaryl, but it is more strongly sorbed than carbaryl on the more acid of the two mineral soils.

Compendio

Se determinó el coeficiente de sorción de carbaril en muestras de dos tipos de suelos, con diferente contenido de materia orgánica. Se usaron para tal fin técnicas espectrofotométricas y de centelleo líquido.

Los resultados obtenidos por los dos métodos de análisis fueron satisfactorios. Los suelos 1 y 1A absorben carbaril de manera similar, y más fuertemente que los suelos 2 y 2A donde existe un bajo contenido de materia orgánica y contenidos altos de hierro y arcillas. En los suelos con alto contenido de materia orgánica, el 1-naftol es sorbido tanto como el carbaril,

pero es más fuertemente sorbido que el carbaril en el más ácido de los dos suelos minerales

Literature cited

- 1 GIANNOTTI, O, ORLANDO, A, PUZZI D., CAVALCANTE, R. D., and MELLO, E.J.R. Noções básicas sobre praguicidas - Generalidades e recomendações de uso na agricultura do Estado de São Paulo. *O Biológico*, 38 (8-9): 223-339, 1972.
- 2 KUHR, R.J. and DOROUGH, H.W. Carbamate Insecticides: chemistry, biochemistry and toxicology. Ohio: CRC Press Inc. 1976 301 p.
- 3 LORD, K.A., HELENE, C.G., DE ANDREA, M.M. and RÜEGG, E.F. Sorption and movement of pesticides on thin-layer plates of Brazilian soils. *Arquivos do Instituto Biológico*, São Paulo 45 (10): 47-52, 1978.
- 4 MONIZ, A.C. comp. Elementos de Pedología Rio de Janeiro, Livros Técnicos e Científicos, 1975. 460 p.
- 5 WEED, S.B. and WEBER, J.B. Pesticide-organic matter interactions. In *Pesticides in Soil and Water*, Ed. Cuenze, W.D. Madison, Wisconsin, Soil Science Society of America, 1974 pp 39-66.
- 6 ZWEIG, G. ed. ANALYTICAL methods for pesticides, plant growth regulators and food additives. Vol. 1-7. New York, Academic Press, 1963-1973.

Notas y Comentarios

Aumentando la resistencia del algodón a los insectos

Conforme se vuelven más resistentes a los insecticidas, ciertos insectos del algodón, como los gusanos de la bellota (*Heliothis virescens* y *H. zea*), pueden ocasionar problemas severos a los productores. Un programa de control integrado que use una variedad de métodos reduce la oportunidad de que los insectos adquieran tolerancia o evadan el control.

Las variedades de plantas resistentes a los insectos constituyen una parte importante de este programa. Las variedades de algodón sin nectarios, glabras y ricas en gopipol son menos susceptibles al daño de insectos, según afirman Maurice J. Lukefarh, del Cotton Research Laboratory de Brownsville, Texas, y Ernesto Salgado, del Centro de Investigaciones de Tamaulipas (CIAT), México (*Agricultural Research*, November 1978).

En un programa cooperativo de algodón entre Estados Unidos y México, los científicos han logrado obtener dos cosechas por año, una en el Valle de Río Grande en Texas y otra en la zona de Tampico en México. Este programa ha permitido una evaluación crítica de características de algodones silvestres o ferales que podrían ser deseables para usarlos en algunas variedades cultivadas.

El carácter de ausencia de nectarios fue transferido de *Gossypium tomentosum*, un algodón silvestre de Hawaii. Lo

más valioso de esta característica es que reduce las poblaciones de insectos al privar a los adultos de *Heliothis* de una fuente de alimentos, lo que afecta su longevidad y fertilidad. Sin embargo, las mariposas de *Heliothis* son capaces de alimentarse lejos de sus lugares de postura de huevos debido a sus fuertes hábitos de vuelo, lo que reduce algo la eficacia del carácter de ausencia de nectarios.

Los algodones glabros han sido desarrollados para evitar a los insectos en los algodones comerciales. El setenta por ciento de los huevos de *Heliothis* son depositados sobre los puntos de crecimiento de las plantas, los que contienen 500 a 1000 pelos epidérmicos (o tricomas) por centímetro cuadrado. La ausencia de pelos da lugar a una reducción de 50 por ciento en la postura de huevos. A su vez, la reducción de huevos significa menos larvas.

Los algodones de alto contenido de gopipol produjeron una mortalidad de 50 por ciento de las larvas en el segundo y tercer instar. Los algodones normales tienen un contenido de gopipol de 0,05 por ciento en las yemas pero los algodones ricos en gopipol tienen un contenido de 1,2 por ciento.

En una prueba en Tampico en 1974, los algodones resistentes a *Heliothis* tuvieron rendimiento, más alto que el cultivar 'Stoneville 7A' en una proporción de tres a uno. De igual manera, en 1975, las líneas que tenían las tres características de resistencia cuatuplicaron los rendimientos de las variedades comerciales. Las variedades resistentes no sólo son altamente eficaces contra las poblaciones de *Heliothis*, sino que pueden alcanzar también altos rendimientos.