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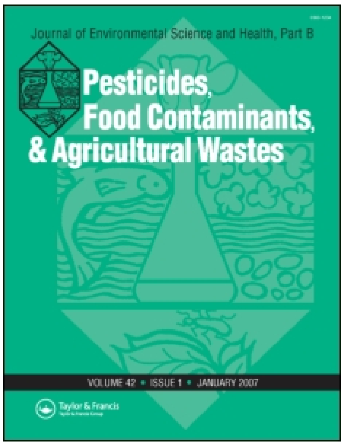

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Monitoring of pesticide residues in a cotton crop soil

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MONITORING OF PESTICIDE RESIDUES IN A COTTON CROP SOIL

Key Words: Multiresidue analysis, clean up, recovery, pesticides, soil

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ABSTRACT

This paper reports on the residues of methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate), trifluralin (α, α, α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine), endosulfan [(1, 4, 5, 6, 7, 7-hexachloro-8, 9, 10-trinorborn-5-en-2, 3-ylenebismethylene) sulfite] and dimethoate (O, O-dimethyl S-methylcarbamoylmethyl phosphorodithioate) in a cotton crop soil. Soil samples (0-15 cm) were collected at different periods from the cotton crop farm and subjected to Soxhlet extraction. The extracted material was analysed after clean-up by a HP5890 II gas chromatograph equipped with a ^{63}Ni electron-capture detector (ECD-^{63}Ni) and fitted with a 25m x 0,2mm i.d. fused silica capillary column [Ultra-2 (5% phenylmethyl polysiloxane)]. The recoveries of the pesticide residues from the spiked control soil were determined after Soxhlet extraction and C_{18} cartridges clean-up by using radiotracer techniques with the corresponding ^{14}C-pesticides. The results show that in the cotton crop soil the pesticide residues under study were present in the range of 0.1 to 0.4 mg · kg^{-1}. Endosulfan was found to be rapidly degraded in the soil and formed a sulfate metabolite.

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INTRODUCTION

The increasing use of pesticides in Brazil is becoming of concern to the agroecosystem pollution as a consequence of the remaining residues in the soil environment. The chemicals utilized for controlling pest organisms and weeds belong to different groups of organochlorine, organophosphorus, carbamates and pyrethroids insecticides. These pesticides may reach the soil surface either directly as a result of spraying or indirectly by weathering or falling leaves. They may then become mixed into the soil and release the residues which may become available to subsequent crops (Kearney and Helling, 1982). The soil is the last reservoir for some of these compounds thereby representing a source from which residues can be released to the atmosphere, ground water and living organisms. Therefore, the soil dynamics of pesticides need to be understood (Luchini, 1997).

Brazil is the fifth world consumer of pesticides, and the extensive use of these compounds needs to be monitored. Although the legislation on the use of pesticides in agriculture is more and more restrictive, there is very little information available the residue contamination by pesticides in Brazilian soils. There is a need for developing analytical procedures to detect the minimum residue levels of the commonly used pesticides and their metabolites in the Brazilian soils in order to assess their behaviour in the agroecosystem. This paper describes the soil extraction and clean up procedures of some organophosphate (methyl parathion and dimethoate), organochlorine (endosulfan) and dinitroaniline (trifluralin) pesticides, as well as the methodology for the simultaneous determination of these pesticides residues by gas chromatography with electron capture detector (GC-ECD). The methodology was checked by the determination of the residue levels from a real agricultural cotton crop soil , which is also reported.

EXPERIMENTAL

Reagents

The commercial pesticides methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate), trifluralin (α, α, α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine), endosulfan [(1, 4, 5, 6, 7, 7-hexachloro-8, 9, 10-trinorborn-5-en-2, 3-ylenebismethylene) sulfite] and dimethoate (O, O-dimethyl S-methylcarbamoylmethyl phosphorodithioate) were investigated according to their use in the studied area. Analytical grade pesticides were used to prepare the standard calibration curves for GC-ECD. All solvent utilized were residue analysis grade. The corresponding radiolabelled ^{14}C-pesticides were used to determine the recoveries after the extraction and clean-up methods.

Samples and standards

Soil samples were collected at different time intervals from a cotton crop farm in Tatuí (Sao Paulo State, Brazil) from the surface layer (0 to 15cm) of the soil profile. Physico-chemical characteristics of the soil were: 2.5% of organic matter; 41% of sand; 51% of clay, 8% of silt, and pH of 5.7.

For the analytical procedures, stock solution (1 mg· mL^{-1}) containing the pesticides: methyl parathion, trifluralin, endosulfan and dimethoate were prepared in pure methanol and stored at - 4 ^{0}C. Working standards solutions (0.1, 1, 10, 50 and 100 μg · mL^{-1}) were prepared by dilution with methanol.

Fortification procedure

Standard solutions of ^{14}C-pesticides (endosulfan, methyl parathion and trifluralin) containing from 4.22 kBq to 6.48 kBq were directly added to (3 ×) 10g of untreated moist soil samples. The samples were allowed to stand for one hour before extraction with the solvent.

Apparatus

Gas chromatography: A Hewlett-Packard 5890 II gas chromatograph equipped with a split/splitless injector; ^{63}Ni electron capture detector (GC-ECD), and HP ChemyStation terminal to integrate peak areas, was employed. The used column was a Ultra-2 fused silica cappilary column (cross-linked 5% phenylmethyl polysiloxane), 25m x 0.2 mm i.d., and nitrogen was used at 30mL/min as the carrier gas. Injector and detector temperature were 280 and 320 ^{0}C, respectively. A 1 μL aliquot of each fortified and field soil sample extract was injected in the splitless mode with the following temperature programme: 200 °C, increase at 5 °C/min. to 280 °C (10 min.).

Liquid Scintillation Countings

To measure the ^{14}C-pesticide residues recoveries, a Packard 1600 TR liquid scintillation counter (LSC) equippement with quench correction by the external channel ratio method was used after addition of 10 mL of scintillation cocktail to each extraction sample (Mesquita and Ruegg, 1984).

Procedure

Linearity: Linearity of the responses in the GC-ECD was studied by three injections of a calibration curve of the pesticides with concentrations varying from 0.1 to 100μg/mL of pesticide standard solutions in methanol.

Sample extractions and clean-up: After thoroughly homogeneization of the soil collected in the cotton field, (3 ×) 50g of soil sub-samples as obtained from field were extracted for 8 hours with 150 mL of methanol by Soxhlet. Aliquots of 100 mL of the organic extracts were concentrated to dryness, resuspended in 2 mL of methanol which were cleaned-up in a Sep-pack C_{18} bonded-phase silica cartridges. The pesticides were eluted with 10 mL of methanol and the recovered volume was concentrated in a rotary evaporator to a suitable volume (2 mL) which was analyzed by GC-ECD.

Extraction and clean-up methodology recoveries: The extractions and clean-up recoveries were performed using radiotracer techniques, by spiking untreated soil samples with ^{14}C-pesticide followed by extraction with methanol, clean-up in Sep-pack C_{18} bonded-phase silica cartridges and the ^{14}C-pesticide quantification of 1 mL aliquots by LSC. Aliquots of spiked extracted soil samples were also analysed by GC to comprove the ^{14}C-recovery.

For monitoring the pesticide residues in a real situation, the soil samples were collected from a cotton farm before the first pesticide application of the 1995/96 crop season and during the crop growths of 95/96, 96/97 and 97/98. The pesticides were applied to the field in response to the appearence of the pests in the cotton crop. The compounds applied in 96/97 (in $L \cdot ha^{-1}$) were: dimethoate (1.0); endosulfan (1.2 and 2.0); methyl parathion (1.0), and again endosulfan (2.0). Trifluralin (2.0) was applied between the crop seasons. In 1997, they were applied as follow: endosulfan (1.25 and 1.20); endosulfan plus methyl parathion

(1.0, 1.5 and 2.0 of each); endosulfan alone (1.2), and methyl parathion (0.25). Again, trifluralin (2.0) between the crops. In 97/98, methyl parathion (1.2) and endosulfan (1.0) were again applied.

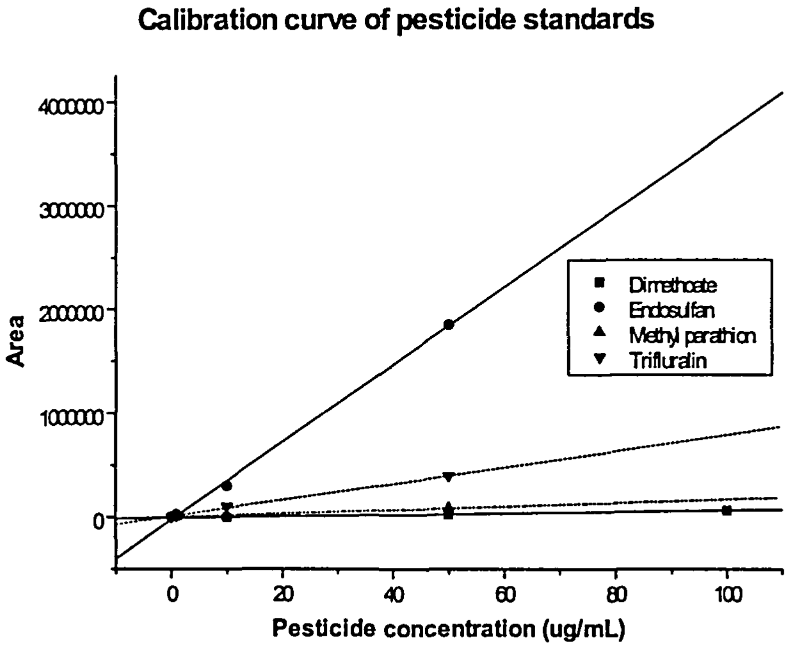
All data are reported on oven-dry soil basis.

RESULTS AND DISCUSSION

The calibration curves and the regression equations obtained by plotting area versus pesticides concentration for 1μL injections, were linear over the ranges shown in Figure 1. Under the experimental conditions used, the R_t (retention times) of the pesticides under study were (in minutes): 3.53 for trifluralin; 4.25 for dimethoate; 5.78 for methyl parathion; 10.65 for endosulfan, and 12.07 for endosulfan sulfate. Results showed the linearity of the responses to the different pesticides in the studied range, with correlation coefficients higher than 0.99 for all pesticides (Fig. 1).

The range of recoveries for extraction and clean-up of the ^{14}C-pesticides from fortified untreated soils using these methods is presented in Table 1. Typical chromatograms of standards, untreated and treated extracted soil samples are shown in Figures 2, 3 and 4. The Ultra-2 capillary column provided excellent resolution of all studied pesticides.

According to Durand et al. (1991), the extraction with methanol by Soxhlet is as a very good system to extract the pesticides. The high recoveries obtained for all pesticides investigated in the present study support the suggestion. Since the Soxhlet extraction with methanol tend to extract also endogenous material from soil, which might interfer with the chromatographic peaks in the analysis (Redondo et al., 1996), a C_{18}-column was utilized in this study for clean-up procedures to avoid interfering peaks. This method was satisfactory because no interfering peaks were observed in any soil extract. Results (in mg · kg^{-1}) of the pesticide residues in the soil under cotton crop obtained by gas chromatographic analysis with electron capture detector after extraction with methanol and clean-up in C_{18} cartridges are shown in the Figure 5.



```
Linear Regression for Dimethoate
Y = A + B * X
--------------------------------
Param   Value     sd
--------------------------------
A       -6033,6   1595,1
B       713,8     24,6
--------------------------------
R = 0,99941
```

```
Linear Regression for Methyl parathion
Y = A + B * X
--------------------------------
Param   Value     sd
--------------------------------
A       1980,9    1751,3
B       1673,3    68,6
--------------------------------
R = 0,99832
```

```
Linear Regression for Endosulfan
Y = A + B * X
--------------------------------
Param   Value      sd
--------------------------------
A       -25410,1   25538,1
B       37423,2    1001,4
--------------------------------
R = 0,99928
```

```
Linear Regression for Trifluralin
Y = A + B * X
--------------------------------
Param   Value     sd
--------------------------------
A       8821,9    7486,9
B       7822,5    293,6
--------------------------------
R = 0,99859
```

FIGURE 1
Calibration curve and linear regression parameters obtained by GC-ECD for dimethoate, endosulfan, methyl parathion and trifluralin standards.

TABLE 1
Recoveries of Extraction and Clean-up of Pesticides in Soil

Pesticide	Extraction Recovery (%)	S.D.[a]	Clean-up Recovery (%)	S.D.[a]	GC Recovery (%)	S.D.[a]
Trifluralin	93.1	1.1	79.7	1.7	89.3	10.8
Methyl parathion	94.9	2.7	90.5	0.3	111.1	3.4
Endosulfan	91.5	2.0	96.7	1.8	98.6	11.0

[a] Standard deviations (n = 3)

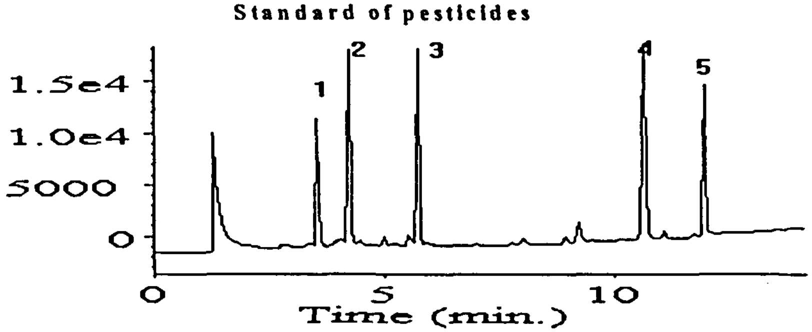


FIGURE 2
Gas-liquid chromatogram of trifluralin (1), dimethoate (2), methyl parathion (3), endosulfan (4) and endosulfan sulfate (5) standards.

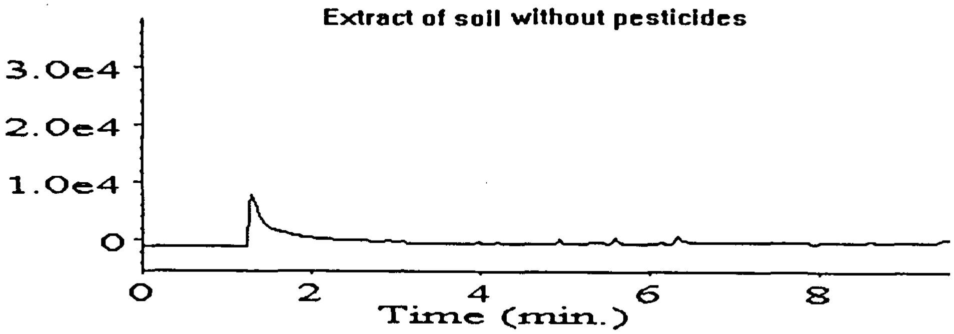


FIGURE 3
Gas chromatogram obtained from methanol extract of a untreated soil sample.

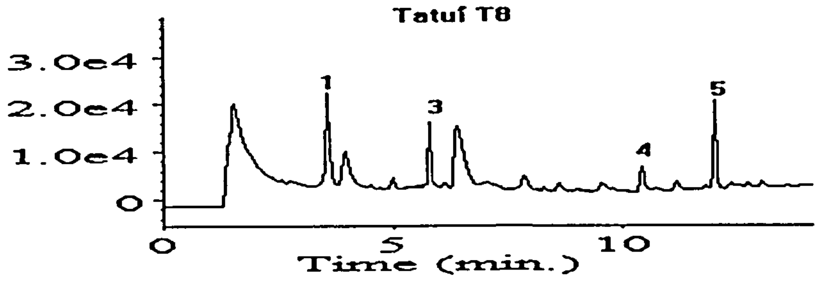


FIGURE 4
Representative gas chromatogram of methanol extract of soil sample from a cotton field farm: 1= trifluralin, 3 = methyl parathioRn, 4 = endosulfan and 5 = endosulfan sulfate.

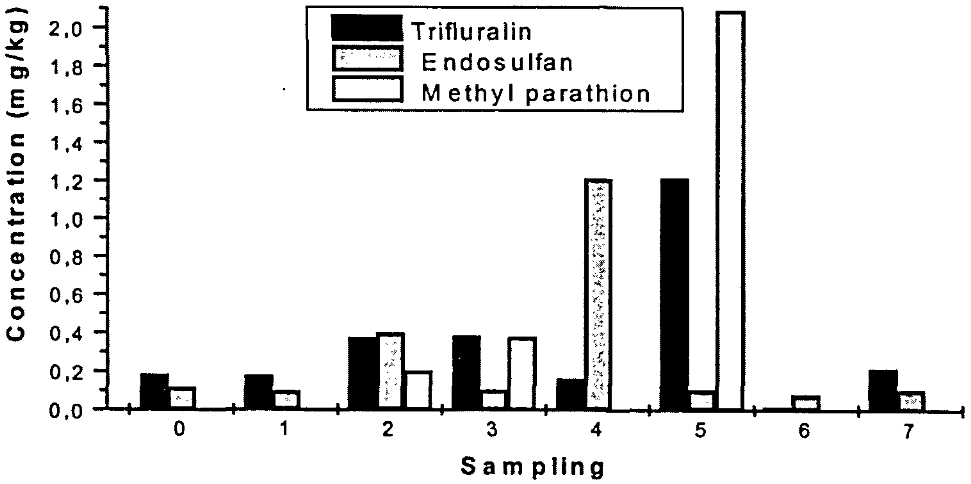


FIGURE 5
Concentration of pesticides in soil from a cotton crop field at different sampling (0 = between crop seasons; 1 and 2 = during 95/96 crop season; 3, 4 and 5 = during 96/97 crop season; 6 = between crop seasons; 7 = during 97/98 crop season).

Most pesticide residues were found in the range from 0.1 to 0.4 mg · kg^{-1} of soil. At sampling 4 and 5 (Figure 5), more than 1.2 mg of endosulfan and 2.0 mg of methyl parathion were detected per kg of soil. These high levels were observed in the soil which received these pesticides just before the soil sampling. However, trifluralin was detected in the amount of approximately 1.2 mg · kg^{-1} of soil at sampling 5, about 6 months after its last application. This indicates that trifluralin residues can persist in the soil. On the other hand, endosulfan was detected in higher amounts just after its application, but it dissipated rapidly as in the subsequent soil sampling the amounts of its residues was about 0.1mg · kg^{-1}. Furthermore, its sulfate metabolite presence was confirmed by comparing the GC retention time whith the authentic standad. This metabolite is known to be as toxic as the parent coumpond (Worthing and Hance, 1991).

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