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Persistence and Leaching of Some Residual Herbicides in Uncropped Soils

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Disappearence of pesticides from field soils results from interactions between various processes such as chemical decomposition, microbiological degradation, volatilization, runoff, leaching, photodecomposition and uptake by plants

With most compounds degradation is the main route for loss, and the rate of degradation of most herbicides, under normal agricultural conditions, exceeds 80% per year It is therefore unlikely that accumulation of residues would occur following repeated annual applications

The main residual herbicides used for weed control in citrus are atrazine, bromacil, diuron, simazine, terbacil, terbuthylazine, terbumetone, terbutryn and trifluralin. In Spain, Gómez de Barreda et al. (1991) conducted a survey of sites where these types of herbicide had been used for more than 20 years, and found no evidence of residue accumulation in the soil.

Occasionally, due to treatment mistakes or soil erosion, it is possible to find some areas within an orchard where herbicide concentrations are several times higher than expected. On other occasions, in order to increase persistence, growers can apply higher rates, particularly in highly adsorptive soils, without damage to the adult trees.In these circumstances it is interesting to know if these chemicals are completely degradated within one season, under Mediterranean climate.

The purpose of the present experiments was to study the persistence and leaching of atrazine, bromacil, diuron, simazine, terbuthylazine, terbumetone and terbutryn in a loam soil typical of many areas in Easter Spain. The experiments were made in two consecutive years and the application rates were high compared with normal field use.

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MATERIALS AND METHODS

The experiment was conducted in 2 adjacent fields (named A and B) with uncropped replicated plots measuring 4 x 2 m, in a field of the IVIA farm at Moncada (Valencia-Spain). The soil characteristics are shown in Table 1, and the layout of the experiment is illustrated in Figure 1. The rate of application was 10 kg ai/ha, which represents, on average, about 5 times the commercial doses (2 kg ai/ha).

Table 1: Soil characteristics of the experimental plot

Organic matter (%)	1.1
Sand (%)	63.4
Silt (%)	24.6
Clay (%)	12.0
Calcium carbonate (%)	21.1
pH (1:2.5 soil:water)	7.8
Water holding capacity (w:w)	44
Cation exchange capacity(meq/100g)	13

One day after herbicide application the soil was flood irrigated with 50 mm depth of water; thereafter, irrigation with the same amount of water was applied whenever the cumulative evaporation from a nearby class A evaporation pan exceeded 60 mm. Soil samples were taken 3 times each year. The first sampling was about 2 weeks after herbicide application and the first irrigation. Each sample comprised soil from three sampling points, and soil was taken from 10 cm increments down to 30 cm depth. The soil was air dried and analyzed immediately or stored at -20°C Diuron was analysed by HPLC (Cotterill, 1980) bromacil by GLC (Pease 1966) , and the triazines by GLC (Byast et al. 1977; Ramsteiner et al. 1974).

For bromacil and the s-triazines extraction in an acetone/water mixture was followed by separation with dichloromethane and determination by gas chromatography with a thermoionic specific detector (NPD)

A mixture of acetone: water (7:3; 200 ml) was added to dry soil (100 g) and the mixture was shaken on a rotatory shaker for 30 min. The extract was filtered and placed in a separation funnel and extracted twice with dichloromethane (50 ml) The two organic phases were combined and filtered through anhydrous sodium sulphate. The dichloromethane extract was evaporated to dryness in a rotary evaporator at 40°C The residue was redissolved in ethyl acetate and injected in the gas chromatograph

The analytical equipment used and the conditions during the analyses were: gas chromatograph, Hewlett Packard 5890, automatic injector, Hewlett Packard 7674 A, data station, Vectra QS/20 HP; column, fused silica capillary column crosslinked 5% phenylmethyl silicone (column id. 0.20 mm, column length 250 m, film thickness 0.33 m), injection, mode split 25:1; column temperature, 120°C (hold 5 min) to 180°C (hold 5 min) at 4°C/min; helium flow rate, 1 cm^3/ min. The detection limit for the

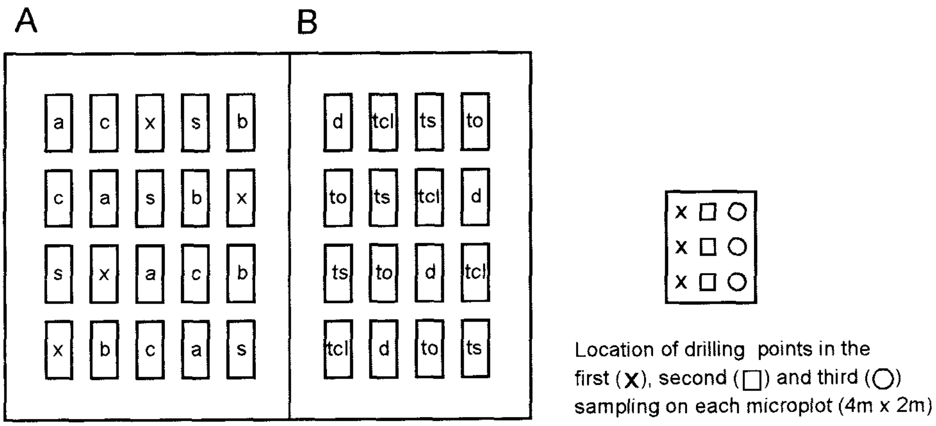

Figure 1. Layout of the experiment at the I.V.I.A. farm. Two fields A & B. Three samplings each year. Treatment dates for field A were 29 June 1989 and 3 September 1990, and for field B were 17 april 1990 and 24 June 1991. Samplings depths were 0-10, 10-20 and 20-30 cm (a = atrazine, b = bromacil, s = simazine, c = (tcl 15% + to 15% + ts 20%), x = check, tcl=terbuthylazine, to=terbumetone, ts=terbutryn. d=diuron).

simazine (n=8)

Diuron was extracted from soil (25g) by shaking with methanol (50 ml) for 1 hour The soil slurry was filtered and an aliquot was evaporated to dryness in a rotary evaporator at 40°C The residue was then redissolved in HPLC mobile phase (1 ml) and filtered through a 0.45-pm Millipore (Millex-HV4) filter.

The identification of substances was by comparison of retention times and UV absorption spectra, which was carried out using a spectra library search The HPLC apparatus used and the analytical conditions were. System, HP 1090 (USA); detector, HP DAD, 250 nm; bandwidth 20 nm; reference, 390 nm (100 nm), column, Lichrosorb RP-18.5 µm, 250 x 4.6 mm, Merck (Germany), mobile phase, methanol:water (70.30), flow rate, 1.3 ml/min; injection volume, 10 µl; integrator, HP chemstation (Pascal Series)

The detection limit for diuron residues in soils was 0.04 mg/kg. The recovery test results were 74±4.(n=8).

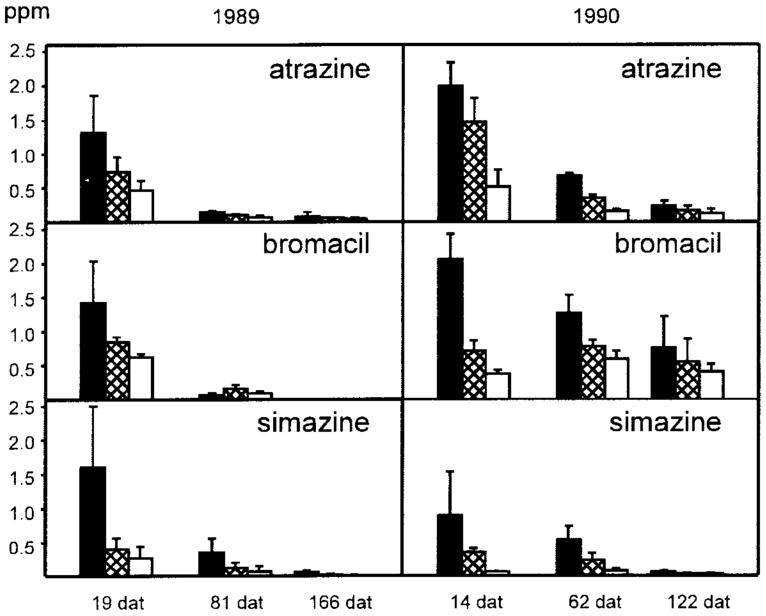

Figure 2. Field A. Herbicide concentration in the soil samples taken at different times after application. dat = days after treatment. Sample depth (cm): ■ 0-10; ▨ 10-20; □ 20-30. Vertical bars indicate standard deviations.

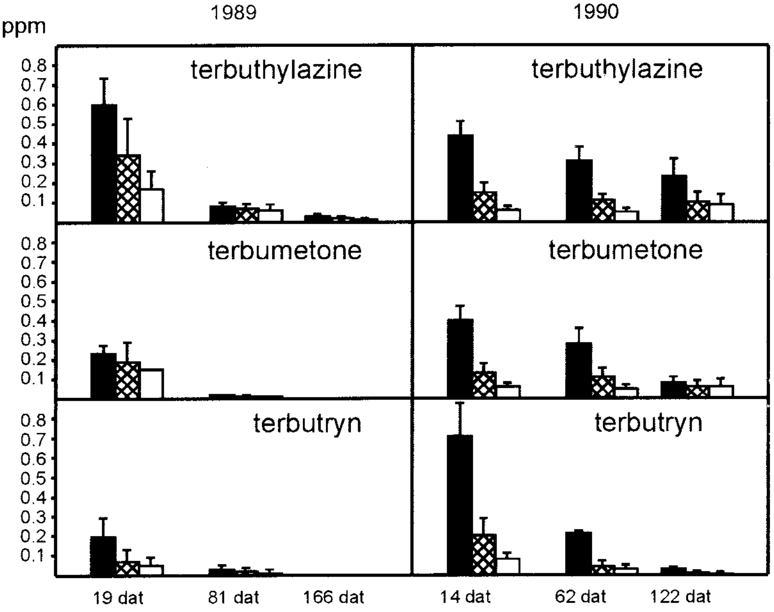

Figure 3. Field A. Herbicide concentration in soil samples. The plots were treated with 20 kg/ha of a commercial mixture equivalent to 4.0 kg/ha of terbutryn, 3.0 kg of terbuthylazine and 3.0 kg/ha of terbumetone. Sample depth (cm): ■ 0-10; ▨ 10-20; □ 20-30. Vertical bars indicate standard deviations.

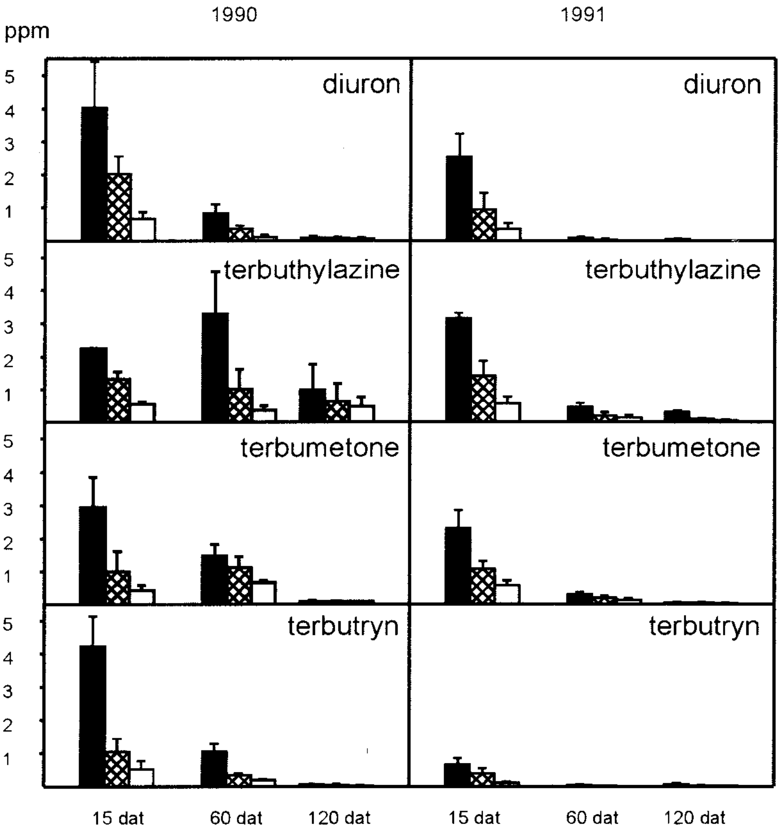

Figure 4. Field B. Herbicide concentration in soil samples at different times after application of diuron, terbuthylazine, terbumetone and terbutryn. dat = days after treatment. Sample depth (cm): ■ 0-10; ▨ 10-20; □ 20-30. Vertical bars indicate standard deviation.

RESULTS AND DISCUSSION

The results are presented in Figures 2, 3 and 4 in which the values shown are averages of the data from the 4 replicate plots together with the standard deviations In general, the highest soil residues were found in the 0- 10 cm layer, although residues of all of the compounds were found at 20-30 cm In a column study conducted in the laboratory, Gómez de Barreda et al.(1993) demonstrated that the leaching of these chemicals decreased in the order bromacil > atrazine > terbumetone, terbuthylazine, simazine, diuron > terbutryn. The patterns shown by the present data are in general agreement with these earlier results.

The degradation behavior of the different compounds was similar in the two years, but the residues of atrazine and, in particular, bromacil were much higher in 1990 than in 1989. This may have been due in part to the shorter time intervals to sampling in 1990, but will also reflect some differences in weather pattern.

Figure 3 shows the behaviour of the commercial triazine mixture (20% terbutryn + 15% terbuthylazine + 15% terbumetone) in field A. Degradation of terbuthylazine was somewhat slower than that of terbumetone or terbutryn, and similar differences were observed in field B. The results with the individual compounds (Figure 4) indicate again the longer persistence of terbuthylazine compared with the other two compounds, and they show that, in general, terbutryn was the least persistent and least mobile of the three triazines examined. The data in Figure 4 also show that diuron residues 120 dat were negliglible under the conditions of these experiments.

The results demonstrate that even after aplication at very high rates, under the conditions studied which are typical of irrigated soils in a Mediterranean climate, degradation of the six residual herbicides was almost complete within one year. Consequently repeated annual applications of the herbicides are unlikely to lead to a build-up of residues in the soil. This agrees with the conclusion of Walker (1994) who carried out a computer modelling excercise using soil parameters and weather data from Valencia (Spain) to make prediction of herbicide persistence in Mediterranean areas. His results suggested that repeated use of even moderately persistent chemicals should not be associated with an unacceptable accumulation of residues, particularly when high inputs of irrigation are part of the crop production system.

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