DISAPPEARANCE OF PENDIMETHALIN IN SOIL AND ITS RESIDUE IN RIPE FENNEL

ZANIKANIE PENDIMETALINY W GLEBIE I JEJ POZOSTAŁOŚCI W KOPERKU

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ABSTRACT

Disappearance of pendimethalin in soil, a herbicide widely used for control of weeds on vegetable crops, has been studied. A simple and rapid multiresidue analytical procedure for the quantification of the substance has been applied using a Hewlett Packard 5890A gas chromatograph, equipped with a nitrogen – phosphorus detector (GC-NPD). Disappearance trend followed first order kinetics seemed to be the best approximation. The average pendimethalin residues have decreased according to equations: $y = 0.236e^{-0.0115x}$ (exponential) and $y = -0.0018x + 0.226$ (linear) with excellent coefficient of determination in both cases. Half-lives obtained from those equations were 60 and 62 days, respectively. Low pendimethalin residue in plants indicate that fresh fennel may be used as additive in baby food. On the other hand, the experimental results indicate that pendimethalin is quite stable compound and may cause problems with follow-up crops.

Key words: pendimethalin, residues in soil, residues in fennel, South-Eastern Poland

STRESZCZENIE

W pracy przedstawiono wyniki badań nad zanikaniem pendimetaliny w glebie. Pozostałości tej substancji oznaczano za pomocą chromatografu gazowego Hewlett Packard 5890A, wyposażonego w detektor azotowo – fosforowy (NPD). Przebieg zanikania początkowych pozostałości pendimetaliny najlepiej opisuje równanie kinetyczne pierwszego rzędu. Średnia jej zawartość w glebie obniżała się zgodnie z równaniem wykładniczym $y = 0,236e^{-0,0115x}$ i liniowym $y = -0,0018x + 0,226$. Okresy połowicznej przemiany wyznaczone na podstawie tych równań wyniosły odpowiednio 60 i 62 dni. W dojrzałym koperku pozostałości pendimetaliny wystąpiły na niskich poziomach a zatem świeży koperek uzyskany z pola odchwaszczanego za pomocą tego herbicydu może być stosowany do produkcji żywności dla dzieci.

Słowa kluczowe: pendimetalina, pozostałości w glebie, pozostałości w koperku, południowo-wschodnia Polska

STRESZCZENIE SZCZEGÓŁOWE

Herbicydy są powszechnie stosowane w uprawie warzyw gruntowych. Mogą być źródłem licznych problemów, np. mogą zawierać pozostałości ich substancji aktywnych. Aby ocenić możliwość wystąpienia pendimetaliny w koperku przeznaczonym do produkcji żywności dla dzieci przeprowadzono badania nad jej zanikaniem w glebie. Pobór próbek gleby rozpoczęto 10 dni po zabiegu. Pozostałości pendimetaliny oznaczano za pomocą chromatografu gazowego Hewlett Packard 5890A, wyposażonego w detektor azotowo – fosforowy (NPD) i wyrażano w mg/kg. Przebieg zanikania początkowych pozostałości pendimetaliny najlepiej opisuje równanie kinetyczne pierwszego rzędu. Średnia początkowa jej zawartość w glebie wyniosła 0,228 mg/kg, a następnie obniżała się zgodnie z równaniem wykładniczym: $y = 0{,}236e^{-0{,}0115x}$ i liniowym: $y = -0{,}0018x + 0{,}226$. Okresy połowicznej przemiany wyznaczone na podstawie tych równań wyniosły odpowiednio 60 i 62 dni. W dojrzałym koperku pozostałości pendimetaliny nie przekroczyły poziomu 0,01 mg/kg, a zatem świeży koperek, pozyskany z pola odchwaszczanego za pomocą tego herbicydu, może być stosowany do produkcji żywności dla dzieci.

INTRODUCTION

Herbicides play an important role in the production of vegetables but their residues may cause numerous environmental problems. First of all, they may contaminate surface and groundwater through leaching and run-off. They may also remain on the soil surface and potentially affect quality and yield of the next crop cultivated on the same field. Finally, stable herbicides may be taken up by a plant forming unwanted residues. Therefore, the use of persistent herbicides requires a thorough understanding of their dissipation and movement on fields. Unfortunately, little research has been undertaken on the behaviour of some herbicides.

The dinitroanilines include benfluralin, butralin, ethalfluralin, fluchloralin, oryzalin, pendimethalin, trifluralin, and some others. These substances are selective herbicides used for pre-emergent control of annual grasses and broadleaf weeds in corn, winter cereals, potatoes, some vegetables and ornamentals. Most of them are so volatile that they must be incorporated into soil to avoid vapour loss. Trifluralin, the common name of N,N-di-n-propyl-2,6-dinitro-4-trifluoromethylaniline, is one of the selective pre-emergence herbicides belonging to dinitroaniline group that has been in agricultural use since the early 1960s. Its behaviour in sandy soil was characterised by fast initial loss followed by slow subsequent dissipation. Half - life in the surface soil calculated on the basis of first order kinetics was found to be 27 and 30 days [2]. However, some studies showed that trifluralin was a very persistent herbicide and after 1.5 years its residue in surface soil layer was still high [11]. In Poland, trifluralin is commonly used in various vegetables in formulations: Triflur 480 EC, Triflurex 480 EC, Triflurotox 250 EC and Triflurotox 480 EC and its residues have been detected in carrots [7].

Very few data have been published about persistence of pendimethalin in soils in experiments carried out in the field. Behaviour of pendimethalin deposits in soils of cotton fields indicate that the compound is more persistent than trifluralin [8]. This paper reports the dissipation of pendimethalin deposits in soil. The other aim of the tests was to control the level of pendimethalin residues in ripe fennel destined for the production of baby food.

MATERIALS AND METHODS

The experimental field was located in Świlcza, small village about 15 km west of Rzeszów and 30 km of the meteorological station where precipitation data were recorded every day. Pendimethalin was applied pre-emergence on fennel plantation on 26 June at recommended rate (3 l of Stomp 330 EC per ha) two days after sowing (24 June) using commercial formulation Stomp 330 EC. The field received no pendimethalin before that experiment. Pendimethalin residue in soil was monitored from the 10th day after application date to 12 September. At each sampling time four soil samples were taken with steel cores (5.0 cm diameter and 20 cm length) from randomly selected rows of fennel plants. At the end of that test, four samples of ripe fennel plants were taken at the harvest time and pendimethalin residues were determined. Because of bad weather the yield was very pure. Therefore the grower decided to sow once more the fennel on the same field. The soil and fennel samples were taken in the same way. That time none herbicide was used and at the end of that second test four samples of ripe fennel plants were taken at the harvest time and pendimethalin residues were determined.

Soil samples were air-dried, ground and stored at room temperature prior to analysis but no more than three days. Subsamples (20 g) were extracted by shaking for one hour with 100 ml of dichloromethane-acetone mixture (9:1, v:v) on a rotary shaker. The extract obtained, was decanted by a layer of anhydrous sodium sulphate and the soil was rinsed two times with 10 ml of dichloromethane [1, 3, 4, 6]. The extract was cleaned using florisil [10]. The analysis of the extract was performed using a Hewlett Packard 5890A gas chromatograph, equipped with a nitrogen – phosphorus detector (GC-NPD). The column used in this study was an HP fused – silica capillary column coated with cross-linked methyl silicone (length 25 m, ID 0.31, film thickness 0.52 μm). Nitrogen was used as both the carrier and make-up gas at a flow rate of 30 ml/min. Hydrogen was used at a flaw rate of 3.5 ml/min., and air at 120 ml/min. The oven temperature was programmed as follows: initial temperature 150°C (1min.), rate of 10°C/min. and final temperature 250°C.

Recovery studies were carried out regularly by spiking analytical samples with stock solution of pendimethalin standard. In addition of the in-house quality assurance programme, in 2006 the laboratory successfully participated in proficiency testing schemes organised and run by the Food Analysis Performance Assessment Scheme (Central Science Laboratory in York) and by European Commission (University of Almeria). The results obtained by Rzeszów Laboratory of Institute of Plant Protection in both cases were acceptable.

Acetone, dichloromethane and petroleum ether were of analytical grade. Pendimethalin standard was purchased from Ehrenstorfer (Germany) and its stock solution (10 μg/ml) was prepared in acetone and stored at 4^0C. Working standard solution (0.2 μg/ml) was obtained by diluting the stock solution with petroleum ether.

RESULTS AND DISCUSSION

Pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) is a selective dinitroanaline herbicide used for pre-emergent control of annual grasses and broadleaf weeds in corn, winter cereals, potatoes, some vegetables and ornamentals. It inhibits cell division and cell elongation. In Poland, pendimethalin is available as emulsifiable concentrates (Stomp 330 EC, Panida 330 EC, Escort 263 EC), or a suspension concentrate for use in various crops (Stomp 400 SC)[9].

Immediately after treatment, the average pendimethalin residue in the plough layer of the soil was found to be 0.228 mg/kg with low variation coefficient (Relative Standard Deviation, RSD) indicating that Stomp 330 EC was evenly distributed on field surface (Table 1). With passing time pendimethalin residues decreased successively and finally reached the average level of 0.103 mg/kg. Therefore, some disappearance parameters for pendimethalin residues were calculated on the basis of first order kinetics and regression equations. The

Table 1. Occurrence of pendimethalin residues in soil and ripe fennel
Tabela 1. Występowanie pozostałości pendimetaliny w glebie i dojrzałym koperku

Sampling date	Day after treatment	Sample	Residue [mg/kg]						RSD
			I	II	III	IV	mean	s	%
6.07	10	soil	0.186	0.225	0.166	0.334	0.228	0.075	33
20.07	24	soil	0.276	0.216	0.104	0.119	0.179	0.082	46
1.08	36	soil	0.122	0.168	0.180	0.087	0.139	0.043	31
		fennel	0.016	0.011	0.011	0.010	0.012	0.003	23
16.08	51	soil	0.038	0.048	0.020	0.355	0.115	0.160	139
25.08	60	soil	0.181	0.036	0.182	0.090	0.122	0.072	59
12.09	78	soil	0.078	0.036	0.078	0.221*	0.103	0.081	79
		fennel	0.004	0.003	0.005	0.008*	0.005	0.002	49

*soil sample and sample of plants with the visible changes in their appearance

Table 2. Dissipation of pendimethalin residues in the plough layer (0-20 cm) during the periods: 26.06-1.08, 15.08-12.09, and 26.06-12.09
Tabela 2. Zanikanie pozostałości pendimetaliny w wierzchniej warstwie gleby (0-20 cm) w okresach: 26.06-15.08, 15.08-12.09 i 26.06-12.09

Period of time	Equation		R_0	R^2	$t_{1/2}$
26.06-1.08	first order kinetics	$y = 0.283e^{-0.019x}$	0.283	0.9967	36
	regression line	$y = -0.0034x + 0.265$	0.265	0.9998	38
15.08-12.09	first order kinetics	$y = 0.121e^{-0.0048x}$	0.121	0.6002	144
	regression line	$y = -0.0005x + 0.121$	0.121	0.5788	-
26.06-12.09	first order kinetics	$y = 0.236e^{-0.0115x}$	0.2360	0.9064	60
	regression line	$y = -0.0018x + 0.226$	0.226	0.8585	62

x – time after pendimethalin application [days], *y* – pendimethalin residue in soil [mg/kg],
R_0 - initial residue derived from equation [mg/kg], R^2 - coefficient of determination; $t_{1/2}$ - half-life period [days]

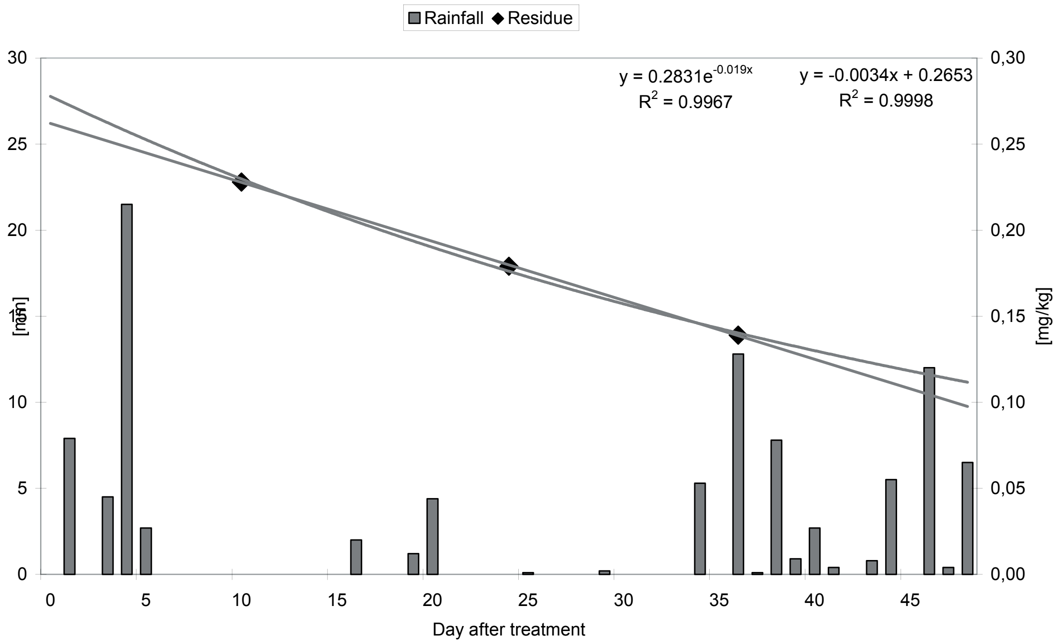

Fig. 1. Precipitation and disappearance trend of pendimethalin residues in soil within five decades after treatment (26.06-15.08),

Rys. 1. Opad deszczu i przebieg zanikania pozostałości pendimetaliny w glebie w okresie pięciu dekad po zabiegu (26.06-15.08)

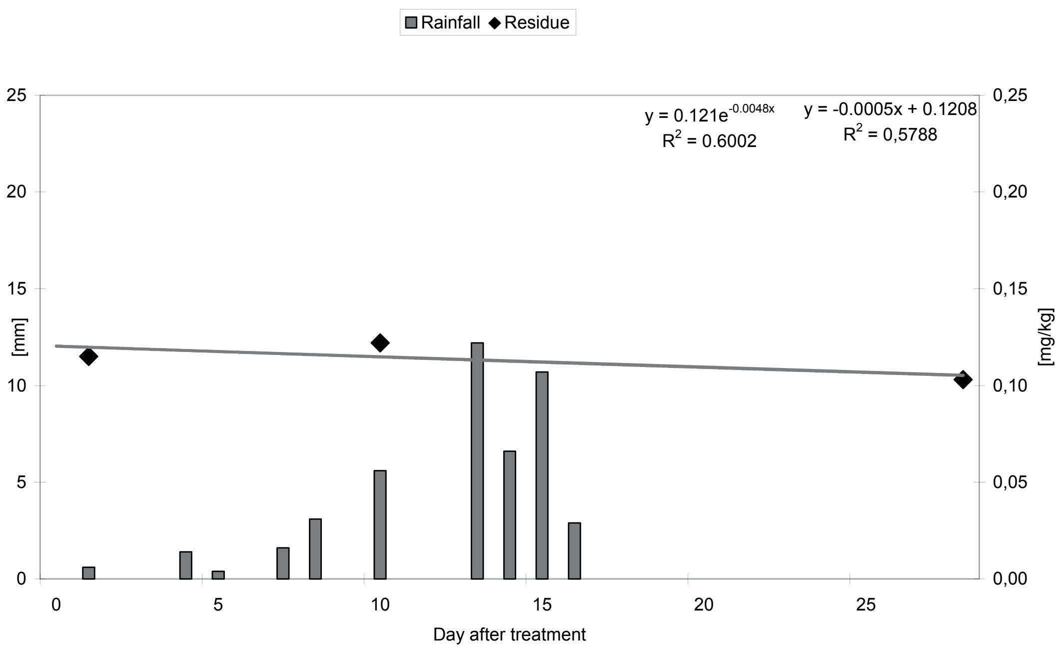

Fig. 2. Precipitation and disappearance trend of pendimethalin residues in soil within the next three decades after treatment (15.08-12.09)

Rys. 2. Opad deszczu i przebieg zanikania pozostałości pendimetaliny w glebie w okresie trzech kolejnych dekad po zabiegu (15.08-12.09) disappearance trends of initial deposits of pendimethalin residues on soil surfaces, determination coefficients, and half-life times are shown in Table 2.

Results obtained indicated that the main factor influencing dissipation of pendimethalin deposits seems to be rainfall. July 2006 was particularly dry and the first stormy rain had place after third sampling date. By this time, average pendimethalin residues decreased according to equations: $y = 0.2831e^{-0.019x}$ (exponential) and $y = -0.0034x + 0.2653$ (linear) with excellent coefficient of determination in both cases (Fig. 1). Half-lives obtained from those equations were 36 and 38 days, respectively. The rainfall of the August and September was intensive and affected on transport of pendimethalin within tested field resulting uneven redistribution of pendimethalin on soil surface expressed by variation coefficient reaching the highest level of 139%. During that period of time, the average pendimethalin residues decreased according equations: $y = 0.121e^{-0.0048x}$, and $y = -0.0005x + 0.121$ (Fig.2) and in practice stayed on the same level during 30 days.

Finally, taking into account all the analysis results, the trends of pendimethalin disappearance in the soil within the period from its application (June 26) to the crop of the second fennel crop (September 12) have been pointed out (Fig. 3). It has been stated that the course of the pendimethalin disappearance within this period reflected the exponential equation: $y = 0.236e^{-0.0115x}$. According to this equation, the initial residues of this herbicide lowered by half after 60 days from the application date of the Stomp 330 EC preparation. Half-life time of pendimethalin residues estimated on the level of linear trend of the disappearance was formed at a bit higher level.

The other aim of the study was to estimate residue levels resulting from pendimethalin residues in soil. Analyses of ripe fennel samples indicated that despite of high level of pendimethalin residues present in soil surface, only trace pedimethalin residues (on average 0.012 and 0.005 mg/kg) were found in ripe plants. Low pendimethalin residues, and small addition of fresh fennel to a final product of baby food indicate that fresh fennel picked from the field where the weeds were controlled with the use of the Stomp 330 EC, fulfils the requirements of the food producer for babies/children [5].

It has to be emphasised that the rate of the pendimethalin disappearance was slow ($t_{1/2}$=60 days) and its residues in the soil can be locally toxic for the follow-up plants. The proof of this possibility are the observations done on 12 September while picking up the ripe fennel sowed on the same field in the first decade of August. There have been hyper pigmentation and lower growth of some plants

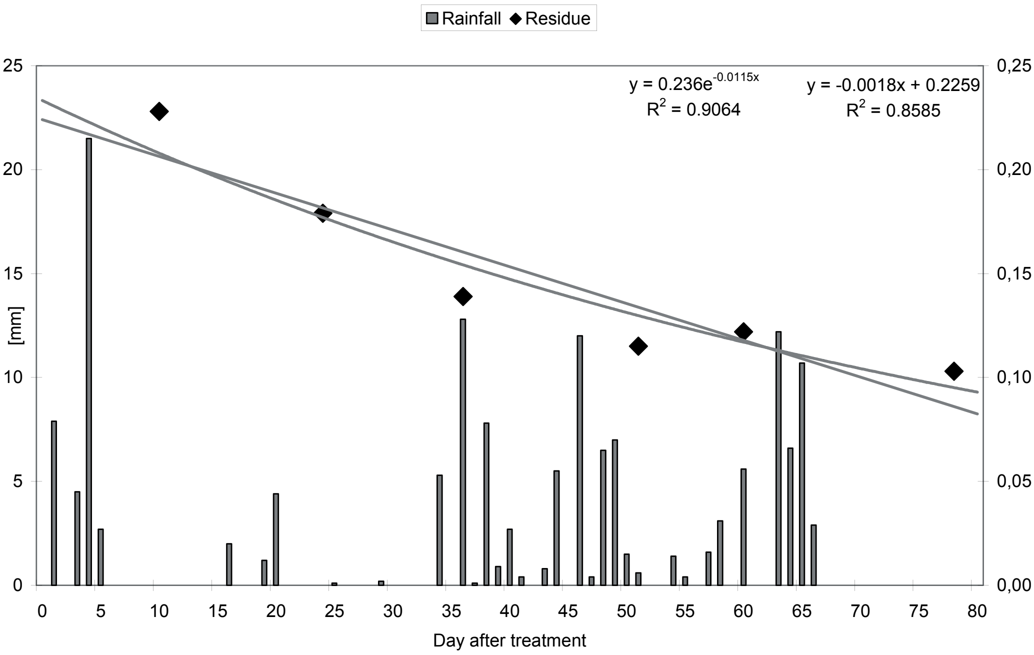

Fig. 3. Precipitation and disappearance trend of pendimethalin residues in soil within eight decades after treatment (26.06-12.09)

Rys. 3. Opad deszczu i przebieg zanikania pozostałości pendimetaliny w glebie w okresie ośmiu dekad po zabiegu (26.06-12.09) observed locally. In order to prove the toxic activity of the pendimethalin from the place different because of changes in plants' appearance, the plant and soil sample have been taken from their vicinity. The residues of pendimethalin in plants have not exceeded the level of 0.01 mg/kg, whereas in the soil it was of 0.221 mg/kg, and were 3 times higher than in other samples of the soil taken in the period of crops (Table. 1).

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