

Sorption–desorption and dissipation of trifluralin in agricultural soils of the Žitný ostrov (the Danubian Lowland)

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Abstract

Leaching of any herbicide through the soil profile to groundwater depends mainly on the sorption–desorption and dissipation processes. In this study, batch sorption, desorption and dissipation experiments were performed with dinitroaniline herbicide trifluralin and three soil types collected from their soil horizons in the Žitný ostrov (SW Slovakia). Trifluralin was strongly sorbed by all soils with Freundlich sorption coefficient and distribution coefficient values between 32.8–239 mg^(1-1/n) l^{1/n} kg⁻¹ and 34.8–243 l kg⁻¹, respectively. Statistical analysis of the results confirmed significant positive correlations of trifluralin sorption with organic components of the soils ($r = 0.99$, $p < 0.001$). Only low proportions of the sorbed trifluralin could be released from soils into aqueous solution after four successive desorption steps (2.30–6.23 %), indicating an irreversibility of trifluralin sorption. Both sorption and desorption were depth-dependent, when the A soil horizons exhibited higher retention capacity of the herbicide than B or C soil horizons. Trifluralin persisted more in the A soil horizons than the corresponding B or C soil horizons with dissipation half-life values ranging from 57.8 to 99 days in topsoils and from 46.2 to 77 days in subsoils. The stronger the sorption of trifluralin in the soil, the higher its persistence as indicated by positive correlation of distribution coefficients with dissipation half-lives ($r = 0.90$, $p < 0.01$). It was concluded that trifluralin had no risk of leaching to groundwater, and therefore its past use for agricultural purposes in the study area was safe.

Key words: dissipation, leaching, pesticide, sorption, soil, trifluralin

Introduction

Dinitroaniline compounds are an important class of agricultural herbicides. Their properties regarding the mode of action as blockers of cell division in plant roots led to their worldwide uses for protection of many crops against weeds. One of the most commonly used dinitroaniline herbicides is trifluralin (α, α, α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine), which controls broadleaf weeds and grasses in a large variety of crops including sunflowers, soybeans, sugar beets and corns. It is applied pre-emergently and due to its high volatilization losses, trifluralin is incorporated directly into the soil (Helling, 1975). Therefore, soils appear as the ultimate sink for residues of trifluralin.

Agricultural use of dinitroaniline herbicides necessitates evaluation of the risks resulting from the surface- and groundwater contamination via run-off of these compounds from agricultural fields and their movement through the soil, respectively. Sorption–desorption and dissipation (a general term including degradation of herbicide in soil via multiple processes, such as volatilization, microbial degradation,

hydrolysis, etc.) are two interrelated processes occurring in soil-water systems and determine the final fate of any dinitroaniline herbicide in the soil environment, including mainly its persistence and transfer into the natural waters (Kim and Feagley, 1998). Both sorption and dissipation of these herbicides in soils are dependent on the complex relationships among the physico-chemical properties of herbicides, the composition and texture of soils and environmental conditions (temperature, water content in soil, redox status, application dose, etc.; Zimdahl and Gwynn, 1977; Francioso et al., 1992; Cooke et al., 2004). Generally, dinitroaniline herbicides were shown to be highly sorbed by soils, categorizing them as immobile (Peter and Weber, 1985; Boivin et al., 2005). Nevertheless, they were frequently detected in both surface- and groundwaters, where adversely affect aquatic life and fish-eating wildlife (Gilliom, 2007; Ensminger et al., 2013). Soil organic matter content correlates positively with sorption of these pesticides in soils but clay minerals may have also an importance when organic matter content of the soils is low. Dissipation of dinitroaniline herbicides in soils, which occurs mainly via microbial degradation, is

relatively slow under aerobic conditions with mean dissipation half-life values (DT_{50}) ranging from 20 days for oryzalin to 180 days for trifluralin (FOOTPRINT, 2006). On the other hand, microbially mediated degradation of these herbicides in soils under anaerobic conditions may proceed very quickly (McFarland et al., 1996; Tor et al., 2000).

This study is specifically focused on the laboratory determination of sorption–desorption and dissipation characteristics of trifluralin in three different soil types, which are representative of agricultural fields in the Danubian Lowland, mainly in the region of Žitný ostrov. Recently, trifluralin has not been used in Slovakia since 2010 because it was deleted from the list of allowed herbicides by European Commission. However, at the time of experimental studies in 2009, trifluralin was one of the most used herbicides in the Žitný ostrov. The Žitný ostrov is a large region with an area of 1 900 km² characterized by the advanced and intensive agricultural activities, which are associated inevitably with the use of herbicides. Moreover, the whole region is well-known for its large groundwater resources (~1 x 10⁶ km³), supplying drinking water to more than 700 000 inhabitants. The groundwater table may underlie shallow in several parts of Žitný ostrov with a range from 0.5 to 3 m from the surface, and varies by ±1 m during a year. Hence, groundwaters of the region are susceptible to contamination by herbicides used in agriculture. As a first step in evaluating the potential of herbicides to contaminate groundwater is usually to determine the extent of their sorption, desorption and disappearance in soils as well as factors affecting these processes.

Therefore, the main aims of this study were (i) to determine the sorption, desorption and dissipation of the herbicide trifluralin in representative agricultural soils of the Žitný ostrov under aerobic conditions, (ii) to identify soil properties, which affect sorption, desorption and dissipation of trifluralin, and (iii) to evaluate the potential risk of herbicide leaching through the soil to groundwater using a simple mobility index Groundwater Ubiquity Score (GUS).

Materials and methods

Chemicals

Trifluralin of analytical grade (98 %) used in this study was purchased from Dr. Ehrenstorfer GmbH (Germany). It has a relatively high hydrophobicity ($\log K_{ow} = 5.27$ at 20 °C and pH 7) and low water solubility with a value of 0.221 mg · l⁻¹ at 20 °C (FOOTPRINT, 2006). All other chemicals used were of analytical reagent grade or better.

Soil sampling and characterization

The sampling area is located in the upper part of the Žitný ostrov (SW Slovakia). Three soil types are typical for this area and cover approximately 98 % of the land: Calcaro-Haplic Chernozem (53 %), Fulvi-Calcaric Phaeozem (27 %), and Calcaric Fluvisol (18 %). The soil samples representative of the Žitný ostrov were taken from manually excavated soil pits (2 x 1 m) at various depths correspon-

ding to the occurrence of individual soil horizons (Tab. 1). Soil samples were air-dried, passed through a 2 mm sieve, and thoroughly mixed. The same soils were previously used in the sorption studies of herbicides MCPA and acetochlor (Hiller et al., 2012; Tatarková et al., 2014).

Total organic carbon content (TOC) was determined using dichromate oxidation (Nelson and Sommers, 1996). Humic and fulvic acids (C_{HA} and C_{FA} , respectively) were extracted by a solution of 0.1 M Na₄P₂O₇ + NaOH using a ratio of extractant to sample of 10:1, and to precipitate humic acid, the supernatant was acidified to pH 2 with H₂SO₄. The TOC associated with each fraction of HA and FA were determined by dichromate oxidation and measurement of the absorbance at 590 nm (Sims and Haby, 1971). Soil pH was measured by an electrode in a 1:2.5 (wt:wt) soil-water (active pH) and soil-1.0 M potassium chloride solution (exchangeable pH) suspensions. Calcium carbonate content (CaCO₃) was measured using a volumetric device (Jackson, 1958). For the determination of the particle size distribution, the pipette method was used (Gee and Bauder, 1986). Cation exchange capacity (CEC) was measured with 1.0 M ammonium acetate at pH 7 (ISRIC, 1995). Amorphous Al and Fe oxides (Al_{ox} and Fe_{ox} , respectively) were determined by extraction with acidified ammonium oxalate in the dark (McKeague and Day, 1966) and clay minerals were identified by X-ray diffraction analysis. The physico-chemical and textural properties of the tested soils are given in Tab. 1.

Sorption–desorption

The stock solution of trifluralin with an initial concentration of ~100 mg · l⁻¹ was prepared in methanol of chromatographic purity due to low solubility of trifluralin in the water. For pre-equilibration, 1 g of each soil was shaken in 15 ml glass tubes with 9.75–9.997 ml of 0.01 M CaCl₂ and 0.0015 M NaN₃ solution for 24 h at 20 °C in the dark. Calcium chloride and sodium azide are used to keep ionic strength of the soil solution constant and to inhibit microbial activity, respectively. Then, an adequate volume of the stock solution of trifluralin prepared in methanol was added to the suspensions to reach a final volume of 10 ml with five initial concentrations of trifluralin: 0.017, 0.258, 0.410, 1.17, and 2.35 mg · l⁻¹. These concentrations were selected with respect to the expected concentration of the herbicide in the topsoil and the detection limit of the analytical method. Moreover, volume fraction of methanol in the tubes was enough low to have any effect on the sorption of trifluralin in soils. Tubes were rotated for another 24 h to reach the sorption equilibrium and subsequently centrifugated at 1 160xg for 15 min. Supernatants were transferred in glass vials, extracted, and analysed for trifluralin concentrations by gas chromatography (GC) as described below.

Desorption experiments followed immediately after sorption with the highest equilibrium concentration on an isotherm. After the removal of 8 ml of supernatant, the same volume of aqueous solution containing no herbicide was added and the tubes were rotated for 24 h in the dark, centrifuged, extracted, and the supernatant was analysed.

Desorption procedure was repeated four times. All sorption–desorption experiments were performed in two replicates. The control samples for each concentration without soil were also included and used to account for possible losses due to volatilization or sorption of trifluralin onto the glass tube surface.

Trifluralin in aqueous solutions from sorption–desorption experiments was extracted with dichloromethane (CH_2Cl_2) in three consecutive steps. The extracts were combined, dried using a column filled with sodium sulfate (Na_2SO_4), then evaporated and redissolved in isooctane. The mean extraction recovery of trifluralin from aqueous samples was 96 % and the detection limit was $0.001 \text{ mg} \cdot \text{l}^{-1}$.

Dissipation

A set of 20 g portions of each soil was placed in the dark at $20 \text{ }^\circ\text{C}$ and at the soil moisture content of 15 % by

weight in glass batches covered with perforated aluminum foil. The soils were incubated for one month before the start of dissipation experiments and periodically irrigated with deionized water to the original soil moisture content. After one month, soils were spiked with trifluralin dissolved in methanol to obtain an initial trifluralin concentration in soil $10 \text{ mg} \cdot \text{kg}^{-1}$. The soil moisture in all glass batches was adjusted to 70 % of the maximum water holding capacity by adding appropriate amounts of deionized water and weighed. The soils were thoroughly mixed and placed in the dark at $20 \text{ }^\circ\text{C}$ for an incubation period of 100 days. To maintain the soil water content constant throughout the experiment, water was added every other day for evaporation loss if necessary. The possible losses of water from batches were determined by weighting every other day. Two replicates were taken at each time point (after 1, 5, 14, 30, 60, and 100 days) to determine trifluralin concentrations remaining in the soil. Trifluralin remaining in the soils after

Tab. 1
Selected physico-chemical and textural properties of the soils. The same soils were used in previous studies by Hiller et al. (2012) and Tatarková et al. (2014)

Soil type	Calcaro-Haplic Chernozem			Fulvi-Calcaric Phaeozem		Calcaric Fluvisol	
	S1A	S1B	S1C	S2A	S2B	S3A	S3B
Location	Most pri Bratislave			Lehnice		Most pri Bratislave	
Vegetation at sampling time	Sugar beet			Oilseed rape		Maize	
Soil depth (cm)	0–15	30–40	90–110	0–15	30–40	0–15	40–60
TOC ^a (%)	2.09	1.39	0.58	4.41	2.31	1.47	0.89
C_{HA}^{b} (%)	0.42	0.30	0.13	0.89	0.53	0.23	0.13
C_{FA}^{b} (%)	0.29	0.23	0.10	0.76	0.34	0.28	0.17
$C_{\text{HA}}/C_{\text{FA}}^{\text{c}}$	1.45	1.30	1.30	1.17	1.56	0.82	0.76
$C_{\text{HA}}/\text{TOC}^{\text{d}}$	0.20	0.22	0.22	0.20	0.23	0.16	0.15
Active pH	7.83	8.03	8.24	7.69	7.99	7.91	8.12
Exchangeable pH	7.28	7.55	7.67	7.31	7.53	7.42	7.55
CaCO_3 (%)	19.2	28.0	9.30	16.1	27.4	24.3	27.4
CEC ^e ($\text{cmol}^+ \text{kg}^{-1}$)	26.2	26.5	21.1	41.6	33.0	19.3	18.7
$\text{Fe}_{\text{ox}}^{\text{f}}$ ($\text{mg} \cdot \text{kg}^{-1}$)	220	226	94.8	457	176	321	361
$\text{Al}_{\text{ox}}^{\text{f}}$ ($\text{mg} \cdot \text{kg}^{-1}$)	217	263	135	484	374	154	127
Sand (%)	22.7	21.9	18.9	39.4	42.9	29.1	31.1
Silt (%)	62.3	61.7	63.4	53.4	43.9	60.1	59.0
Clay (%)	15.0	16.4	17.7	7.20	13.2	10.8	9.90
Clay minerals ^g	Ch/III	Ch/III/Sm	Ch/III/Sm	Ch/III	Ch/III	Ch/III/Sm	Ch/III/Sm
Clay/TOC ^h	7.19	11.8	30.6	1.63	5.71	7.33	11.2

^atotal organic carbon content

^bhumic and fulvic acid carbon contents

^cratio of humic acid carbon to fulvic acid carbon – an indication of soil humus quality

^dratio of total organic carbon content to humic acid carbon content – humification degree

^ecation exchange capacity

^fammonium oxalate extractable iron and aluminium

^gCh-Chlorite, III-illite, Sm-Smectite

^hratio of clay content to total organic carbon content

degradation was extracted mechanically twice with 40 ml of acetonitrile and water (99:1 by volume) for 90 min. The extracts were concentrated on rotary evaporator (model 461 Buchi Rotavapor) and then subjected to solid-phase extraction using Supelco Envi-C₁₈ cartridges. The cartridge was eluted with 3 ml of hexane and the same volume of isooctane, and the evaporated extract was dissolved in isooctane and analysed for trifluralin by GC (see section Analytical method section). The recovery efficiencies of the extraction were determined by analysing all soil samples after their spiking with trifluralin at two concentration levels of 5 and 10 mg · kg⁻¹. Recovery efficiencies of trifluralin from soils ranged from 86 % to 93 %. The detection limit of the analytical method used was 0.05 mg · kg⁻¹.

Analytical method

Trifluralin concentrations in all extracts from sorption and dissipation experiments were analysed by a gas chromatography (GC; HP model 5890A Series II) equipped with NP detector. The column used was BD-5 (15 m x 0.53 mm i.d.; 0.5 µm). Oven and injector temperatures were 280 °C and 230 °C, respectively. Helium was used as a mobile phase with a flow rate of 5 ml · min⁻¹. Peak areas were estimated using an integrator (HP model 3396 Series II). Retention time of trifluralin was 6.90 min under these chromatographic conditions and uncertainty of the measurement was ±15 %. External solution standards were used to establish linear calibration curves for a NP detector.

Data analysis

The amount of trifluralin sorbed per unit weight of soil was calculated as the difference between the initial and equilibrium concentrations of trifluralin in solution using the equation:

$$S = \frac{(C_0 - C) \times V}{m} \quad (1)$$

where S (mg · kg⁻¹) is the amount of trifluralin sorbed per unit weight of soil, C_0 and C (mg · l⁻¹) are the initial and equilibrium trifluralin concentrations in solution, respectively, V (l) is the volume of solution and m (kg) is the weight of soil.

The amount of trifluralin desorbed from soil in each desorption step was calculated as:

$$S_d = \left[C_d - \left(C \times \frac{V - V_r}{V} \right) \right] \times \frac{V}{m} \quad (2)$$

where S_d (mg · kg⁻¹) is the amount of herbicide desorbed from soil, C_d (mg · l⁻¹) is the analytically measured concentration of desorbed herbicide in solution and V_r (l) is the volume of solution removed from each tube and replaced by the same volume of trifluralin-free calcium chloride solution; in this case V_r is equal to 0.008 l.

Sorption and desorption isotherms were obtained by plotting the amount of trifluralin sorbed by soil versus

its equilibrium concentration in solution. Sorption and desorption data were fitted to the logarithmic form of the Freundlich isotherm equation:

$$\log S = 1/n_{s/d} \log C + \log K_{fs/d} \quad (3)$$

where K_{fs} and K_{fd} (mg^(1-1/n) l^{1/n} kg⁻¹) are the Freundlich sorption and desorption coefficients, respectively, and $1/n$ is the Freundlich exponent, which indicates curvature of the isotherm. The hysteresis (H) was calculated as the ratio between $1/n_d$ and $1/n_s$, corresponding to desorption and sorption Freundlich exponents, respectively.

If determined sorption or desorption isotherms are linear, they fit to the Henry's law isotherm, which is given by the equation:

$$S = K_d \times C \quad (4)$$

where K_d (l · kg⁻¹) is the distribution coefficient. Assuming that soil organic carbon acts as the sole sorbent, organic carbon distribution coefficient (K_{oc} , l · kg⁻¹) can be calculated from the equation:

$$K_{oc} = \frac{K_d}{\text{TOC}(\%)} \times 100\% \quad (5)$$

where TOC (%) is the total organic carbon content of a given soil (Hamaker and Thompson, 1972).

The rate of disappearance of trifluralin from all soils was described by the linear form of the first-order kinetic equation:

$$\ln C_t = -k \times t + \ln C_0 \quad (6)$$

where C_0 and C_t (mg · kg⁻¹) are the initial herbicide content in soil and the herbicide content in soil at time t , respectively, k (day⁻¹) is the first-order rate constant and t (day) is the time. From the obtained k values, the dissipation half-life values (DT₅₀, day) were calculated using the equation:

$$\text{DT}_{50} = \frac{\ln 2}{k} \quad (7)$$

Groundwater Ubiquity Score was calculated using the following equation:

$$\text{GUS} = \log(\text{DT}_{50}) \times [4 - (\log K_{oc})] \quad (8)$$

According to GUS values, Gustafson (1989) divided the leaching potential of a pesticide into three categories. When GUS <1.8, pesticide can be classified as non-leacher, when GUS >2.8, pesticide may pose a risk of leaching to groundwater, and GUS between 1.8–2.8 means that pesticide has transitional tendency to be leached.

Relationships among variables were tested using Pearson's correlation coefficient (r) at a significance level (p) of 0.05 or lower. Statistical analysis was performed by a program SPSS Statistics.

Results and discussion

Sorption

Because the measured sorption isotherms were essentially linear for all soil samples as indicated by $1/n_s$ values close to 1 (Fig. 1; Tab. 2), K_{fs} could be considered as equivalent to distribution coefficient K_d . It can be seen from K_{fs} and K_d values given in Tab. 2 that sorption of trifluralin in soils is very high. Based on both the K_{fs} and K_d values, the extent of trifluralin sorption in each soil type decreased with increasing soil depth (Tab. 2). Considering all the soil samples, the order of decreasing sorption was: horizon A of Phaeozem > horizon B of Phaeozem > horizon A of Chernozem > horizon B of Chernozem > horizon A of Fluvisol > horizon B of Fluvisol > horizon C of Chernozem, and corresponded fully to the decrease of total organic carbon content in the soils. Statistical analyses (Tab. 3) showed that the sorption of trifluralin in soils was correlated strongly with TOC ($r = 0.99$, $p < 0.001$), and C_{HA} and C_{FA} ($r = 0.99$ and 0.96 , $p < 0.001$, respectively). The fact that capability of a soil to sorb trifluralin is determined mostly by total organic carbon content of the soil was confirmed also in previous studies (Cooke et al., 2004; Boivin et al., 2005; Hiller et al., 2008; Kodešová et al., 2010; Leovac et al., 2015). From the obtained K_d values, organic carbon sorption coefficient (K_{oc} , $l \cdot kg^{-1}$) was calculated from the equation (5). In sorption theory, this distribution coefficient (K_{oc}) expresses the amount of pesticide sorbed per unit of soil organic carbon. Assuming that organic matter is the only constituent of soils contributing to sorption and it sorbs similarly in all soils, the K_{oc} values of a pesticide will be essentially constant for a group of soils and can be used to compare the relative mobility of a pesticide in soils (Hamaker and Thompson, 1972; McCall et al., 1980). In this study, the calculated K_{oc} values were very similar among the soils and varied only by a factor of 1.36 ($K_{oc} = 4\,414\text{--}6\,027\,l \cdot kg^{-1}$; Tab. 2), confirming that organic matter of the soils had almost identical sorption affinity for trifluralin. However, still observed low variation in K_{oc} values indicates that qualitative properties of soil organic carbon appear to be important for trifluralin sorption in soils. In fact, there were significant positive correlations between the K_{oc} values and the C_{HA}/C_{FA} ratio ($r = 0.90$, $p < 0.01$) or the C_{HA}/TOC ratio ($r = 0.91$, $p < 0.01$). This shows that more humified organic matter is a better sorbent of trifluralin and increases overall capability of the soil to sorb the herbicide. A few of previous studies confirmed that humification degree of soil organic matter played an important role in the sorption not only of relatively apolar pesticides, such as atrazine and acetochlor (Dousset et al., 1994; Hiller et al., 2009), but also of highly polar pesticides like MCPA (López-Piñeiro et al., 2013; Peña et al., 2015). The values of K_{oc} for trifluralin determined in this study are comparable with those given in some previous studies. For example, Cooke et al. (2004) obtained K_{oc} values for trifluralin in five agricultural soils from UK in a range of $5\,202\text{--}7\,838\,l \cdot kg^{-1}$ or Hiller et al. (2008) recorded trifluralin K_{oc} values between $3\,750\text{--}9\,253\,l \cdot kg^{-1}$ for six agricultural soils. On the other hand, much higher K_{oc} values of trifluralin in soils

($27\,250\text{--}51\,670\,l \cdot kg^{-1}$) found Francioso et al. (1992) due to the high content of clay fraction in their soils, which might significantly contribute to the overall sorption of trifluralin in these soils, and thus increase the value of K_{oc} . Interestingly, there was also a positive significant correlation of K_{fs} and K_d values with Al_{ox} contents ($r = 0.94$ and 0.93 , $p < 0.01$, respectively). However, positive influence of non-crystalline to poorly crystalline Al oxides on trifluralin sorption would be unlikely due to positive significant relationship between Al_{ox} and TOC ($r = 0.92$, $p < 0.01$). Unfortunately, there are no studies regarding the adsorption of dinitrobenzenamides onto Al oxides, but Clausen et al. (2001) confirmed that uncharged herbicides like isoproturon and atrazine did not adsorb on the Al-surfaces of α -alumina.

Desorption

Desorption of pesticides from soils is the opposite process to their sorption, when pesticides are released from soil into the soil solution, and therefore determines the final distribution of pesticides between soil and water and their propensity to be leached into the surface- and groundwaters. Desorption isotherms are presented in Fig. 1, following four desorption cycles with $0.01\,M$ $CaCl_2$ aqueous solution. Desorption isotherms were adequately described by the linear form of the Freundlich equation and the Freundlich desorption parameters K_{fd} and $1/n_d$ are given in Tab. 2. The extent of trifluralin desorption from all soil samples was far lower than its sorption as shown by low percentages of trifluralin desorption (P_d) after four successive cycles and very low values of H (Tab. 2). Only 2.30–6.23 % of the total amount of trifluralin sorbed in soils could be desorbed, indicating that sorption is not reversible process, i.e. a hysteresis exists in the sorption–desorption of trifluralin in the studied soils. The extent of desorption from the soils was almost fully opposite to its sorption and the following order of decreasing desorption was obtained based on the values of P_d : horizon B of Fluvisol > horizon A of Fluvisol > horizon B of Chernozem > horizon C of Chernozem > horizon B of Phaeozem > horizon A of Chernozem > horizon A of Phaeozem. This desorption order showed that less trifluralin desorbed from soils, which had high organic carbon content and vice versa. Statistical analysis (Tab. 3) confirmed that percentages of trifluralin desorbed were negatively correlated to soil organic carbon content ($r = -0.78$, $p < 0.05$) and even more significantly to humic acid carbon content ($r = -0.84$, $p < 0.05$). Cooke et al. (2004) and Boivin et al. (2005) also observed a low extent of trifluralin desorption from soils when fractions of desorbed trifluralin ranged between 3.90–15.2 % and on average 17.3 %, respectively. The authors pointed out that soils having high total organic matter content retained trifluralin more strongly in comparison to those with low TOC, and concluded that the herbicide was highly immobile, thereby preventing its leaching into groundwaters. Additionally, there was a significant negative correlation between the K_d values and the P_d values ($r = -0.84$, $p < 0.05$) (Tab. 4), indicating that the higher and stronger the sorption of trifluralin in the soil, the more difficult its desorption.

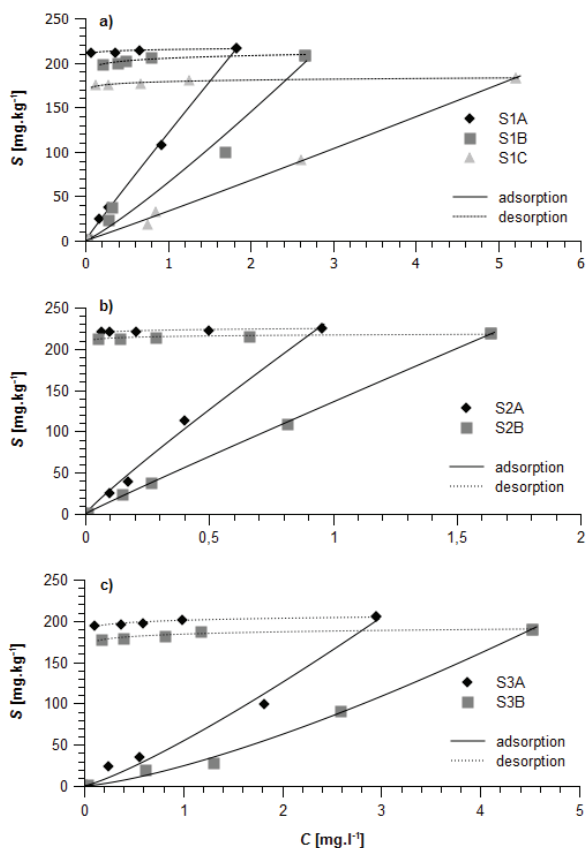


Fig. 1. Sorption and desorption isotherms of trifluralin in the soils. **a)** soil samples S1A, S1B, and S1C represent soil horizons A, B, and C of Calcaro-Haplic Chernozem, respectively; **b)** S2A and S2B are soil horizons A and B of Fulvi-Calcaric Phaeozem, respectively; **c)** S3A and S3B denote soil horizons A and B of Calcaric Fluvisol, respectively. Lines are the fitted Freundlich sorption and desorption isotherms. Each point represents mean value calculated from two duplicate samples.

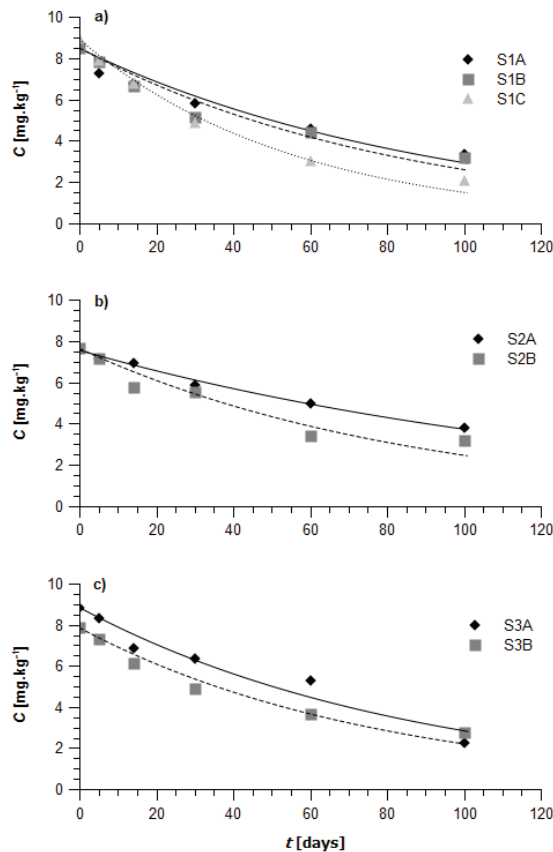


Fig. 2. Dissipation curves of trifluralin in soil samples. **a)** symbols S1A–C denote A–C horizons of the Calcaro-Haplic Chernozem; **b)** S2A and B are A and B horizons of the Fulvi-Calcaric Phaeozem, and **c)** S3A and B denote A and B horizons of the Calcaric Fluvisol. Lines are the fitted first-order degradation kinetics. Each point represents mean value calculated from two duplicate samples.

Dissipation

It is known that the main dissipation pathways of trifluralin in soils are volatilization due to its relatively high vapor pressure and microbial degradation. Therefore, its disappearance from soils under laboratory conditions is governed by a combination of the above-mentioned dissipation pathways. Dissipation curves of trifluralin in soil horizons of each soil type are presented in Fig. 2. The rate of disappearance of trifluralin from all soils was described well by the first-order kinetic equation. The obtained values of both dissipation parameters k and DT_{50} are given in Tab. 2. The estimated k values ranged from 0.007 to 0.015 day^{-1} and DT_{50} values varied between 46 and 99 days. These values are similar to those obtained for soils by others under aerobic conditions (Mamy et al., 2005; EFSA, 2009; Sengupta et al., 2009). However, in tropical regions of high temperatures and humidity, much lower DT_{50} values for trifluralin in soils than those in the present study were obtained (Laabs et al., 2000). According to the classification of pesticide persistence based on the DT_{50}

values (Greenhalgh, 1980), trifluralin may be categorized as persistent in the A horizon of Fulvi-Calcaric Phaeozem and moderately persistent in all other soil samples. Considering each soil type, trifluralin disappearance was significantly slower in the A horizons of Fulvi-Calcaric Phaeozem and Calcaro-Haplic Chernozem than in the deeper soil horizons, i.e. rate of its dissipation in soils was depth-dependent. Statistical analysis of the effect of soil properties on the dissipation parameters was performed (Tab. 3). The results of this analysis showed the main effect of TOC and C_{HA} on the persistence of trifluralin in soils ($r = 0.90$ and 0.91 , $p < 0.01$, respectively). This means that trifluralin is more persistent in soils having higher contents of total organic carbon and humic acid carbon, i.e. in the A horizons of the soils, than soils with lower TOC and C_{HA} . Furthermore, as shown in Tab. 4, strong positive relationships between the sorption–desorption parameters K_d , K_{fs} and K_{fd} and the dissipation half-lives were observed ($r = 0.90$, 0.91 and 0.89 , $p < 0.01$, respectively). Thus, the persistence of trifluralin was highly affected by its sorption–desorption in the soils when soils with the elevated capability to retain trifluralin

Tab. 2

Mean values of sorption–desorption and degradation parameters for trifluralin in each soil type and the corresponding GUS values.
For detailed explanation, see text

Soil type	Calcaro-Haplic Chernozem			Fulvi-Calcaric Phaeozem		Calcaric Fluvisol	
	S1A	S1B	S1C	S2A	S2B	S3A	S3B
K_{fs}^a (mg ^(1-1/n) l ^{1/n} kg ⁻¹)	123	78.2	32.8	239	137	66.7	33.3
$1/n_s^b$	0.94	0.94	1.01	0.96	0.94	1.01	0.97
r^2	0.99	0.99	0.99	0.99	0.99	0.98	0.98
K_d^c (l . kg ⁻¹)	119	73.5	34.8	243	134	65.5	39.1
r^2	0.99	0.96	0.99	0.99	0.99	0.97	0.96
K_{oc}^d (l . kg ⁻¹)	5 678	5 296	6 027	5 500	5 797	4 447	4 414
K_{fd}^e (mg ^(1-1/n) l ^{1/n} kg ⁻¹)	215	205	179	225	217	201	184
$1/n_d^f$	0.007	0.021	0.014	0.008	0.008	0.018	0.022
r^2	0.80	0.92	0.92	0.87	0.85	0.86	0.89
H^g	0.007	0.022	0.014	0.008	0.008	0.017	0.023
P_d^h (%)	2.64	4.89	4.69	2.30	2.71	5.29	6.23
k^i (day ⁻¹)	0.009	0.009	0.015	0.007	0.009	0.012	0.011
DT_{50}^j (day)	77.0	77.0	46.2	99.0	77.0	57.8	63.1
GUS ^k	0.46	0.52	0.37	0.52	0.45	0.62	0.64

^aFreundlich sorption coefficient^bFreundlich exponent for sorption^cdistribution coefficient^dorganic carbon distribution coefficient^eFreundlich desorption coefficient^fFreundlich exponent for desorption^ghysteresis index^hpercentage of desorptionⁱfirst-order rate constant^jdissipation half-life^kGroundwater Ubiquity Score

Tab. 3

Pearson's correlation coefficients (r) for relationships between the soil properties and the sorption–desorption (K_{fs} , K_d , K_{oc} , K_{fd} , H and P_d) or dissipation (k and DT_{50}) parameters

	TOC	C_{HA}	C_{FA}	C_{HA}/C_{FA}	C_{HA}/TOC	pH(H ₂ O)	pH(KCl)	CaCO ₃	CEC	Fe _{ox}	Al _{ox}	Sand	Silt	Clay
K_{fs}	0.99****a	0.99***	0.96***	0.36	0.30	-0.86*	-0.70	-0.13	0.96***	0.49	0.94**	0.63	-0.54	-0.52
K_d	0.99***	0.99***	0.97***	0.33	0.27	-0.85*	-0.69	-0.15	0.95***	0.52	0.93**	0.64	-0.54	-0.56
K_{oc}	0.22	0.35	0.12	0.90**	0.91**	0.02	0.08	-0.57	0.48	-0.59	0.39	-0.08	-0.19	0.53
K_{fd}	0.87*	0.89**	0.80*	0.46	0.32	-0.89**	-0.76*	0.17	0.83*	0.36	0.85*	0.57	-0.55	-0.37
H	-0.64	-0.69	-0.54	-0.65	-0.47	0.56	0.55	0.44	-0.65	0.08	-0.59	-0.38	0.45	0.08
P_d	-0.78*	-0.84*	-0.68	-0.74	-0.59	0.67	0.59	0.29	-0.84*	-0.01	-0.79*	-0.43	0.51	0.10
k	-0.80*	-0.81*	-0.75	-0.27	-0.15	0.79*	0.67	-0.39	-0.77*	-0.54	-0.80*	-0.56	0.48	0.47
DT_{50}	0.90**	0.91**	0.86*	0.30	0.23	-0.82*	-0.67	0.18	0.89**	0.57	0.89**	0.57	-0.47	-0.50

^asymbols (***), (**) and (*) denote significant correlations at a significance level (p) of <0.001, <0.01 and <0.05, respectively

were less efficient in the herbicide dissipation and led to its higher persistence (Zimdahl and Gwynn, 1977; Mamy et al., 2005). It has been shown that enhanced sorption and reduced desorption may limit herbicide degradation rate in soil by reducing its concentrations in the aqueous solution (Dyson et al., 2002; Jensen et al., 2004) and consequently, herbicide bioavailability to soil degrading microorganisms (Katayama et al., 2010) because herbicide molecules are more bioavailable in their dissolved state than bound by soils. Therefore, it seems that the dissipation of trifluralin in the studied soils occurred mainly via volatilization rather than microbial degradation because only low proportions of trifluralin could be released from its sorbed state into the aqueous solution (Tab. 2). Various authors pointed out that microbial degradation of trifluralin in soils was not the main dissipation mechanism for this herbicide (Savage, 1973; Laabs et al., 2002). Mamy et al. (2005) performed environmental fate study with ^{14}C -labelled trifluralin in three soils and showed that trifluralin losses from the soils were mostly due to its significant volatilization.

Leaching to groundwater

Taking into account the high capability of the soils to retain trifluralin, the herbicide was unlikely to pose a risk for groundwater quality via its leaching through the soil in the region of Žitný ostrov at the time of its use, i.e. before year 2010. This conclusion was supported by the groundwater monitoring data from this region, which showed that trifluralin was not detected in groundwater samples collected in 2008–2009 (personal communication by Andrea Luptáková from Slovak Hydrometeorological Institute in Bratislava). This is also consistent with the calculated values of Groundwater Ubiquity Score (GUS) (Tab. 2), which includes in a single equation two main factors affecting the behavior of a pesticide in the soil

Tab. 4
Correlation matrix showing relationships between sorption, desorption and dissipation parameters

	K_{ts}	K_{d}	K_{oc}	K_{fd}	H	P_{d}	k
K_{ts}							
K_{d}	0.99****a						
K_{oc}	0.33	0.32					
K_{fd}	0.90**	0.88**	0.26				
H	-0.71	-0.70	-0.67	-0.66			
P_{d}	-0.85*	-0.84*	-0.69	-0.83*	0.93**		
k	-0.81*	-0.80*	-0.04	-0.88**	0.35	0.61	
DT_{50}	0.91**	0.90**	0.17	0.89**	-0.45	-0.70	-0.97***

a symbols (**), (*) denote significant correlations at a significance level (p) of <0.001, <0.01 and <0.05, respectively

environment: sorption as K_{oc} and dissipation as DT_{50} . The values of GUS for trifluralin in each soil type were much less than 1.8, corresponding to the category of non-leacher pesticides. Despite this, although trifluralin was not detected in groundwaters of the Žitný ostrov in the past when it was used extensively, its occurrence was recorded in groundwaters from other countries like USA, Spain and Greece (Gilliom, 2007; Dores et al., 2008; Vryzas et al., 2012). The occurrence of trifluralin in groundwater below agricultural fields was attributed to the colloid-facilitated transport of trifluralin through preferential flow pathways in the soil because this herbicide has strong sorption affinity for natural solid particles.

Conclusions

The results of this study confirmed that sorption of trifluralin in agricultural soils of the Žitný ostrov was strong and high with consecutively low extent of its desorption from soils. Thus, the soils were effective in the immobilization of trifluralin, preventing it to migrate into other environmental compartments, such as groundwater. Trifluralin was shown to be moderately persistent up to persistent in the soils and the persistence was in a direct relationship to the extent of trifluralin sorption, i.e. sorption inhibited the rate of its dissipation in the soils. All three environmental fate processes were depth-dependent. Trifluralin sorption and persistence were higher in the A soil horizons than the corresponding B or C soil horizons of each soil type, and vice versa for its desorption from soils. Sorption–desorption and dissipation of trifluralin in these soils were affected mainly by organic components of the soils, e.g. total organic carbon content, humic and fulvic acid carbons, with negligible or no role of inorganic soil constituents. According to the determined sorption–desorption and dissipation parameters under laboratory conditions and the calculated GUS values, trifluralin did not represent risks to groundwater quality in the region, resulting from its leaching through the soil profiles to groundwater.

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Sorpcia, desorpcia a odbúravanie trifluralínu v poľnohospodárskych pôdach Žitného ostrova (Podunajská nížina)

Distribúcia (napr. sorpcia a desorpcia) a odbúravanie pesticídov v pôdach sú najdôležitejšie biogeochemické procesy, ktoré určujú pohyblivosť týchto zlúčenín v pôdnom prostredí a ich prestup do prírodných vôd. Z praktického hľadiska je štúdium sorpčných a degradačných procesov pesticídov dôležité predovšetkým v tých oblastiach, kde sa nachádzajú podzemné vody určené na ľudskú spotrebu, pretože aplikované prípravky proti škodcom na poliach môžu migrovať pôdnym profilom až k hladine podzemnej vody a znehodnotiť jej chemické vlastnosti. Preto hlavným cieľom tejto práce bolo laboratórne stanovenie sorpčných a degradačných vlastností trifluralínu v základných pôdnych typoch Žitného ostrova s cieľom posúdenia pohyblivosti trifluralínu v pôdnych profiloch. Hoci trifluralín sa už v súčasnosti nepoužíva ako pesticíd na ničenie burín v poľnohospodárstve Slovenskej republiky, v čase realizácie tejto štúdie, teda v roku 2009, patril k najpoužívanejším herbicidom na Žitnom ostrove. Jednotlivé pôdne typy (černozeme, čiernice a fluvizeme) boli odobraté z rôznych horizontov pomocou ručne vykopaných pôdnych sond. Ich základné vlastnosti sú uvedené v tab. 1. Sorpcia, desorpcia a odbúravanie trifluralínu v pôdach boli realizované pomocou nádobkových experimentov.

Stanovená závislosť koncentrácie trifluralínu sorbovaného v pôdach (S) od jeho rovnovážnej koncentrácie v roztoku (C) vyhovovala Freundlichovej adsorpčnej izoterme (rovnica 3) (obr. 1). Hodnoty $1/n_s$ boli buď rovné 1, alebo blízko hodnoty 1 (tab. 2), čo znamená, že medzi S a C je priamo úmerný vzťah, t. j. zistené adsorpčné izotermy majú lineárny tvar, a preto vyhovovali tiež Henryho adsorpčnej izoterme (rovnica 4). Ako naznačujú hodnoty Freundlichovej sorpčnej konštanty (K_{fs}) a distribučného koeficientu (K_d) (tab. 2), intenzita sorpcie trifluralínu vo všetkých pôdach bola vysoká. Štatistickým spracovaním výsledkov sa ukázalo, že najväčší vplyv na sorpciu trifluralínu v pôdach mal obsah pôdneho organického uhlíka ($r = 0,99$; $p < 0,001$) a obsah uhlíka humínových a fulvo kyselín ($r = 0,99$ a $0,96$; $p < 0,001$) (tab. 3). Tieto kladné korelácie dokumentujú, že pôda s vyšším obsahom organickej hmoty má aj vyššiu kapacitu akumulovať trifluralín, a to podľa tohto poradia:

čiernica (A horizont) > čiernica (B horizont) > černozem (A horizont) > černozem (B horizont) > fluvizem (A horizont) > fluvizem (B horizont) > černozem (C horizont). Opačný proces k sorpcii – desorpcia – bol sledovaný v štyroch po sebe nasledujúcich krokoch (obr. 1). Celkový podiel trifluralínu uvoľneného z pôd do vodného roztoku bol nízky ($P_d = 2,30$ až $6,23$ %; tab. 2), pravdepodobne pre nízku rozpustnosť herbicidu vo vode ($0,221 \text{ mg} \cdot \text{l}^{-1}$ pri $20 \text{ }^\circ\text{C}$) a jeho lipofilnú povahu ($\log K_{ow} = 5,27$). Nízka desorpcia trifluralínu naznačuje, že pôdy Žitného ostrova výrazne imobilizujú herbicid a jeho rezíduá nie sú za normálnych okolností transportované k hladine podzemnej vody. Desorbované podiely trifluralínu boli v nepriamej úmere k intenzite sorpcie (tab. 4). Vyšší podiel trifluralínu sa uvoľnil z pôd s nižšou intenzitou sorpcie a naopak ($r = -0,84$; $p < 0,05$).

Odbúravanie trifluralínu v pôdach vyhovovalo rýchlostnej rovnici prvého poriadku (rovnica 6), pričom degradačné krivky sú na obr. 2 a zistené rýchlostné konštanty (k) a polčasy rozkladu (DT_{50}) sú uvedené v tab. 2. Z hodnôt DT_{50} , ktoré boli v intervale od 46 dní až po 99 dní, vyplýva, že trifluralín v A horizonte čiernice možno považovať za perzistentný a v ostatných pôdnych vzorkách za mierne perzistentný. Perzistencia trifluralínu vyjadrená veličinou DT_{50} bola vyššia v pôdach s vyšším obsahom organického uhlíka ($r = 0,90$; $p < 0,01$) a zároveň aj s vyššou intenzitou sorpcie vyjadrenou distribučným koeficientom K_d ($r = 0,90$; $p < 0,01$). To znamená, že perzistencia trifluralínu v týchto pôdach bola ovplyvnená najmä ich sorpčnou kapacitou voči herbicidu. Trifluralín sa odbúraval pomalšie v pôde, ktorá účinnejšie sorbovala herbicid, a naopak.

Zo zistených charakteristických vlastností sorpcie a odbúravania trifluralínu v profiloch troch pôdnych typov, ktoré sa najčastejšie vyskytujú na Žitnom ostrove, vyplýva, že jeho pohyblivosť je nízka a nemal žiadny negatívny vplyv na podzemné vody ani v čase intenzívneho používania na poliach (pred rokom 2010). Nízka pohyblivosť sa potvrdila aj výpočtom hodnôt GUS (rovnica 8), ktoré boli nižšie ako prahová hodnota 1,8 (tab. 2), a absenciou trifluralínu vo vzorkách podzemných vôd v predmetnej oblasti z rokov 2008 – 2009, keď sa tento herbicid používal.