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Short Communication  
**Determination of thiobencarb residues in water and soil using  
solid-phase extraction discs**

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**Abstract**

The movement and degradation of the herbicide thiobencarb was monitored in a rice field near Lake Albufera (Valencia, Spain). This area constitutes an ecological unit of great environmental interest. Soil samples were collected from the surface and the subsurface of the rice field treated with this herbicide. Soil characterization tests for pH, organic matter, moisture and texture were also carried out. At the same time, samples of water were taken from the inundated plot 10 cm below the surface. Both types of sample were extracted by solid-phase extraction using 47-mm discs of octyl-bonded silica sorbent and eluted with ethyl acetate, with average recoveries for this compound of 63 and 93% from soil and water, respectively. The analyses were carried out by gas chromatography with nitrogen–phosphorus detection. Sample components were separated with a 30 m × 0.25 mm I.D. fused-silica capillary column coated with 50% phenylmethylsilicone (DB-17).

**1. Introduction**

Thiobencarb [(*S*)-4-chlorobenzyl diethylthiocarbamate] is a carbamate herbicide that has been widely used for weed control in rice crops. It is normally applied directly on the soil surface or by inundating the rice fields. After application, thiobencarb is distributed in the sediments and water of rice fields.

It has been stated that almost all of the pesticides applied in agriculture fails to reach the target and enters the environment unnecessarily [1]. Research has begun to focus on factors such as selectivity, reduction of application rates and the environmental fate of chemicals. Soil and

surface waters are interesting matrices for these environmental studies. Monitoring samples for pesticide residues requires rapid, simple, accurate and reliable methods for determining the most common polluting pesticides.

Chromatographic analyses are preceded by sample preparation to extract the analyte compounds. This step is more difficult for complex samples, such as soil, than for water samples, so the selection of the extraction process may be one of the most important factors in the optimization of pesticide analyses.

Numerous methods exist for determining carbamate residues in both soil and water samples, but most of them involve partitioning by liquid–liquid extraction or solid-phase extraction. Prior to the partitioning it is necessary, for soil samples, to prepare a supernatant liquid by

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adding the soil to an organic or aqueous solvent, or a combination of the two, and shaking [2–7].

A wide variety of solvents have been used for the extraction of carbamates by traditional liquid–liquid extraction methods. The primary criteria for choosing the solvent have been extraction efficiency, selectivity (reducing the amount of unwanted co-extractives) and reproducibility of residue recovery. Partitioning with methylene chloride for carbamate insecticides [8–10], with chloroform for aldicarb [11] or with *n*-hexane for thiobencarb [12] has been proposed.

Because liquid–liquid extraction can be tedious and time consuming, solid-phase extraction is gaining popularity, principally for water samples [13–15]. The results obtained from application of solid-phase extraction techniques to the extraction of other groups of pesticides from soil samples [16–20] reveal important benefits of using them for carbamate determinations [21].

The purpose of this work was to develop a simple and rapid procedure for the determination of carbamate herbicides in agricultural soil and water samples. This procedure was used to monitor the movement and degradation of thiobencarb in a rice field near Lake Albufera (Valencia, Spain).

## 2. Experimental

### 2.1. Chemicals and reagents

Ethyl acetate and acetone, both of pesticide grade, were obtained from Promochem (Wesel, Germany) and methanol from Romy (Leics., UK). The herbicide standard used was thiobencarb (98.9% purity) from Promochem.

### 2.2. Apparatus

A standard Millipore 47-mm filtration apparatus equipped with 47-mm discs of Empore octyl-bonded silica (Analytichem International, Harbor City, CA, USA) was used.

### 2.3. Gas chromatographic analyses

Gas chromatography was performed with a Hewlett-Packard Model 5890 Series II chromatograph equipped with a nitrogen–phosphorus detector, a Model H-P 7673 automatic injector, an HP 3365 integrator and a 30 m × 0.25 mm I.D. DB-17 capillary column with a film thickness of 0.25 μm. The injector and detector temperatures were 285 and 300°C, respectively.

Injection was performed in the splitless mode with the column oven at 50°C. This temperature was held for 1 min and was then increased at 30°C min<sup>-1</sup> to 140°C, held for 2 min, then increased at 5°C min<sup>-1</sup> to 280°C, which was held for 10 min. Helium was used as the carrier gas at 1.6 ml min<sup>-1</sup>. The detector gases were air at 70.9 ml min<sup>-1</sup>, hydrogen at 3.5 ml min<sup>-1</sup> and helium (make-up) at 18.3 ml min<sup>-1</sup>.

### 2.4. Collection and sample preparation

The plot was treated with thiobencarb at a rate of 3.6 kg ha<sup>-1</sup>. Samples from the same sampling sites had been analysed prior to application and no pesticides could be detected.

Soil samples were taken from three different locations in the plot, from 0–15, 15–30 and 30–45 cm layers. The collection of samples was carried out five times in a period of 4 weeks. After collection the samples were stored at 4°C until analysis.

These samples were thoroughly mixed, and stones and plant materials were removed. Two 5-g portions were drawn, one of which was used for determining the herbicide residues and the other for determining the moisture content, by heating at 105°C for 24 h.

The soils used differ with respect to organic matter content, soil pH levels, sand, silt and clay content. These characteristics are listed in Table 1 and were determined according to the official method [22].

Factors such as temperature and moisture also affect the persistence and rate of degradation of thiobencarb. They ranged from 20 to 26°C and from 24.6 to 37.3%, respectively. The moisture

Table 1  
Characteristics of soil samples

Depth (cm)	Organic matter (%)	pH (H <sub>2</sub> O) <sup>a</sup>	Sand (%)	Silt (%)	Clay (%)
0–15	2.9	7.9	42.1	37.8	20.1
15–30	2.4	8.2	39.9	37.3	22.8
30–45	1.9	8.5	12.7	49.3	38.0

<sup>a</sup> pH (H<sub>2</sub>O) is the pH measured in a water–soil suspension.

not only changes with the depth of the soil layer, but also with the study time.

Water samples were taken from the inundated plot 10 cm below the surface. These samples were filtered to remove plant materials and stored at 4°C until analysed.

### 2.5. Extraction procedure

#### Extraction of soil samples

The method used has been described elsewhere [23]. Briefly, 5 g moist soil sample were added to 5 ml of distilled water and shaken by sonication for 15 min. It was then added to 5 ml acetone and shaken for another 15 min. The suspension was filtered through a Whatman No. 40 filter and washed twice with 5 ml of distilled water.

The polar solution was diluted to about 500 ml with distilled water and passed through a conditioned 47-mm disc of octyl-bonded silica sorbent. The adsorbed residues were eluted with 10 ml of ethyl acetate. The extract was concentrated at 45°C to 1 ml and 1- $\mu$ l samples were injected into the gas chromatograph. The residues were determined by capillary gas chromatography with a nitrogen–phosphorus detector.

#### Extraction of water samples

A volume of 1 l of filtered water was passed through the conditioned solid sorbent and the residues was eluted with 10 ml of ethyl acetate. The extract was concentrated to 1 ml and 1- $\mu$ l samples were injected into the gas chromatograph.

### 3. Results and discussion

In order to judge the efficiency of the analytical procedure, recovery experiments were performed by spiking with thiobencarb soil and water samples that had not received treatment with this herbicide. The spiked concentration levels were 0.06  $\mu$ g g<sup>-1</sup> and 0.2  $\mu$ g l<sup>-1</sup>, respectively. The samples were extracted by the methods described above.

The recoveries (mean  $\pm$  R.S.D.,  $n = 5$ ) were 62.6  $\pm$  4.9% for soil and 92.5  $\pm$  3.2% for water. These values were lower for soil than for water samples owing to adsorption in the soil, a complex phenomenon which makes it difficult to extract the residues. Similar carbamate recoveries were obtained from soil samples using a traditional method involving liquid–liquid extraction with methylene chloride [9,24], as reported in a previous paper [23].

The detection limits are 11.5 ng g<sup>-1</sup> in soil and 34.0 ng l<sup>-1</sup> water. These limits were calculated by extrapolation and represent amounts that produce a chromatographic peak with a height equal to three times the standard deviation of the baseline noise.

Figure 1 shows typical chromatograms of an extract, obtained by the solid-phase extraction procedure described, from a real soil sample before and after treatment with thiobencarb. Similar chromatograms were obtained from a real water sample containing thiobencarb, as illustrated in Fig. 2.

The GC peak with a retention time 26.8 min was identified as the herbicide thiobencarb. Owing to the high selectivity of nitrogen–phosphorus detection, no further purification was

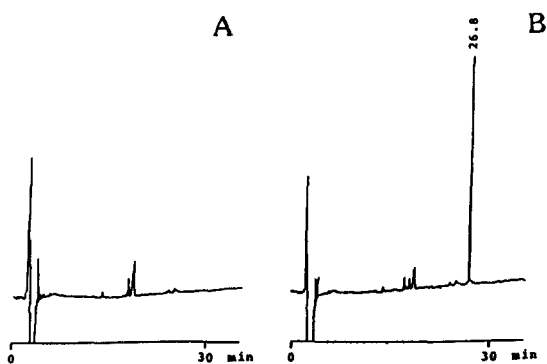


Fig. 1. Chromatograms of extracts obtained by SPE with a  $C_8$  disc from (A) a real soil sample prior to treatment and (B) a real soil sample from the same plot treated with thiobencarb.

needed. The concentrations determined in the soil and water samples are given in Table 2. The herbicide residue levels in a soil sample were subjected to a correction based on the moisture content of the sample and were expressed on a dry mass basis. In Table 2 it can be seen that there was a rapid initial dissipation followed by a slower rate of dissipation from the second sampling to the end of the experiment.

The movement of thiobencarb is considerably less in soil with increased organic matter content (see Table 1), because organic matter is the most important factor involved in adsorption of this herbicide [25]. However, the dissipation was slower below the soil surface than at the surface, which proves that thiobencarb can move vertical-

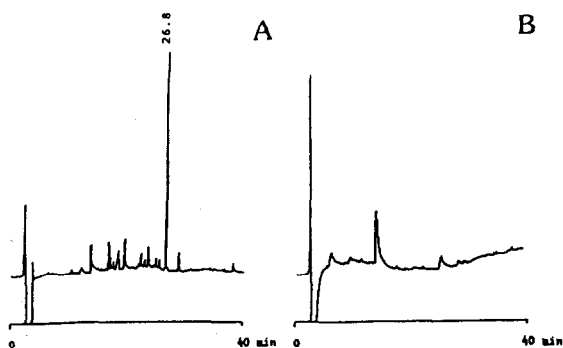


Fig. 2. (A) Chromatogram of an extract obtained by solid-phase extraction with a  $C_8$  disc from a real water sample taken from the inundated plot and (B) blank.

Table 2  
Total thiobencarb concentrations in soil and water

Days after application	Depth (cm)	Concentration in soil ( $ng\ g^{-1}$ )	Concentration in water ( $\mu g\ l^{-1}$ )
5	0–15	743.0	36.3
	15–30	247.2	
	30–45	115.0	
10	0–15	425.3	10.5
	15–30	189.1	
	30–45	121.9	
14	0–15	332.3	9.9
	15–30	135.4	
	30–45	83.5	
21	0–15	291.1	8.0
	15–30	147.2	
	30–45	42.0	
28	0–15	237.2	4.6
	15–30	143.5	
	30–45	42.1	

ly, reaching the deeper layers some days after the application owing to the leaching of the pesticide through the soil. In addition, in the top layer, the combination of degradation and movement leads to a rapid decrease in thiobencarb concentration. Generally, the degradation process of the pesticides is favoured by the presence of oxygen and by aerobic microorganisms [25].

The estimated field half-life was 12 days in the soil surface. This does not agree with values in the literature, which ranged from 14 to 21 days [26]. This can easily be explained by the fact that this parameter is closely linked to the soil characteristics, climate factors and agricultural methods.

#### 4. Conclusions

The methodology proposed may be useful in pesticide residue programmes because it is suitable for the rapid analysis of a large number of samples. The effectiveness of the sorbent discs for extraction and clean-up in the determination of thiocarbamates in soil and water samples has been demonstrated. The application of the method to soil and water samples from an inundated

rice field made it possible to monitor the thiobencarb concentration under field conditions and to determine its rate of dissipation.

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