

Enhanced degradation of propyzamide after repeated application in orchards

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Summary The degradation of propyzamide, a benzamide herbicide mainly acting through soil uptake, has been studied with chemical and biological methods in a field experiment on sandy loam soil in a pear orchard at Melle (Province East-Flanders) with long-term repeated application of propyzamide (1250 g ha⁻¹) on the same plot. With chemical analysis, enhanced degradation of propyzamide was observed in 1998 on plots treated for the 14th time; on these plots, soil half-life time was 10 days only compared to 31 days on plots never treated previously. With greenhouse bioassays, the enhanced degradation of propyzamide could be confirmed at the same time using winter wheat (*Triticum aestivum* L.) to monitor propyzamide dissipation.

Following this detection of enhanced degradation, field experiments were set up in two orchards at Melle and Velm (Province Limburg) respectively, to examine particularly the development of this phenomenon. Therefore, plots were set up receiving 0, 1, 2, 3, or 4 spring applications in consecutive years with propyzamide (1000 g ha⁻¹). To examine the degradation of propyzamide, soil samples were taken on the different plots prior to a new application, mixed with a range of concentrations of propyzamide, incubated at 15°C and sown with winter wheat. After 15 days, foliage fresh weights were taken. An enhancement of the degradation of propyzamide could be observed already after the second application. Using the above mentioned plots, an other set of bioassay experiments was carried out with soil samples taken in the field at different intervals after application. These samples were stored frozen until sowing. Based on foliage fresh weights, the fast appearance of the enhanced degradation of propyzamide in the field was confirmed again.

Keywords Enhanced degradation, propyzamide.

INTRODUCTION

In fruit orchards in Belgium, weeds must be controlled early in the season to reduce the risk of damage to the blossoms by late night frost, and later on, during the fruit setting phase, to prevent damage by weed competition. To maintain the soil weed-free during this whole period chemical weed control systems are used, often based on the application of soil acting

herbicides assisted by foliar, non-residual herbicides. Soil persistence is an important characteristic of the soil acting herbicides as it determines their residual activity against later emerging weeds. High doses of herbicides are given on account of the high organic matter content of the soil in fruit orchards, and the same herbicides are applied year after year.

Herbicide dissipation is mainly due to chemical and microbial degradation. For some microbially degraded herbicides, enhanced degradation has been reported after their repeated application at the same site (Walker and Welch 1991, Hole and Powles 1997). High herbicide doses repeated over a long period can be favourable for generating enhanced degradation.

The benzamides isoxaben and propyzamide are established soil applied herbicides for use in fruit orchards. In a long-term herbicide experiment in a pear orchard on loam soil in Gorseme (Province Limburg), with yearly application of the same herbicides on the same strips since 1987, enhanced degradation of isoxaben could be recorded after 10 years of consecutive spring applications with 500 g ha⁻¹ isoxaben (Rouchaud *et al.* 1997, Eelen *et al.* 1999). A soil half-life of 43 days was recorded, indicating a significantly faster degradation than on first time treated soil (half-life: 101 days). In a comparable long-term herbicide experiment in a pear orchard on sandy loam at Melle (Province East-Flanders) propyzamide has been applied at 1250 g ha⁻¹ yearly since 1985. This article reports on the soil dissipation of propyzamide in this long-term herbicide experiment and on the study of the dynamics (the development) of the enhanced degradation of this herbicide in two experiments in nearby orchards.

MATERIALS AND METHODS

Field experiments Sites 1 and 2 were located in a pear and apple orchard respectively at Melle (Province East-Flanders) on a sandy loam soil (clay 7%, silt 39%, sand 54%; organic matter 3.1%; pH 6.6). Site 3 was located in a pear orchard at Velm (Province Limburg) on a light loam soil (clay 13.8%, silt 70.1%, sand 16.1%, organic matter 1.96%, pH 6.65). At Site 1 the same strips have been treated each year in spring with propyzamide (1250 g ha⁻¹) since 1985. In 1998 (chemical

study), additional control plots were treated with this herbicide for the first time. At Site 2 (starting in 1996) and Site 3 (starting in 1997), plots (two replicates) were treated in spring with propyzamide (1000 g ha^{-1}) in such a way that after four consecutive years, plots were available that had received 0, 1, 2, 3, or 4 applications. Herbicide applications were done with a commercial formulation of propyzamide (Kerb, wettable powder containing 500 g kg^{-1} propyzamide, Protex), using an air-pressurized knapsack sprayer (Azo Sprayers Veeze Ede), equipped with flat fan nozzles (Teejet XR11002) delivering 300 L ha^{-1} at 200 kPa pressure.

Chemical analysis At Site 1, in 1998, plots treated with propyzamide for the first and fourteenth time respectively were sampled at up to 195 days after treatment. Soil samples were taken from the 0–10 cm layer on four replicate plots. Soil cores (15) from each replicate plot were combined and stored at -25°C until analysed.

Propyzamide was extracted from the soil samples and the extracts were subjected to clean-up by repeated thin-layer chromatography. Following elution, the extracts were analysed by gas-liquid chromatography and by combined gas chromatography - mass spectrometry. For full details on these analytical procedures, reference is made to Rouchaud *et al.* (2000). Results were analysed statistically using the SAS software CMS SAS 5.18 (1984, 1986 SAS Institute Inc., Cary, NC) and soil half-lives with their 95% confidence intervals were derived from linear regression of the naperian logarithm of herbicide concentration against time following application.

Bioassay experiments For a first kind of bioassay experiments, soil samples (upper 8 cm) were taken from plots of the field experiments at the end of winter, prior to a new application, to avoid the presence of residues from previous applications. Soil samples were collected by bulking together numerous subsamples taken on both replicates of each treatment. Following sieving ($<4 \text{ mm}$) of the samples and air-drying, propyzamide (at 0, 90, 180 and $360 \mu\text{g kg}^{-1}$ respectively) was incorporated into the soils, in 100 mL of water to 1000 g air-dry soil. Mixed soils were incubated in plastic bags at 15°C either overnight or for 15 days. Levels of remaining herbicide in the soil samples were monitored by setting up small pot experiments with winter wheat ('Torfrida'; 12 seeds per pot) as test plant. Following seeding, pots were kept in the greenhouse and watered by subirrigation when necessary. Foliage fresh weights were recorded after a two week test period by clipping the plants at the soil surface and weighing them.

For the second set of bioassay experiments, soil samples (0–8 cm) were taken on the plots of the field experiments at regular intervals after the spring application, to monitor the dissipation of the herbicide in the field. Soil cores from each replicate plot were combined, sieved over 4 mm and stored at -25°C until used in a bioassay. Maintenance and harvest of the bioassays was as described above.

In all bioassay experiments the experimental design was a split-block with four replicates. Yield data were expressed as a percentage compared to the yields of the corresponding untreated control. Data were subjected to analysis of variance.

RESULTS

Detection A bioassay was carried out with soil samples of Site 1 taken prior to a new treatment in spring 1997. The experiment, with winter wheat as a test plant and with propyzamide incorporated into soil sampled on plots having been treated previously never and 12 times respectively with this herbicide, was able to detect a faster degradation of propyzamide in the soil with long-term repeated pretreatment (Table 1). On soil with 12 previous treatments, the foliage fresh weight was significantly higher from $150 \mu\text{g kg}^{-1}$ propyzamide onwards.

In 1998, with chemical methods, the dissipation of propyzamide in the 0–10 cm soil layer was found to follow first-order kinetics during the sampling period. The propyzamide soil half-life was 31 days in plots treated for the first time (Table 2). A very significant enhancement of the rate of soil dissipation was recorded in 14th time treated soil resulting in a half-life of only 10 days. In the repeatedly treated soil no herbicide could be detected in samples taken 85 days after treatment.

Dynamics For the bioassays with incorporation of propyzamide in propyzamide-pretreated soils, results of the overnight incubated soils are presented (Figure 1), as these exhibit clear differences. The majority of differences were still detectable, but less pronounced, after a prolonged incubation of 15 days.

A clear decline in foliage fresh weight yield could be noticed on never pretreated soil with increasing concentration. Both at Site 2 and Site 3, this resulted in less than 18% foliage fresh weight yield when the highest concentration ($360 \mu\text{g kg}^{-1}$ propyzamide) was incorporated. On the pretreated soils, on the other hand, a reduction in foliage fresh weight was hardly noticeable, not even at the highest concentration and regardless of the number of pretreatments with propyzamide in the field.

Table 1. Foliage fresh weight response (% of corresponding control) of winter wheat to propyzamide incorporated in two soils with a highly differing background of previous treatments with propyzamide. Means followed by the same letter are not significantly different (Duncan P=0.05).

Propyzamide (µg kg ⁻¹)	FFW (%) on soil with following number of previous applications	
	0	12
0	100 a	100 a
75	99 a	94 ab
150	85 b	46 c
300	50 c	10 d

Table 2. Dissipation of propyzamide in first time treated versus long-term treated soil in pear orchard at Melle.

Propyzamide (1250 g ha ⁻¹)	Soil half-life (days) with 95% interval	Herbicide no longer detected at DAT ¹
1st time	30.7 ± 1.5	195
14th time	10.1 ± 0.8	85

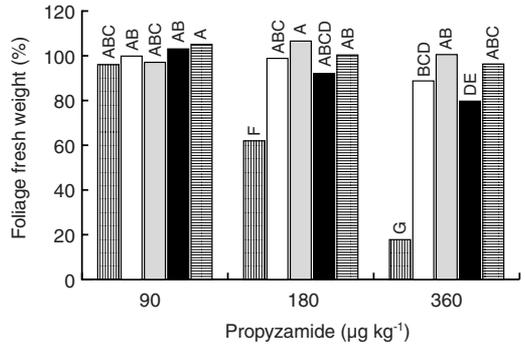
¹ First sampling date (number of days after treatment) at which the herbicide was no longer detectable.

Table 3. Response (% of control soil for the corresponding sampling date) of winter wheat to propyzamide residues in soils from Site 3 pretreated 1, 2, 3 and 4 times respectively with propyzamide (1000 g ha⁻¹) and sampled at different intervals after application. Means followed by the same letter are not significantly different (Duncan P=0.05).

Sampling interval (DAT)	Foliage fresh weight (% of corresponding control) on soils with following number of previous propyzamide applications			
	1	2	3	4
8	5 d	95 ab	101 ab	88 bc
14	8 d	94 ab	93 abc	93 abc
21	15 d	92 abc	92 abc	88 abc
29	75 c	93 ab	100 ab	86 bc
43	100 ab	96 ab	100 ab	106 a

Results of bioassay experiments with soils sampled at different intervals after treatment on plots pretreated with propyzamide, correspond very well with the first set of experiments. Winter wheat growth is inhibited severely on first time treated soil, and this until 21 days after treatment (DAT) (Table 3). At 29 DAT only small, and at 43 DAT no differences in growth could be observed when compared to growth on untreated soil. On soils that were treated for the second, third or

Site 2



Site 3

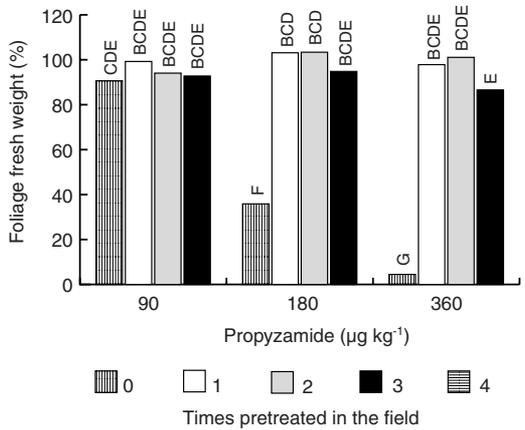


Figure 1. Foliage fresh weight response (% of untreated) of winter wheat to propyzamide incorporated in soil pretreated with 1000 g ha⁻¹ propyzamide and incubated overnight. Treatment means for the same site followed by identical letters do not differ significantly (Duncan P=0.05).

fourth time, no foliage fresh weight reductions could be noticed, not even at the first sampling interval, being as short as 7 days after the application date.

DISCUSSION

The bioassay system made it possible to detect enhanced degradation of propyzamide prior to its confirmation with chemical methods. Fourteen years after the first application, the dissipation of propyzamide as expressed by half-life was enhanced by a factor 3. The adaptation of the soil micro-organisms to degrade propyzamide occurred quite quickly. In soil that received no more than one previous propyzamide application in the field, the rate of propyzamide dissipation is

significantly higher than in never pretreated soil. An increase of the degradation rate after multiple annual field treatments could not be measured with these winter wheat bioassays: no differences in growth could be observed between the soils treated more than once with propyzamide. Remarkable is the fast dissipation of propyzamide in the bioassays with incorporation of the herbicide: already after one day of incubation the activity on the sensitive winter wheat had disappeared almost completely on repeatedly pretreated soil. The conclusion can be made that the enhanced degradation is already present from the second application onwards.

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