Original Research

Degradation of Ethofumesate in Soil under Laboratory Conditions

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Abstract

The aim of our research was to determine the influence of the soil type and adjuvants on the dynamics of ethofumesate degradation in soil. Samples of two types of soil were placed in growth chambers. Ethofumesate was applied at a rate of 800 g·ha^{-1}, alone and in mixture with adjuvant based on methylated crop oil and surfactant adjuvant. Residues of ethofumesate were determined using high-performance liquid chromatography with UV detection. The type of soil influenced the degradation rate of ethofumesate. Significant differences in degradation rate between soils during the first period after treatment (36 days) influenced the DT_{50} indicator. The addition of oil adjuvant slowed down the degradation of ethofumesate and increased the level of residue in soils. The DT_{50} value for mixture ethofumesate + oil adjuvant was about 8-10 days higher in comparison with the DT_{50} for ethofumesate applied alone. No significant differences were observed between degradation rates and the DT_{50} for ethofumesate applied alone and with surfactant adjuvant.

Keywords: oil adjuvant, surfactant, herbicide, HPLC, residue, degradation

Introduction

Ethofumesate, (±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl methanesulfonate, is the active substance of many commercial herbicide products widely used for weed control in strawberry and beet crops [1]. Ethofumesate is absorbed by the emerging shoots (grass coleoptile and broadleaf hypocotyl) and roots with translocation to the foliage. This herbicide inhibits the growth of meristems, retards cellular division and limits the formation of cuticular. Ethofumesate is biologically degraded in soil. DT_{50} [dissipation time (days) for 50% of the initial residue to be lost] ranges from less than 35 days under moist and warm conditions to more than 100 days under dry and cold conditions [2].

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Persistence in topsoil is one of the criteria for pesticide registration at the European Union level [3]. The DT_{50} under field conditions should be less than 3 months unless there are no unacceptable effects on terrestrial organisms and plants [4]. Based on their persistence in soil, herbicides can be divided into three groups: persistent (DT_{50} > 90 d), moderately persistent (DT_{50} = 20-90 d) and not (short-term) persistent – DT_{50} < 20 d [5]. In soil the activity of herbicides may be decreased by chemical or biological degradation of its active ingredients. Adsorption by soil colloids, absorption by plants or leaching to lower layers of the soil profile also influences the biological activity of herbicides in the soil [6]. In plants, the biological activity of herbicides may by decreased by low retention and washing of herbicide from leaf surface by rain, dew and irrigation to the soil [7].

Modeling of field behaviour of pesticides started around 1970, when tools and techniques became available that enabled dynamic simulation of behaviour in the soil and plant system [8]. Walker [9] presented the first model for simulation of pesticide persistence in the top layer of field soil. He considered transformation within the soil as the only loss process and assumed that this process is controlled by soil temperature and soil moisture content. The core of the model is the first-order rate equation for the total amount in topsoil. Presently, many models for pesticide behaviour in the soil and plant are used [10, 11]. The role of environmental fate modeling of pesticides has increased steadily, and it now plays a major role in the assessment of environmental aspects of pesticide behaviour for registration at the EU level [3].

Numerous research studies show that adjuvants applied with herbicide influenced weed-control efficacy [12]. Properties of adjuvant increased herbicide activity through mechanisms such as droplet adhesion, retention, spreading, deposit formation, uptake and translocation [13, 14]. Some research indicates that adjuvants can reduce leaching of herbicide through the soil profile [15]. The listed properties of adjuvants can influence the concentration of herbicide residues in plants and soil.

The aim of the present study was to determine the influence of the soil type and adjuvants on the dynamics of ethofumesate degradation in soil.

Experimental Procedures

The influence of soil type and adjuvants addition on degradation rate of ethofumesate was studied under controlled laboratory conditions. Two kinds of soil (medium silty loam and heavy loamy sand) were collected for the laboratory experiments from the upper soil layer (0-15 cm depth). Soils collected from two sites (Teodorów and Laskowice) had no history of previous ethofumesate use (no residues detected) and are representative of the beet-growing regions of Lower Silesia (southwestern Poland). The properties of the soils are presented in Table 1.

After passing the soil through a 2 mm sieve, it was stored in covered trays in a greenhouse for 10 days and regularly mixed. Soil moisture was measured before the start of the trials by heating to dryness for 24 h at 105ºC and determining the difference in weight. Soil moisture was set at 60% of field capacity and checked at regular intervals and adjusted with distilled water to the initial level.

Soil samples were transferred into 60 mm diameter pots (h=55 mm) that were placed in growth chambers, each variant had four replicates. Day/night temperature regimes were 22/12ºC, and light intensity was 250 ±10 $\mu mol \cdot m^{-2} \cdot s^{-1}$ photosynthetic photon flux, with 16 h day length.

Two days after placing the pots into the growth chambers, a commercial formulation of ethofumesate (Kemiron® 500 SC) was applied at a dose of 800 g $a.s. \cdot ha^{-1}$ alone and in mixture with 1.5 $L \cdot ha^{-1}$ of adjuvant based on methylated oilseed rape oil – Olbras® 88 EC and 0.3 $L \cdot ha^{-1}$ of surfactant adjuvant - Trend® 90 EC (ethoxylated isodecyl alcohol). Application of herbicide and adjuvants was done in a stationary chamber sprayer equipped with a mobile nozzle type TeeJet XR 11003-VS. Doses of herbicide, adjuvants and spraying conditions were the same as for field conditions.

Soil samples (one pot containing ca. 150 g of soil = one sample and one replication) were taken for analyses at 1 hour (initial concentration) and 1, 3, 6, 12, 21, 36, 54, 72, 90 and 120 days after treatment (DAT) respectively.

The analytical procedure was performed at the Institute and described by authors [16]. All samples were analyzed using high-performance liquid chromatography (SHIMADZU® HPLC measuring set) with UV-detection.

The recoveries of the ethofumesate were determined by fortification of soil samples at concentrations of 0.001, 0.01, 0.1 and 1 $mg \cdot kg^{-1}$ soil, respectively, in three replicates. The recoveries for all concentrations were between 78 and 94%. The quantification limit of the method was 0.001 $mg \cdot kg^{-1}$. All results of residue concentration were calculated to a soil dry weight basis.

All experimental data were calculated using the statistical program Statgraphics Centurion, version XV.

Results

Effect of Soil Type

The results of the ethofumesate degradation study in surface soils are shown in Fig. 1. The initial ethofumesate concentration (1 hour after application) amounted for all samples to 0.712 ± 0.021 $mg \cdot kg^{-1}$. The degradation rates of ethofumesate differed significantly between the two soils, being faster in the medium silty loam soil (soil A) and slower in the heavy loamy sand soil (soil B). Up to 36 DAT

Table 1. Properties of the test soils.

pH (in 1 n KCl)	Organic carbon (%)	Sand (%)	Silt (%)	Clay (%)	Soil type	Texture of soil
Soil A – Location: Teodorów						
6.1	2.10	15	34	51	brown soil	medium silty loam
Soil B – Location: Laskowice						
5.5	0.94	63	20	17	podzol soil	heavy loamy sand

degradation rates for both soils were inverted, at 120 days after application, and ethofumesate residue amounted to 0.057 mg·kg^{-1} (8.0% of initial dose) for the medium silty loam soil and 0.035 mg·kg^{-1} (4.9%) for the heavy loamy sand soil.

The degradation data were plotted. Good linearity was found between logarithmic concentration of ethofumesate residues and time, indicating first-order rates of degradation with correlation coefficients (r^2) about 0.97-0.99 for heavy loamy sand soil. Calculated data for degradation of ethofumesate in medium silty loam soil deviated from first-order reaction. Rapid initial degradation followed by a gradual decline was observed in the A soil, suggesting a two-stage degradation process.

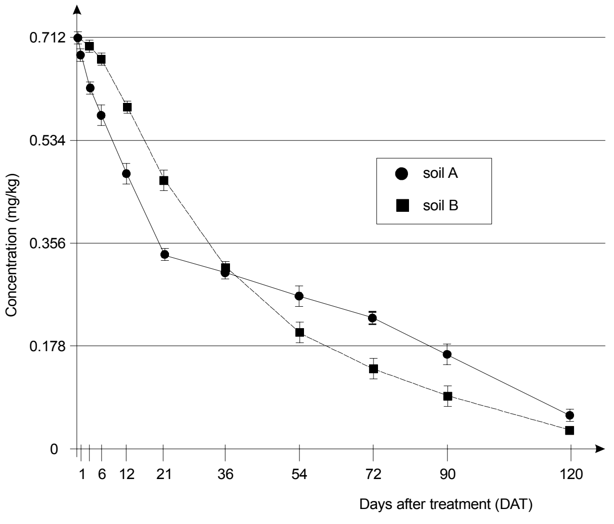

Fig. 1. Degradation of ethofumesate in two soils. Vertical bars represent ± standard errors of means (n = 4). Bars where not present fall within the symbols.
Soil A – medium silty loam soil, Soil B – heavy loamy sand soil.

The DT_{50} values (graphically derived by interpolating the values between successive residue measurements) varied from 20.2 (±0.72) days for medium silty loam soil (soil A) to 31.3 (±0.91) days for heavy loamy sand soil (soil B).

The ethofumesate degradation rate depends on properties of soils. In medium silty loam soil (higher content of silt, clay and organic carbon) the DT_{50} value was shorter than in heavy loamy sand soil, but residues determined 120 DAT in the first soil (0.057 mg·kg^{-1}) were higher than in the second soil (0.035 mg·kg^{-1}).

Effect of Adjuvant Addition

The results of the ethofumesate degradation in soil and influence of adjuvants are shown in Fig. 2 (medium silty loam soil) and Fig. 3 (heavy loamy sand soil).

The degradation pattern differed significantly among the objects: ethofumesate alone and in mixture with oil adjuvant. The addition of oil reduced the degradation rate of ethofumesate in both soils. No significant differences were observed between degradation rates for ethofumesate applied alone and with surfactant adjuvant.

The DT_{50} value for mixture ethofumesate + oil was about 10 days higher for medium silty loam soil and 8 days for heavy loamy sand soil in comparison with DT_{50} for ethofumesate applied alone. Final residues of ethofumesate (120 days after treatment) on objects with oil adjuvant were higher (0.085 mg·kg^{-1}) for the medium silty loam soil and 0.056 mg·kg^{-1} for the heavy loamy sand soil, than in objects, where ethofumesate was used alone (0.057 and 0.035 mg·kg^{-1}, respectively). No significant differences were observed between DT_{50} and final residue level for ethofumesate applied alone and with surfactant adjuvant (for both soil types).

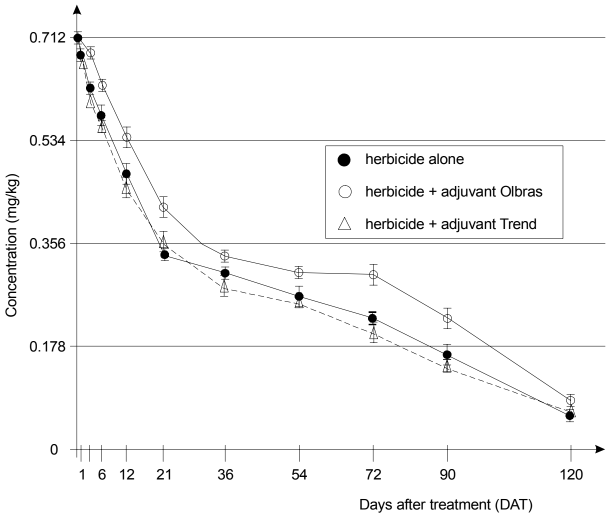

Fig. 2. Influence of adjuvants on degradation rate of ethofumesate in the medium silty loam soil A. Vertical bars represent ± standard errors of means (n = 4).

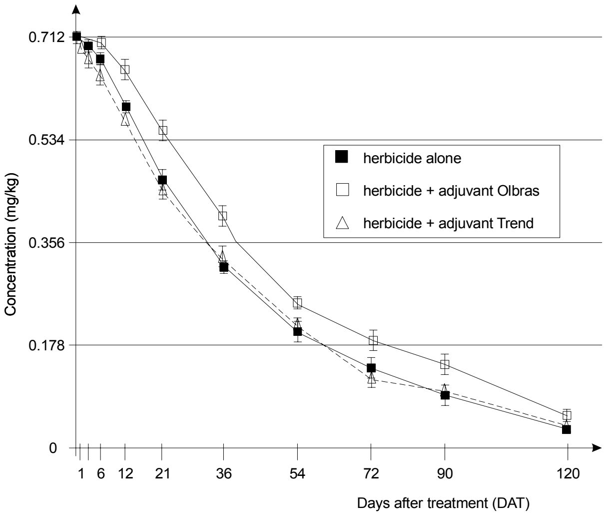

Fig. 3. Influence of adjuvants on degradation rate of ethofumesate in the heavy loamy sand soil B. Vertical bars represent ± standard errors of means (n = 4).

Discussion

Soil texture (content of sand, silt, clay) and the content of organic carbon influenced residues, retention and degradation rates of herbicide. Results of this study showed that soil type (especially clay and organic matter content) could influence speed, run and final residues of ethofumesate in soils. Similar observations for other herbicides were described [17-19]. Good linearity was found between logarithmic concentration of ethofumesate residues and time, indicating first-order rates of degradation for heavy loamy sand soil. Rapid initial degradation was observed in the medium silty loam soil, suggesting a two-stage (rapid followed by slow) degradation process. This apparent two-stage degradation has been noticed before for metsulfuron-methyl [20], triasulfuron [21] and also for other herbicides such as metamitron [22]. However, the reason for such degradation behaviour is still not clear, although attempts have been made to explain it conceptually and empirically using two-compartment models [23].

Significant differences in degradation rate of the herbicide in soil in the first period after treatment influenced the DT_{50} indicator. The DT_{50} values for both soils are consistent with the data of Tomlin [2]. DT_{50} values for ethofumesate obtained from field experiments in sugar beet were different and ranged from 52 to 78 days [24].

The addition of oil adjuvant slowed down the degradation of ethofumesate in heavy loamy sand and medium silty loam soils and increased the level of residue in soils. Swarcewicz et al. [25] described experiments where influence of adjuvants on trifluralin degradation was tested in greenhouse conditions. At 50 DAT, residues of trifluralin amounted to 38% of the initial dose and on objects with adjuvants residues ranged from 42 to 49% of the initial dose. Similar experiment [26] also proved that the addition of adjuvants slowed down degradation and increased the level of phenmedipham residue in soil. The DT_{50} value for the mixture of phenmedipham + adjuvant was about 10 days higher in comparison with the DT_{50} for phenmedipham applied alone.

The effect of organic additives, especially oil substances, on increased herbicide retention, mobility and immobilizatoin in soil top layer were described by other authors [27-31]. In these experiments saw no significant differences beetwen DT_{50} and residue level for ethofumesate applied alone and with surfactant adjuvant. A study by Rodriguez-Cruz et al. [32] on leaching of linuron and atrazine compounds was studied in columns of a natural clayey soil and the same clayey soil modified by direct injection of the surfactant. Breakthrough curves indicated total immobilization of these substances in modified soils and a decrease in the leaching kinetics compared to what was obtained in the natural soil. This study and cited references inform that the addition of adjuvants, especially oil adjuvants, could influence speed of degradation and increase herbicide residues in soil, but usually adjuvants are applied with herbicides in reduced doses (70-80% of recommended) and herbicidal residues determined at harvest time are lower than those obtained from objects, where full (recommended) doses of herbicide (without adjuvant) were applied [33].

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