Bull. Environ. Contam. Toxicol. (1997) 58:752–757

Bulletin of Environmental Contamination and Toxicology

Enhanced Soil Biodegradation of Prosulfocarb Herbicide in Barley Crop

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Received: 6 November 1996/Accepted: 24 January 1997

Enhanced soil biodegradation of a carbamate insecticide, appearing after repeated applications of the same insecticide made in the past, has been observed with carbofuran, bendiocarb, and carbaryl, but not with aldicarb (Racke and Coats, 1988a). The organophosphorus insecticides isofenphos, fonofos and fenamiphos also presented enhanced soil biodegradation, but not chlorpyrifos, ethoprop, terbufos and phorate, indicating that the phenomenon of enhanced soil microbial degradation of soil insecticides may exhibit some degree of specificity (Racke and Coats, 1988b; Racke et al., 1990; Chung and Ou, 1996).

Enhanced soil biodegradation is also observed with the thiocarbamate herbicides EPTC and butylate (Dowler et al., 1987; Tal et al., 1990). On the other hand, enhanced soil biodegradation has not been observed with the herbicides atrazine, cyanazine and metolachlor (Harvey, 1987).

Accelerated herbicides soil biodegradation decreases the weed control efficiencies. Such decrease however may also be due to increased weed resistance to the herbicides. In order to apply an efficient remedy, it is necessary to know the true cause of the fall of the herbicide efficiency.

The recent prosulfurocarb herbicide (S-(phenylmethyl) dipropylcarbamothioate) is efficiently applied pre- or post-emergence at the rate of 3.2 to 4 kg ha^{-1} for protection of winter wheat and barley against grass and broad-leaved weeds. It is applied alone or in mixture with isoxaben (60-70 g ha^{-1}). To our knowledge, nothing so far has been published about the possible accelerated soil biodegradation of prosulfocarb. This is the object of the present study. During the year preceding barley sowing and its prosulfocarb treatment made just before sowing, each field plot was treated with only one prosulfocarb repeated treatments scheme. Several different repeated treatments schemes were compared on different field plots. These schemes were different among themselves by the number of prosulfocarb treatments and the intervals between them. For the prosulfocarb applied just before sowing, its soil half-life was measured in each plot during barley crop, and compared according to the repeated prosulfocarb treatments scheme applied during the year preceding sowing (Table 1). This was done in order to observe the effect of the repeated prosulfocarb treatments made in the past, on the

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Table 1. The repeated prosulfocarb treatment schemes applied during the year preceding winter barley sowing (12-10-1995) and the prosulfocarb treatment made two days before sowing. At each treatment date, 4 kg prosulfocarb ha^{-1} was applied.

Repeated prosulfocarb treatment schemes			
1 (Control)	2	3	4
Dates at which 4 kg prosulfocarb ha^{-1} was applied (months before sowing)			
		21-11-1994 (11 months)	21-11-1994 (11 months)
		13-12-1994 (10 months)	13-12-1994 (10 months)
		20-2-1995 (8 months)	20-2-1995 (8 months)
	20-4-1995 (6 months)	(20-4-1995) (6 months)	
	5-9-1995 (1 month)	5-9-1995 (1 month)	

rate of prosulfocarb soil biodegradation.

MATERIALS AND METHODS

A 40 x 40 m field at Melle, Belgium (clay 8%, silt 35%, sand 57%, organic matter 1.8%, pH 6.5, sandy loam) was tilled on 18-11-1994 (day-month-year) to a depth of 25-28 cm, and prepared as for sowing. The field was divided into 10x10 m plots. Four repeated prosulfocarb treatments schemes applied at different frequencies and intervals during the year preceding sowing were compared (Table 1). Onto each field plot, only one repeated prosulfocarb treatments scheme was applied. For each repeated prosulfocarb treatments scheme there were 4 replicate plots. At each prosulfocarb treatment, 4 kg prosulfocarb ha^{-1} was applied by spraying the emulsion of Defi (800 g prosulfocarb l^{-1}) in water (600 l ha^{-1}). The repeated treatment schemes were compared as to their influence on the rate of soil biodegradation of the prosulfocarb applied just before sowing. The following prosulfocarb repeated treatment schemes applied during the year before sowing were compared: Scheme 1 (control): no prosulfocarb treatment made in the past during the year which preceded sowing. Scheme 2: a first prosulfocarb treatment on 20-4-1995 (6 months before sowing and the prosulfocarb treatment made at sowing) and a second one on 5-9-1995 (one month before sowing). Scheme 3: a first prosulfocarb treatment on 21-11-1994 (11 months before sowing), a second one on 13-12-1994 (10 months before sowing), a third one on 20-2-1995 (8 months before sowing), a fourth one on 20-4-1995 (6 months before sowing), and a fifth one on 5-9-1995 (one month before sowing); Scheme 4: a first prosulfocarb treatment on 21-11-1994 (11 months before sowing), a second one on 13-12-1994

(10 months before sowing), and a third one on 20-2-1995 (8 months before sowing). On 10-10-1995, the entire field was rotary tilled to 15 cm depth, and made ready for sowing, and all field plots were treated with 4 kg prosulfocarb ha^{-1}. On 12-10-1995, winter barley (CV. Express) was sown, except a 2 m broad band on one side of each plot which was sown with rye-grass (plant sensitive to prosulfocarb). At several intervals after sowing, and its treatment with prosulfocarb made just before, soil samples were taken separately (and analyzed separately) in the 0-10 cm surface soil layer of each of the four replicate plots of each of the four repeated prosulfocarb treatments schemes (Table 2). At each sampling date, and for each treatments scheme, there were thus 4 different replicate analyses. In addition, on 13-11 and 14-12-1995, single samples were taken separately from the 10-20 cm soil layer in each of the 4 replicate plots; each soil sample was analyzed separately, one analysis being thus made with the soil of each replicate plot of each of the treatment schemes. For each soil sample, 15 cores (2.5 cm diameter) were taken from each replicate plot at random points, the cores from each replicate plot were bulked together and then stored at -25°C until analyzed.

Thin-layer chromatography (TLC) was made by using silica gel 60 F254 20 x 20 cm, 0.2 mm thick plates. The sample was applied as a band. The prosulfocarb standard was applied on another part of the TLC plate, next to the band of the sample solution.

Gas-liquid chromatography (GLC) conditions were the following. Flame photometry detection in the sulfur mode. Injection at 250°C, and detection at 180°C. Glass column 1.80 m x 2 mm i.d. containing 5% SE 30 on Gas-Chrom Q 80-100 mesh. Nitrogen carrier gas was at 40 ml min^{-1}, column oven at 220°C, and prosulfocarb retention time was 3.3 min.

Infra-red (IR) spectra: KBr discs, cm^{-1}. Nuclear magnetic resonance (^{1}H-NMR) spectra δ, ppm/tetramethylsilane in $CDCl_3$. Mass (MS) and gas-liquid mass (GC-MS) spectra: 70 eV, electron impact; m/e, relative abundance, %.

Prosulfocarb analytical standard was made as following: the solution of Defi (800 g prosulfocarb l^{-1}; 82 g) in dichloromethane (700 ml) was washed four times (4 x 250 ml) with a saturated solution of NaCl in water, sodium dodecyl sulfate (1 to 2 g) being added to help phases separation. The dichloromethane solution was dried (Na_2SO_4, and evaporated to dryness, giving prosulfocarb (62 g, 95%) whose purity was greater than 99%. Spectra of prosulfocarb: IR: 2963, 2872, 1649, 1495, 1454, 1404, 1385, 1221, 1123, 1101, 1030, 949, 892. ^{1}H-NMR 0.89 (t, 6 H, $CH_2CH_2CH_3$); 1.61 (m, 4 H, $CH_2CH_2CH_3$); 3.16-3.38 (m, 4 H, $CH_2CH_2CH_3$); 4.16 (s, 2 H, $CH_2C_6H_5$); 7.19-7.38 (m, 5 H, C_6H_5). MS: 251 (M^+, 48); 162 (M-$NCOSCH_2$-H, 12); 128 ($(CH_3CH_2CH_2)_2NCO$, 87); 91 ($C_6H_5CH_2$, 49); 43 ($CH_3CH_2CH_2$, 100).

For analysis of prosulfocarb in soil, soil (100 g) was stirred in acetone/water (8/2 vol./vol., 200 ml) at room temperature (40 min). The mixture was filtered, and the

extraction repeated. The filtrates were combined, water (100 ml) was added, and the acetone was removed in a vacuum rotary evaporator (30°C). The pH of the aqueous solution was adjusted to 7.0 by successive addition of $NaHCO_3$ and Na_2CO_3. Sodium chloride (15 g) was added, and the aqueous solution was extracted two times with ethyl acetate (2 x 200 ml), the ethyl acetate solution was dried (Na_2SO_4), concentrated to 40 ml in a vacuum rotary evaporator (30°C), and then concentrated further to 0.5 ml under a slow stream of nitrogen (20°C). The concentrate was applied to a TLC plate, with the prosulfocarb standard on another part of the plate. Elution with ether/hexane, 1/9 vol./vol. , gave a band at R_f=0.35 containing prosulfocarb. The band was scraped off, the silica gel extracted with ethyl acetate (40 ml) in a small glass column, the extract concentrated to 0.2 ml under a slow stream of nitrogen (20°C) and the extract was analyzed by GC and, in several cases, by OC-MS. At the 0.5 and 0.1 mg prosulfocarb kg^{-1} level in soil, recoveries respectively were 85-98 and 81-91%. The analytical limit of sensitivity was 0.01 mg prosulfocarb kg^{-1} dry soil.

During the first two months period following the prosulfocarb application made just before sowing, there was a linear relationship ($\ln y = kt + b$) between the naperian logarithms of the prosulfocarb soil concentrations ($y = 100 \times$ mg kg^{-1} dry soil) against time t (days) following the prosulfocarb application made just before sowing. The prosulfocarb soil half-lives with their 95% confidence intervals were obtained using the SAS logicial CMS SAS 5.18 (1984, 1986, SAS Institute Inc., Cary, NC 27512).

RESULTS AND DISCUSSION

In each of the field plots, and thus with each of the repeated prosulfocarb treatments schemes applied during the year before sowing, prosulfocarb was not detected in the soil layer at 10 to 20 cm depth, the analytical limit of sensitivity being 0.01 mg prosulfocarb kg^{-1} dry soil. There was thus no detectable leaching of prosulfocarb in soil.

During the two first months following the prosulfocarb application made just before sowing, the rates of prosulfocarb soil biodegradation followed apparent first order kinetics (Table 2). This occurred in each of the field plots treated with one of the repeated prosulfocarb treatments scheme during the year preceding sowing; There was indeed a linear relationship between the logarithms of the prosulfocarb soil concentrations, and the time elapsed since the prosulfocarb application made just before sowing.

The repeated prosulfocarb treatments -made during the year preceding sowing and its prosulfocarb treatment made just before- much enhanced the rate of prosulfocarb soil biodegradation in the barley crop. The three prosulfocarb treatments made during the 8 to 11 months period before sowing (Treatments Scheme 4) however didn't much reduce the prosulfocarb soil half-life (30 days), relatively to its soil half-life (38 days) in the control plots (Treatments Scheme 1) not treated with prosulfocarb during the year preceding sowing. On the other hand,

Table 2. Concentrations of prosulfocarb in the 0-10 cm superficial soil layer of a barley crop treated with 4 kg prosulfocarb ha^{-1} two days before sowing. During the year preceding barley sowing and its prosulfocarb treatment made just before sowing, repeated prosulfocarb treatment schemes were applied on separated field plots and compared.

Sampling date, year 1995	Days after the at sowing prosulfo-carb treatment	Cumulati-ve rainfall, mm	Repeated prosulfocarb treatments scheme			
			1 (Control)	2	3	4
			Prosulfocarb soil concentration (mg kg^{-1} dry soil) in the 0-10 cm superficial soil layer. Means of 4 replicates ± s.d. nd=non detected			
8-10	-2		nd	0.32±0.02	0.29±0.02	nd
13-10	3	0	2.71±0.14	2.95±0.15	3.08±0.15	2.85±0.14
23-10	13	1	2.42±0.12	l.66±0.08	1.50±0.08	2.33±0.12
31-10	21	7	2.01±0.10	1.25±0.06	1.00±0.05	2.02±0.10
7-11	28	19	1.81±0.09	0.98±0.05	0.74±0.04	1.60±0.08
13-11	34	19	1.60±0.08	0.70±0.04	0.53±0.03	1.35±0.07
1-12	52	53	1.13±0.06	0.30±0.02	0.20±0.01	0.93±l.05
14-12	65	54	0.53±l.03	0.15±0.01	0.10±0.01	0.38±0.02
Correlation coefficient			-0.9887	-0.9963	-0.9967	-0.9915
y Intercept			5.69	5.79	5.80	5.75
Slope, $days^{-1}$			-0.01818	-0.04537	-0.05432	-0.02346
Prosulfocarb soil half-life, days, with its 95% confidence interval			38±1.9	15±0.8	13±0.6	30±1.5

the prosulfocarb treatments applied during the 6 months period preceding sowing (Treatments Scheme 2) considerably reduce the prosulfocarb soil half-life (15 days). When the prosulfocarb treatments were repeated 5 times during the whole year preceding sowing (Treatments Scheme 3), the prosulfocarb soil half-life (13 days) was not significantly different from the one (15 days) in the plots repeatedly treated with prosulfocarb during the only 6 months period preceding sowing (Treatments Scheme 2).

The repeated prosulfocarb treatments made during the 6 months period before sowing thus were the most efficient to induce enhanced soil biodegradation. They indeed were the nearest to the prosulfocarb treatment made at sowing. Above all, these treatments were made during spring and summer, seasons during which the soil microbial activity is highest -relatively to winter-, and thus has the greatest capacity to adapt itself to prosulfocarb soil metabolism.

Weed counting during the first two months period following barley sowing, indicated a better weed control in the plots where Treatments Schemes 1 and 4 were applied, relatively to the plots treated with Treatments Schemes 2 and 3 (Callens and Bulcke, 1996). Moreover, the rye-grass (which is sensitive to prosulfocarb) sown on a band on the side of each plot, practically did not grow in the plots treated with Treatments Schemes 1 and 4, but normally grew on the plots treated with Schemes 2 and 3.

In the agronomy practice, repeated applications of prosulfocarb on the same field could occur, according to the crops succession practized in crops rotation. Barley or winter wheat indeed could be sown on the same field after barley and winter wheat crops, which themselves could have been sown after a potato crop. Prosulfocarb could have been applied onto each of these crops at sowing or planting. Results however indicate that care should be given not to repeat at a too high frequency the same prosulfocarb treatment on the same soil, the weeds control efficiency being able to be reduced by enhanced soil biodegradation.

Acknowledgments. Mass spectra were recorded by C. Moulard (Université Libre de Bruxelles, Brussels, Belgium). The research was supported by the Research and Development Department of the Ministry of Middle Classes and Agriculture, Brussels, Belgium.

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