

## Article

# Dissipation Kinetics, Leaching, and Ecological Risk Assessment of S-Metolachlor and Benfluralin Residues in Soil

Paraskevas Parlakidis <sup>1,\*</sup>, George S. Adamidis <sup>1</sup>, Georgios D. Gikas <sup>2</sup>, Sofia Vasiliou <sup>1</sup>, Melpomeni Kissa <sup>1</sup>, Konstantinos Doitsinis <sup>1</sup>, Christos Alexoudis <sup>1</sup> and Zisis Vryzas <sup>1</sup>

- <sup>1</sup> Laboratory of Agricultural Pharmacology and Ecotoxicology, Faculty of Agricultural Development, Democritus University of Thrace, 193 Pantazidou, 68200 Orestias, Greece; gadamidi@agro.duth.gr (G.S.A.); sofiavasiliou@gmail.com (S.V.); menikissa@gmail.com (M.K.); kostasdoitsinis@gmail.com (K.D.); calexoud@agro.duth.gr (C.A.); zvryzas@agro.duth.gr (Z.V.)
- <sup>2</sup> Laboratory of Ecological Engineering and Technology, Department of Environmental Engineering, School of Engineering, Democritus University of Thrace, 67100 Xanthi, Greece; ggkikas@env.duth.gr
- \* Correspondence: pparlaki@agro.duth.gr

**Abstract:** The use of selective herbicides is one of the best methods for weed management. However, the extensive use of herbicides can have adverse impacts on non-target organisms. The goals of this study were to assess the dissipation kinetics, leaching, and ecological risk assessment of S-metolachlor and benfluralin residues in silty loam soil planted with chickpea (*Cicer arietinum* L.). The experimental setup included four different layers with four replications corresponding to an experimental randomized complete block design consisting of 16 plots. The application doses of S-metolachlor and benfluralin were 1350 and 1920 g a.i./ha, respectively, according to manufacturer recommendations. Soil samples were split into four depths, 0 to 20 cm (Layer A), 20 to 40 cm (Layer B), 40 to 60 cm (Layer C), and 60 to 80 cm (Layer D), to determine the dissipation kinetics and the leaching behavior of the herbicides. Gas chromatography coupled with the electron capture detector (GC-ECD) method was developed and validated for the determination of S-metolachlor and benfluralin residues in soil. The analytes were extracted from the soil with distilled water and ethyl acetate followed by solid-phase extraction (SPE). The limit of quantification (LOQ) of the method was 0.1 µg/g, and the recoveries of S-metolachlor and benfluralin were in the ranges 81% to 97% and 88% to 101%, respectively, with relative standard deviations (RSD) of less than 9.7%. The dissipation kinetics of S-metolachlor and benfluralin in soil (0–20 cm) followed first-order kinetics with half-lives of 21.66 and 30.13 days, respectively. The results for samples obtained from the 20–80 cm soil profile showed that both benfluralin and S-metolachlor presented high leaching, following preferential flow. Also, a soil ecological risk assessment was conducted in the top 0–20 cm soil profile, estimating the toxicity–exposure ratio (TER) for four soil organisms and the risk quotient (RQ). The mean herbicide levels found at the studied soil profile at 0 days (2 h) and 60 days of the experiment were used for risk assessment. In the first case, the mean pesticide concentration (MPC) gives a worst-case scenario (ws); in the second case, a dissipation scenario (ds) is given using the respective MPC. In all cases, both TER and RQ values showed that benfluralin corresponds to a higher risk than S-metolachlor for soil organisms.

**Keywords:** S-metolachlor; benfluralin; dissipation; leaching; preferential flow; ecological risk assessment; GC-ECD



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## 1. Introduction

Soil pollution is an international issue with both natural and anthropogenic causes. Compounds, chemicals, and chemical agents have been used as a result of urbanization, industrialization, and rising food consumption, which over time has led to the dispersion and buildup of pollutants in the environment [1]. Heavy metals, pesticides, and polycyclic aromatic hydrocarbons (PAHs) are typical soil contaminants [2]. The European Commission

has already named eight soil concerns in the 2006 EU Soil Strategy: soil erosion, soil contamination, floods and landslides, reduction in soil organic matter, salinization, soil compaction, soil sealing, and soil biodiversity [3]. The newly released “EU Soil Strategy for 2030” highlights the advantages of healthy soils for people, food, nature, and climate, demonstrating how the soil will be treated in the future [4].

The environmental behavior of pesticides can be influenced by several factors and mechanisms. The run-off, adsorption, and leaching potential of pesticides is significantly influenced by the soil’s properties, including its organic carbon content, texture, pH, type of clay mineral, dissolved organic matter, and cation exchange capacity, and the physicochemical characteristics of the pesticides, such as their ionization, water solubility, volatility, octanol–water partition coefficients, and thermo-, photo-, and hydrolysis stability all have an impact on pesticide fate [5]. The intensity of rainfall and irrigation, biological processes (biodegradation), and agricultural techniques also affect pesticide fate [6].

Pesticides that have not been absorbed or broken down while moving through the soil, a process known as leaching, move down into the lower soil layers with percolating water. If appropriate filtration procedures are lacking, pesticides which have leached from the soil and are moving through the rock layer are likely to pollute groundwater. Evaluating pesticides’ leaching behavior in agricultural soils is crucial to prevent the contamination of groundwater [7].

Weed infestation raises production expenses, lowers yields, and degrades product quality. The use of selective herbicides is one of the best methods for weed management [8]. Herbicides are used to prevent weeds and crops from competing with each other. Herbicides are applied at the highest concentrations of active chemicals per hectare of all pesticides. They can efficiently suppress weeds when used alone or in mixes, but they can also cause unexpected side effects on organisms inside and beyond the treated field. The amount of herbicide that reaches the target plants is frequently less than 0.1%, with the remainder absorbed by the crop, left in the soil, or polluting the environment [9].

Both terrestrial and aquatic environments have started to demonstrate the negative impacts of herbicides’ excessive use on non-target species, either directly or indirectly. Species that play significant ecological roles in agroecosystems, such as nematodes, earthworms, collembolans and isopods, spiders, and insects, have shown the physiological and behavioral consequences of exposure at the organism level [10].

Ecological risk assessment is required for the safe usage of pesticides and the sustainable management of soil ecosystems. The key aspects of the EFSA’s risk assessment process are the evaluation of exposure and the characterization of risk. The toxicity–exposure ratio (TER), which measures the relationship between toxicity and exposure concentrations, determines the risks caused by pesticides [11]. The risk quotient (RQ) approach is frequently used in the environmental risk assessment of pesticides and other chemicals to assess risk quantitatively. A basic formula for calculating RQ is to divide a number for environmental exposure by a value for the toxicity endpoint. The RQ is the ratio of exposure to effect as a result. Risk analysts and other decisionmakers can then utilize the RQ to determine whether the value exceeds established threshold levels of concern [12].

S-metolachlor (GAS name: (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl) acetamide) is regularly used on more than 70 crops and has been available for more than 60 years. S-metolachlor is a selective chloroacetamide herbicide approved for use on a variety of high-value, small-acreage crops, including several vegetables and small fruits as well as major field crops including cotton, corn, soybeans, and cotton. It performs effectively on small-seeded broadleaf plants and annual grasses. S-metolachlor’s residual activity increases its usefulness for managing weeds that are resistant to post-emergence herbicides [13]. It is classified as an inhibitor of very-long-chain fatty acid formation [14].

Dinitroaniline pesticide benfluralin (GAS name: (N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl) benzenamine) is used as a pre-emergence herbicide to manage grasses and broad-leaved weeds in numerous crops, such as alfalfa, clover, lettuce, bean, pea, and other crops. It disrupts the mitotic cycle of weeds, which stunts their growth [15,16]. By 12

August 2023, the member states of the EU must revoke authorizations for plant protection products that use benfluralin as an active ingredient. However, other countries with significant agricultural sectors, such as the UK, have approved its use [16]. Any grace time given to member states in accordance with Article 46 of Regulation (EC) No. 1107/2009 will expire on 12 May 2024 [17].

According to our knowledge, the majority of studies describe adsorption or degradation experiments, dissipation kinetics, and leaching behavior for S-metolachlor and benfluralin in laboratory conditions, usually using batch experiments or soil columns [10]. In our opinion, a similar experiment in field conditions could fill a research gap.

Validation of the methods for the qualification and quantification of the two herbicides is necessary to show that it is appropriate for the intended purpose and to ensure the reliability of the results, and is frequently lacking in published studies. This can be achieved through a variety of tests, which can allow researchers to pinpoint important technique and performance characteristics, such as selectivity, limits of detection and quantitation, working range, sensitivity, trueness, precision, and measurement uncertainty [18]. Similarly, pesticide risk assessment studies are usually missing, even though they are mandatory for pesticide registration.

The well-known solid-phase extraction (SPE) technique and gas chromatograph systems equipped with electron capture detectors (GC-ECD) provide satisfactory analytical methods for numerous pesticides. Surprisingly, SPE paired with the GC-ECD method for S-metolachlor and benfluralin determination in soil is missing in the literature. Therefore, the objectives of this study are (a) to validate a simple, sensitive, and effective method to determine S-metolachlor and benfluralin residues in soil under chickpea cultivation based on SPE using GC-ECD, (b) to study the persistence, dissipation, and leaching of S-metolachlor and benfluralin in soil, and (c) to determine whether herbicide residues pose a risk to soil organisms, such as earthworms (*Eisenia fetida*), enchytraeids (*Enchytraeus crypticus*), springtails (*Folsomia candida*), and mites (*Hypoaspis aculeifer*), as well as nitrogen and carbon mineralization microorganisms, according to the EFSA's guidelines [19].

## 2. Materials and Methods

### 2.1. Reagents and Materials

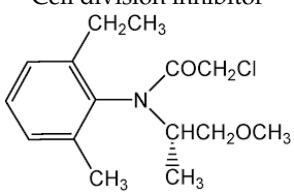
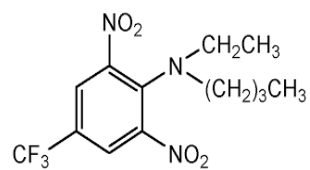
S-metolachlor and benfluralin analytical standards (purity 99.5%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Table 1 presents the physico-chemical parameters of the herbicides. Methanol and ethyl acetate of HPLC-grade purity and n-hexane of proanalysis grade were obtained from Riedel de Haen (Seelze, Germany). They were utilized for the cleanup and elution of the samples. Sodium chloride was purchased from Sigma-Aldrich (Zwijndrecht, The Netherlands) and was used during the herbicide extraction process. C18 cartridges (1000 mg, 6 mL; Thermo Scientific™, Vantaa, Finland) were used for solid-phase extraction (SPE). The commercial formulations Dual Gold 96 EC (S-metolachlor) and Bonalan 18 EC (benfluralin) were provided by Syngenta Hellas S.A. (Thessaloniki, Greece) and Gowan Crop Protection Limited (Yuma, AZ, USA), respectively.

### 2.2. Experimental Setup

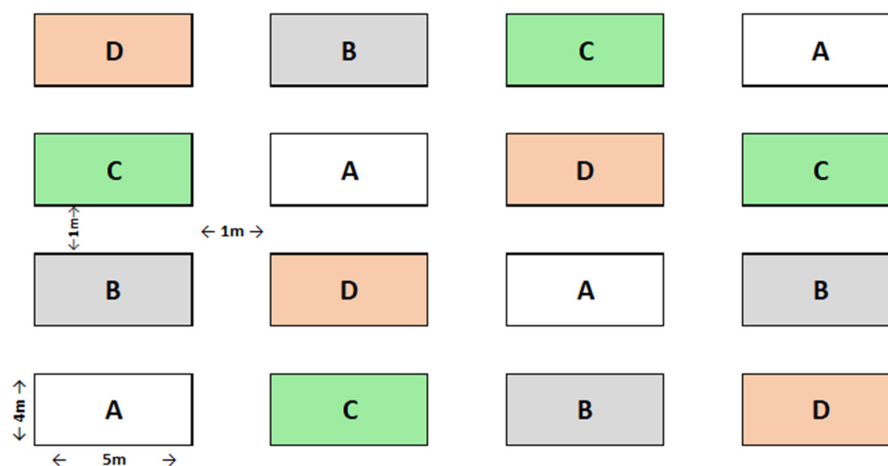
The supervised field experiment was conducted at the Democritus University experimental farm, Orestiada, Thrace, Northern Greece (41°30'08.7'' N, 26°32'25.6'' E), to determine the persistence, behavior, and ecological risk assessment of S-metolachlor and benfluralin in soil. The farm had never previously received S-metolachlor or benfluralin treatment. The experimental setup included four different layers with four replications corresponding to an experimental randomized complete block design consisting of 16 plots. Each experimental plot had a surface area of 20 m<sup>2</sup>. A distance of one meter separated the plots and blocks from one another. Samples were randomly pulled from each plot. Soil samples were split into four depths, 0 to 20 cm (Layer A), 20 to 40 cm (Layer B), 40 to 60 cm (Layer C), and 60 to 80 cm (Layer D), to determine the dissipation kinetics and the leaching behavior of the herbicides (Figure 1). The soil (1 kg) samples were collected randomly at 0

(2 h), 7, 15, 30, 45, and 60 days after application in triplicate. The soil samples were drawn from the soil at random, using a soil auger. The collected samples were transferred to the analytical laboratory for sample preparation and instrumental analysis.

**Table 1.** Physicochemical properties and characteristics of S-metolachlor and benfluralin [16,20].

Parameter	S-Metolachlor	Benfluralin
Molecular formula	C <sub>15</sub> H <sub>22</sub> ClNO <sub>2</sub>	C <sub>13</sub> H <sub>16</sub> F <sub>3</sub> N <sub>3</sub> O <sub>4</sub>
Substance group	Chloroacetamide	Dinitroaniline
Mode of action	Cell division inhibitor	Microtubule assembly inhibitor
Structural formula		
Molecular weight (g/mol)	283.79	387.82
Dissociation constant (pKa) at 25 °C	No dissociation	−0.59
Vapour pressure at 20 °C (mPa)	3.7	1.8
Water solubility at 20 °C (mg/L)	480	0.064
Henry's law constant at 25 °C (Pa m <sup>3</sup> /mol)	2.20 × 10 <sup>−3</sup>	9.5
Octanol–water partition coefficient (25 °C) LogK <sub>ow</sub>	3.05	5.19
Adsorption coefficient K <sub>foc</sub> (mL/g)	200.2	10,777
Soil degradation DT <sub>50field</sub> <sup>1</sup>	23.17	53

<sup>1</sup> Half-life for field studies.



**Figure 1.** Schematic layout of the experimental randomized complete block design in the field. The four different sampling depths were: 0 to 20 cm (Layer A), 20 to 40 cm (Layer B), 40 to 60 cm (Layer C), and 60 to 80 cm (Layer D).

The farm was planted with chickpea *Cicer arietinum* L. (cv. Amorgos). During the experiment, all cultivation tasks were carried out according to good agricultural practices. Chickpea is considered a non-irrigated crop and thus irrigation was not applied. The commercial formulations Dual Gold 96 EC (S-metolachlor) and Bonalan 18 EC (benfluralin) were applied using an experimental Azo field plot sprayer (length 2.4 m) equipped with six flat fan nozzles. The spray volume was 300L/ha, and the pressure was set at 2.8 atm. Dual Gold 96 EC and Bonalan 18 EC were applied on 20 March, pre-emerged to chickpeas. The application doses of S-metolachlor and benfluralin were 1350 and 1920 g a.i./ha, respectively, according to the commercial formulation's recommended doses. Herbicides were incorporated into the soil. The soil was silty loam with 47.5% silt, 35% clay, 17.5% sand, 1.5% organic matter (OM), and a pH of 8.5. Throughout the trial (from 20 March to 21 May), the average minimum and maximum temperatures were 11.38 °C and 21.61 °C,

respectively. Average humidity ranged from 56% to 81% and average soil moisture from 33.6% to 62.9% (measured by the gravimetric method). Light average rainfall was logged during the experimental period, ranging from 20.3 to 48.71 mm.

### 2.3. Sample Preparation

The soil (1 kg) samples were collected in triplicate using a soil auger. Initially, large stones were removed from each soil sample, and then the soil samples were air-dried, homogenized using a mortar and a pestle (clods smashed), and sieved (small stones removed) with a 2 mm sieve. An amount of 250 g was obtained from the samples following the quartering method, and a representative amount (10 g) of each soil sample was placed in a 50 mL centrifuge tube. Then, 5 mL of ethyl acetate and 20 mL of water were added. Extraction was performed by ultrasonication for 20 min. About 5 g of sodium chloride was added, and the mixture was vigorously shaken for 1 min. Centrifugation at 3000 rpm for 5 min followed. The aliquot of the upper layer was treated with SPE [21].

For the cleanup, C18 cartridges were used. The cartridges were initially conditioned with 3 mL of ethyl acetate, 3 mL of methanol, and 2 mL of distilled water. Samples were loaded onto C18 cartridges connected to a SPE vacuum manifold, with a flow rate of about 5 mL/min. The elution was conducted with 3 mL of ethyl acetate and 1 mL of hexane. The eluent was collected, evaporated to near dryness using a vacuum rotary evaporator at 30 °C, and evaporated to complete dryness under a nitrogen stream. The pesticide residues were dissolved in 2.5 mL ethyl acetate for GC-ECD analysis [22].

### 2.4. Instrumental Analysis

A Shimadzu gas chromatograph GC-17A (Duisburg, Germany) equipped with an ECD detector and an HP-5 (30 m 0.32 mm 0.25  $\mu$ m) capillary column was used to quantify and qualify S-metolachlor and benfluralin. The injection volume was 2  $\mu$ L, and the injector was run at 220 °C. The temperature of the oven was set to start at 80 °C with a holding time of 2 min, then increase to 220 °C at 20 °C/min, be held for 4 min, and finally increase to 250 °C at 10 °C/min and be held for 30 min. The carrier gas was helium, flowing at a rate of 1.5 mL/min. The detector was operated at 290 °C.

### 2.5. Method Validation

Mixed standard stock solutions were created separately for herbicides in ethyl acetate at 1 mg/mL. Using a serial dilution method, the calibration standard solutions were created from secondary stock solutions. The calibration standard solutions were prepared at the different concentration rates of 0.1, 0.2, 0.5, 1, 2, and 5  $\mu$ g/L in ethyl acetate. To prove the linearity of the matrix-matched calibration curve, standard solutions were added to a blank soil matrix in the range 0.1–5  $\mu$ g/L. The linearity of the calibration curve in ethyl acetate was also tested.

The SANTE guidelines [23] were followed in the development and validation of the quantitative analytical method, which was assessed using the validation criteria of specificity, linearity, sensitivity, trueness, precision, and matrix effect (ME). To test specificity by integrating the peaks at the target retention time for the eluted S-metolachlor and benfluralin, blank samples were spiked with S-metolachlor and benfluralin at the limit of quantification and injected into the GC-ECD instrument. The average area of the blank sample was divided by the average area of the standard at the reporting limit and then multiplied by 100 to obtain the specificity. Linearity was determined by plotting concentrations against the peak area derived from the GC-ECD chromatogram. The sensitivity of the method was assessed by reaching the limit of detection (LOD) and limit of quantitation (LOQ) by spiking the S-metolachlor and benfluralin with soil at the lowest concentration level complying with the analytical method's specifications. The LOD was evaluated as three times the signal-background-noise ratio on each chromatogram, and the LOQ was the concentration of the lowest spiked level in samples giving reliable and reproducible results. To conduct the recovery studies, blank (control) samples of soil were spiked with standard

solutions of S-metolachlor and benfluralin at concentrations of 0.1, 0.5, and 1 µg/g. Spiking levels were replicated five times. Ten grams of the soil sample were fortified by the addition onto the soil of the initial standard solution (1mg/mL). The fortification was performed by adding the initial solution volumes of 1 mL, 5 mL, and 10 mL for the levels 0.1, 0.5, and 1 µg/g, respectively. The repeatability (RSD %) of the procedure was also evaluated for each spiking level.

Calibration curves prepared with standards in ethyl acetate were compared with matrix-matched calibration curves in soil to determine a potential matrix effect. To prevent false negative or false positive reports, MEs (signal suppression and enhancement) were investigated [24]. ME was assessed utilizing the following equation:

$$ME = \left( \frac{\text{slope of the calibration curve in matrix}}{\text{slope of the calibration curve in solvent}} - 1 \right) \times 100\% \quad (1)$$

## 2.6. Ecological Risk Assessment

### 2.6.1. Exposure Assessment

The ecological risk assessment was conducted in the top 0–20 cm soil profile, according to Bhadari et al. [11]. The mean herbicide levels found at the studied soil profile at 0 (2 h) and 60 days of the experiment were used for risk assessment. In the first case, the concentration gives a worst-case scenario (MPCws), and, in the second case, a dissipation scenario is given (MPCds).

The no-observed-effect concentration (NOEC) and/or the lethal concentration at which 50% of investigated organisms demonstrate mortality (LC<sub>50</sub>), along with the median effective concentrations (EC<sub>50</sub>) for organisms including the earthworm (*E. fetida*), the enchytraeid (*E. crypticus*), the springtail (*F. candida*), the mite (*H. aculeifer*), and nitrogen and carbon mineralization microorganisms are used to evaluate the ecological risks of pesticides. Any study evaluating pesticides for approval by the EFSA for the European Union must take these organisms into account. The current investigation was predicated on the available NOEC endpoints, even though pesticides found in soil have LC<sub>50</sub> and EC<sub>50</sub> values.

The predicted no-effect concentration (PNEC) for the most vulnerable species was calculated using the NOEC value. The PNEC value was calculated as the lowest long-term NOEC divided by the assessment factor (AF), to overcome challenges like incomplete toxicity data, errors, and inaccurate results from the conservative method. To obtain the PNEC with an AF and take into account potential chronic effects, the most sensitive organism for each pesticide was chosen. The EU's 2002 guidance document (SANCO/10329/2002 rev 2 final) served as the basis for selecting the AF, which can number between 10 and 1000: (a) when data from a long-term assay was available, an AF of 100 was used, (b) when at least one LC<sub>50</sub> at one ecological level was available, an AF of 1000 was used, and (c) when two or more NOECs were available, AFs of 50 and 10, respectively, were used [25]. Based on the long-term NOECs that were available, we used AFs of 100, 50, and 10 in the current investigation (Table 2). The ecological risk assessment was conducted using the toxicity–exposure ratio (TER) [25] and the risk quotient (RQ) [26].

**Table 2.** Ecotoxicology (NOEC and NSDE in µg/g) of herbicides for *E. fetida*, *E. crypticus*, *F. candida*, *H. aculeifer*, and N and C mineralization organisms.

Pesticide	<i>E. fetida</i> . NOEC <sup>1</sup>	<i>F. candida</i> NOEC	<i>E. crypticus</i> NOEC	<i>H. aculeifer</i> . NOEC	NSDE <sup>2</sup> for N/C Mineralization Microorgan- isms	Critical Con- centration	PNEC <sup>3</sup> AF <sup>4</sup>	PNECs <sup>5</sup>
S-metolachlor [16]	26.65	na <sup>6</sup>	na	na	na	26.65	100	0.27
Benfluralin [27]	30.8	5.5	na	1000	11	5.5	10	0.55

<sup>1</sup> No-observed-effect concentration. <sup>2</sup> No significant adverse effects. <sup>3</sup> Predicted no-effect concentration. <sup>4</sup> Assessment factor. <sup>5</sup> Lowest long-term PNECs of the most susceptible species/AF. <sup>6</sup> Information not available.

### 2.6.2. Toxicity–Exposure Ratio

The TER method connects exposure and toxicity based on EC [25]. Using the TER for the test organisms and the following Equation (2), the TER for each pesticide was calculated:

$$\text{TER} = \frac{\text{NOECs}}{\text{MPC}} \quad (2)$$

where NOEC is the no-observed-effect concentration for all species and MPC is the mean pesticide concentration in the soil.

Acceptable risk for the organisms was indicated by TER values of  $\geq 10$  or  $\geq 5$ , which are acceptable trigger point values for acute and chronic exposure, respectively.

### 2.6.3. Risk Quotient

The following Equation (3) was used to determine the risk quotient of a pesticide, which served as an index for the risk of a single pesticide:

$$\text{RQ} = \frac{\text{MPC}}{\text{PNECs}} \quad (3)$$

where PNECs is the predicted no-effect concentration for the most sensitive species.

According to Vryzas et al. [28], the risk quotient was divided into four categories: no risk ( $\text{RQ} < 0.01$ ), lesser risk ( $0.01 \leq \text{RQ} \leq 0.1$ ), moderate risk ( $0.1 \leq \text{RQ} < 1$ ), and higher risk ( $\text{RQ} \geq 1$ ).

## 2.7. Dissipation Kinetics

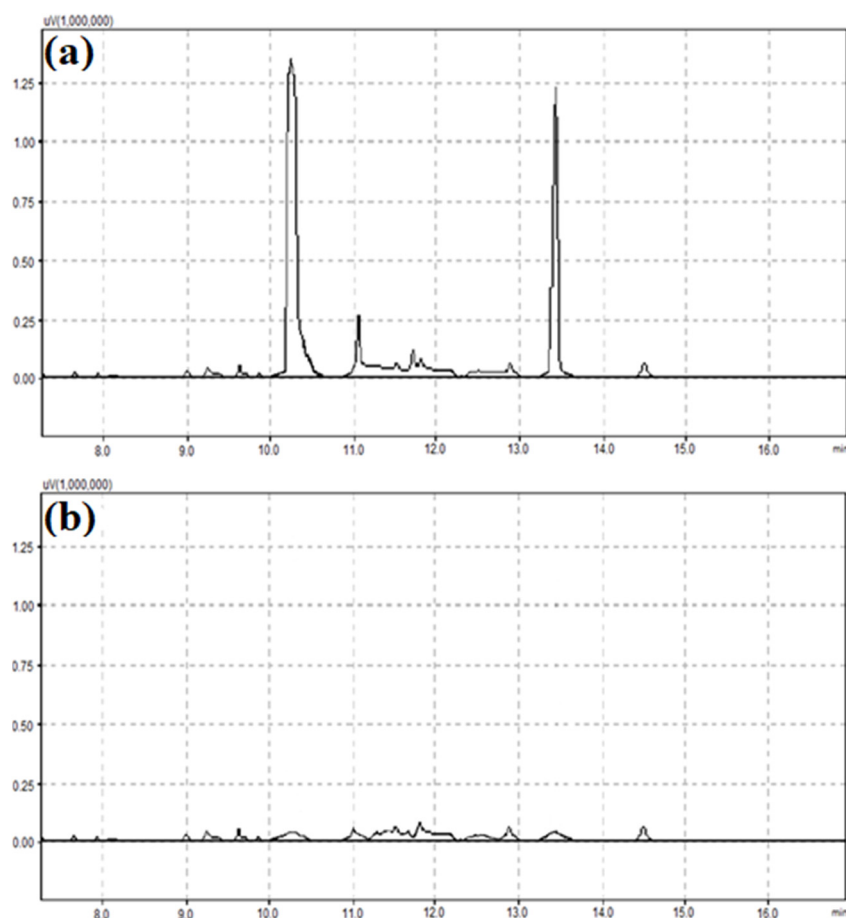
The field experiment data on S-metolachlor and benfluralin residues obtained from the 0–20 cm sampling depth zone were subjected to the first-order dissipation kinetics equation  $C_t = C_0 e^{-kt}$ , where  $C_t$  is the herbicide concentration at time  $t$  (day),  $C_0$  is the initial concentration ( $\mu\text{g/g}$ ), and  $k$  is the dissipation rate constant. The herbicides' half-lives were calculated as  $\text{DT}_{50} = \ln 2/k$  [29].

## 3. Results and Discussion

### 3.1. Method Validation Results

A GC-ECD analytical method was developed and validated. The instrument parameters were optimized to detect, confirm, and quantify S-metolachlor and benfluralin residues in soil. With the set operating chromatographic conditions, S-metolachlor and benfluralin were separated and eluted. The approximate retention times of S-metolachlor and benfluralin were 13.438 and 10.236 min, respectively. The blank soil and herbicide chromatographs are shown in Figure 2.

Both matrix-matched standards and standards in ethyl acetate were used in the creation of calibration curves, which were then examined in three replicates. Calibration curves prepared with pesticide standards in a solvent were compared with matrix-matched calibration curves in soil to determine a potential ME. Both of them were linear, presenting  $R^2 > 99\%$ . The matrix effect of S-metolachlor was  $-17.3\%$  and that of benfluralin was  $-4.86\%$  (signal suppression). When the effect ranges from  $-20\%$  to  $20\%$ , there is a mild ME [24] (Table 3). Therefore, the matrix calibration curves were used for the quantification of herbicides in the current study.



**Figure 2.** GC-ECD chromatograph of (a) the spiked soil matrix with S-metolachlor and benfluralin (1  $\mu\text{g/g}$ ) and (b) blank soil. The approximate retention times of S-metolachlor and benfluralin were 13.43 and 10.23 min, respectively. The injection volume was 2  $\mu\text{L}$ , and the injector was run at 220  $^{\circ}\text{C}$ . The temperature of the oven was set to start at 80  $^{\circ}\text{C}$  with a holding time of 2 min, then increase to 220  $^{\circ}\text{C}$  at 20  $^{\circ}\text{C}/\text{min}$  and be held for 4 min, and finally increase to 250  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$  and be held for 30 min. The carrier gas was helium, flowing at a rate of 1.5 mL/min. The detector was operated at 290  $^{\circ}\text{C}$ .

**Table 3.** Analytical method parameters for S-metolachlor and benfluralin.

Analytical Method Parameter	S-Metolachlor	Benfluralin
Calibration curve in solvent	$y = 306918x + 71.3$ ( $R^2 = 99.5$ )	$y = 554044 + 18304.8$ ( $R^2 = 99.7$ )
Calibration curve in blank soil	$y = 253821x + 380.1$ ( $R^2 = 99.3$ )	$y = 431600 + 3753.9$ ( $R^2 = 99.1$ )
Matrix effect (%)	-17.3	-22.1
LOD ( $\mu\text{g/g}$ )	0.01	0.015
LOQ ( $\mu\text{g/g}$ )	0.1	0.1

LOD = limit of detection; LOQ = limit of quantitation.

The LOD and LOQ were calculated according to guidelines provided by SANTE [23]. The LOD was determined as the signal corresponding to three times the background noise on each chromatogram, whereas the LOQ was considered the concentration at the lowest spiked level in samples giving accurate and precise quantified results. For S-metolachlor, the LOD and LOQ values were 0.01 and 0.1  $\mu\text{g/g}$ , whereas for benfluralin they were 0.015 and 0.1  $\mu\text{g/g}$ , respectively. The accuracy of the method was determined by spiking blank samples with S-metolachlor and benfluralin at three concentration levels (0.1, 0.5, and 1  $\mu\text{g/g}$ ) ( $n = 5$ ). The average recovery rates of S-metolachlor and benfluralin in soil were from 81% to 97% and from 88% to 101%, respectively (Table 4). The RSDs (%) for



S-metolachlor and benfluralin were from 6.6% to 8.5% and from 8.7% to 9.7%, respectively (Table 4). These values were acceptable and reached the conditions of analysis of pesticide residues, since SANTE [23] guidelines demand recovery ranges of 70–120% and RSDs up to 20%.

**Table 4.** Recovery rates and RSDs for S-metolachlor and benfluralin in soil.

Matrix	Spiked Level ( $\mu\text{g/g}$ )		Average Recovery (%)		RSD (%) (n = 5)	
	S-Metolachlor	Benfluralin	S-Metolachlor	Benfluralin	S-Metolachlor	Benfluralin
Soil	0.1		81	88	8.5	9.7
Soil	0.5		90	85	6.6	8.7
Soil	1.0		97	101	7.9	9.1

In the last three decades, various techniques have been developed to detect S-metolachlor and benfluralin residues in soil. However, the majority of them have not been presented in detail, excluding the method validation description. Table 5 summarizes the analytical methods to determine S-metolachlor and benfluralin levels in soil reported by previous studies.

**Table 5.** Comparison of detection methods for S-metolachlor and benfluralin in soil.

Herbicide	Method	LOQ <sup>1</sup> ( $\mu\text{g/g}$ )	Retention Time	Reference
S-metolachlor	GC-MS/MS <sup>2</sup> (scan mode)	na <sup>10</sup>	7.31	[13]
	QuEChERS <sup>3</sup> with online SPE-UHPLC <sup>4</sup> -MS-MS (MRM <sup>5</sup> )	na	na	[30]
	GC-MS (scan mode)	na	na	[31]
Benfluralin	DLLME <sup>6</sup> with GC-MS/MS (SRM <sup>7</sup> mode)	2	8.1	[32]
	GC/NPD <sup>8</sup>	0.5	14	[33]
	GLC <sup>9</sup> /NPD	na	na	[34]

<sup>1</sup> Limit of quantification. <sup>2</sup> Mass spectrometer. <sup>3</sup> Quick, easy, cheap, effective, rugged, safe. <sup>4</sup> Ultra-high-performance liquid chromatograph. <sup>5</sup> Multiple reaction monitoring. <sup>6</sup> Dispersive liquid-liquid microextraction. <sup>7</sup> Elected reaction monitoring, <sup>8</sup> nitrogen-phosphorus detector. <sup>9</sup> Gas-liquid chromatograph. <sup>10</sup> Information not available.

### 3.2. Dissipation and Leaching of S-Metolachlor and Benfluralin

A field experiment was conducted at a farm to determine the persistence and behavior of S-metolachlor and benfluralin in soil. The initial deposits of S-metolachlor and benfluralin residues obtained from the 20 cm sampling depth zone were 1.003 and 2.64  $\mu\text{g/g}$  at the recommended doses of 1350 and 1920 g a.i./ha, respectively. Both herbicides showed a faster dissipation rate during the initial seven days compared with that at 15 days. In particular, S-metolachlor and benfluralin showed 33.90% and 21.10% dissipation rates, respectively, from 0 to 7 days, while from 7 to 15 days the dissipation rates were 21.93% and 17.54%, respectively. From 15 days to 60 days, the dissipation rates of the herbicides did not exceed a percentage of 15%. The final S-metolachlor and benfluralin residue levels (60 days) in the soil in the first layer were 0.13 and 0.61  $\mu\text{g/g}$ , which correspond to 87.04% and 76.89% of the initial concentration, respectively (Tables 6 and 7). The dissipations of S-metolachlor and benfluralin were well-fitted in the first-order dissipation kinetics equation with high regression coefficients  $R^2$  of 0.946 and 0.963, respectively. The half-life ( $DT_{50}$ ) of benfluralin was higher (30.13 days) than the  $DT_{50}$  value for S-metolachlor in soil (21.66 days). The rate constant (k) for S-metolachlor dissipation was 0.032  $\text{d}^{-1}$ , and the rate constant for benfluralin dissipation was 0.023  $\text{d}^{-1}$  (Figures 3 and 4).

**Table 6.** Residues and dissipation parameters for S-metolachlor in soil at 1350 g a.i./ha in the top 0–20 cm soil profile.

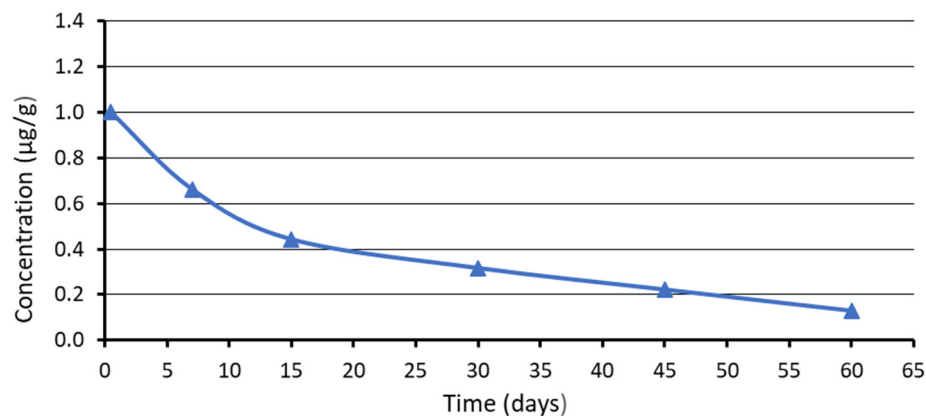
Days after Application	Residue ( $\mu\text{g/g}$ ) <sup>1</sup>	Dissipation (%)
0 (2 h)	1.003	-
7	0.663	33.90
15	0.443	55.83
30	0.317	68.39
45	0.223	77.77
60	0.130	87.04
k (rate constant)	0.032	-
R <sup>2</sup>	0.946	-
DT <sub>50</sub> (days) <sup>2</sup>	21.66	-

<sup>1</sup> Mean concentration. <sup>2</sup> Half-life.

**Table 7.** Residues and dissipation parameters for benfluralin in soil at 1920 g a.i./ha in the top 0–20 cm soil profile.

Days after Application	Residue ( $\mu\text{g/g}$ ) <sup>1</sup>	Dissipation (%)
0 (2 h)	2.640	-
7	2.083	21.10
15	1.620	38.64
30	1.236	53.18
45	0.886	66.44
60	0.610	76.89
k (rate constant)	0.023	-
R <sup>2</sup>	0.963	-
DT <sub>50</sub> (days) <sup>2</sup>	30.13	-

<sup>1</sup> Mean concentration. <sup>2</sup> Half-life.

**Figure 3.** The dissipation curve for S-metolachlor (mean concentration) in the top (0–20 cm) soil profile.

The leaching potential of the herbicides was estimated by collecting samples from three different depth zones. Leaching depths for S-metolachlor and benfluralin are presented in Tables 8 and 9, respectively. S-metolachlor and benfluralin concentrations in the 20–40, 40–60, and 60–80 cm sampling zones were below the LOD of the analytical method 2 h after herbicide application. From 7 to 45 days, S-metolachlor residues in the 20–40 cm sampling zone ranged from 0.104 to 0.202  $\mu\text{g/g}$ . In the sampling zone at 40–60 cm, S-metolachlor was detected only on Day 7, at a concentration equal to 0.127  $\mu\text{g/g}$ . In the 60 to 80 cm soil profile, no S-metolachlor residue was detected on Day 60. From 7 to 60 days, benfluralin residues in the 20–40 cm sampling zone ranged from 0.121 to 0.230  $\mu\text{g/g}$ . In the depth zone at 40–60 cm, benfluralin residues ranged from 0.111 to 0.166  $\mu\text{g/g}$ , but no benfluralin residue was found on Day 60. In the 60 to 80 cm soil profile, benfluralin was detectable only on Day 7.

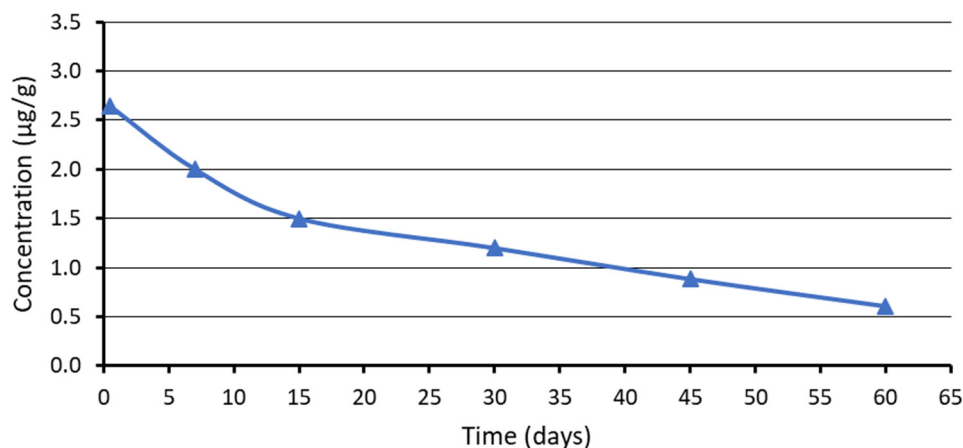


Figure 4. The dissipation curve for benfluralin (mean concentration) in the top (0–20 cm) soil profile.

Table 8. Mobility of S-metolachlor in the 0–80 cm soil profile.

Days after Application	S-Metolachlor (µg/g)			
	0–20 cm	20–40 cm	40–60 cm	60–80 cm
0 (2 h)	1.003 <sup>1</sup>	Nd <sup>2</sup>	nd	nd
7	0.663	0.202	0.127	nd
15	0.443	0.185	nd	nd
30	0.317	0.157	nd	nd
45	0.223	0.104	nd	nd
60	0.130	nd	nd	nd

<sup>1</sup> Mean of four replicates. <sup>2</sup> Not detectable.

Table 9. Mobility of benfluralin in the 0–80 cm soil profile.

Days after Application	Benfluralin (µg/g)			
	0–20 cm	20–40 cm	40–60 cm	60–80 cm
0 (2 h)	2.640 <sup>1</sup>	nd <sup>2</sup>	nd	nd
7	2.083	0.230	0.166	0.112
15	1.620	0.187	0.129	nd
30	1.236	0.201	0.134	nd
45	0.886	0.230	0.111	nd
60	0.610	0.121	nd	nd

<sup>1</sup> Mean of four replicates. <sup>2</sup> Not detectable.

According to Badou-Jeremie et al. [13] and Wołejko et al. [14], dissipation is a complex process that is affected by several physicochemical and biological changes, which cause the active substance’s concentration to decline over time. Residue degradation can be affected by several factors, including the pesticide’s stability in the soil and plants, the rate and frequency of application (initial concentration), the weather (sunlight, temperature, humidity, and wind), microorganisms, the pH of the soil and water, and the species of cultivated plants. In general, processes such as leaching, runoff, volatilization, adsorption, photodegradation, plant uptake, and biodegradation can impact the dissipation of herbicides in the field [35].

In our study, during the experimental period, air temperatures were moderate and rainfall was low, which could affect the dissipation and fate of S-metolachlor and benfluralin. As the temperature rises, pesticide vapor pressures can also rise. Because the herbicides used in this study have low vapor pressures (Table 1), losses due to volatilization were

low. After herbicide application, soil incorporation was conducted. As a result, the photodegradation of pesticides was also low [36].

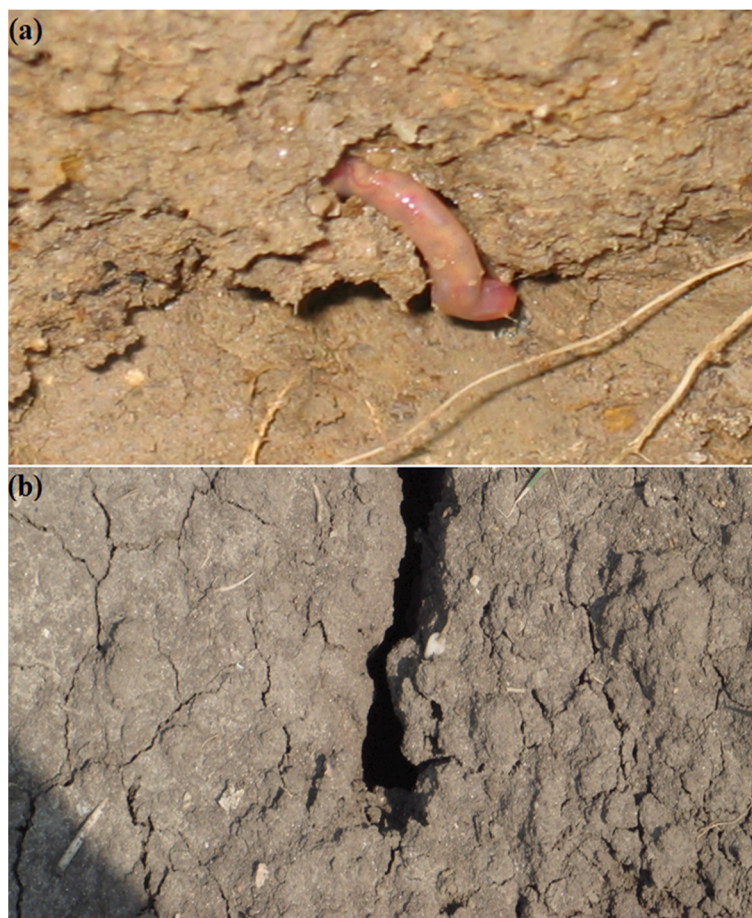
The GUS (groundwater ubiquity score) is an experimentally estimated value that connects pesticide half-life and  $K_{oc}$ . The GUS can be used to categorize pesticides by their possibility of moving towards groundwater [37]. The GUS was used by Hyun et al. [38] to assess the potential of certain pesticides in the soil of Jeju Island to pollute groundwater. They listed pesticides including alachlor, metolachlor, bromacil, ethoprophos, carbofuran, and metalaxyl as groundwater pollutants if their GUS index was greater than 2.8. On the other hand, in Hawaii's soil, the transport of certain pesticides was predicted using GUS values, and pesticide leaching was investigated [39]. With GUS 1.8, it was projected that the fungicide trifloxystrobin would not be leached. S-metolachlor and benfluralin have GUS values of 2.32 and  $-0.62$ , respectively [16,20]. Consequently, a moderate leaching potential for S-metolachlor and a low leaching potential for benfluralin are expected. However, in our study, both herbicides presented high leaching.

The high mobility of herbicides in the soil profile is due to the observed preferential flow. Preferential flow can happen in dry soils when partially water-repellent layers weaken the wetting front, creating fingered flow, or when flow is concentrated via recently developed cracks. Near-positive pore water pressures in soils that are getting close to saturation can push water out of the matrix and into highly conductive macropores, making the entire flow considerably more preferential [40]. Additionally, earlier studies indicate that preferential flow has a significant influence on herbicide leaching in the studied area due to the poor adsorption capacity for the herbicides atrazine and metolachlor in the soil profile. This is due to the fact that pollutants might avoid degradation by entering the saturated zone of the aquifer by preferential flow channels, such as plant roots, shrinking clay minerals, and earthworm burrows, rather than going through chromatographic flow within the unsaturated zone [41,42]. In our experiment, a short but intensive rainfall that temporarily created flood conditions after a dry period appeared to enhance preferential flow in the soil profile. Also, the chickpea root system and earthworms created channels in the soil, which facilitated preferential flow. Figure 5 shows earthworm, root, and crack channels in the soil profile.

The soil was silty loam with 47.5% silt, 35.0% clay, 17.5% sand, 1.5% OM, and a pH of 8.5. OM content and clay percentage in soils have a key role in the rate of adsorption. High clay and OM content in the soil promotes and facilitates greater pesticide molecule adhesion [43]. The soil and the herbicides's physicochemical properties are both essential for herbicide adsorption in the soil. Pesticides with high  $K_{oc}$  ( $K_{oc} > 1000$  L/kg) and low water solubility (water solubility  $< 10$  mg/L) exhibit strong pesticide adsorption in soil and organic matter fractions [39,40]. S-metolachlor and benfluralin have water solubility values of 480 and 0.064 mg/L and respective  $K_{oc}$  values of 200.2 and 646 L/kg [16,20]. Therefore, moderate adsorption of S-metolachlor and benfluralin in the soil was anticipated. Milan et al. [43] demonstrated the possibility of S-metolachlor leaching at values greater than  $0.25$   $\mu\text{g/L}$ . According to Alleto et al., S-metolachlor adsorption in soil is low to moderate, with adsorption coefficients of  $K_d = 1.3$  to  $8.7$  and a mean of  $3.0$  L/kg, which have been recorded from soils taken from fields with various crops and tillage practices [44]. Nevertheless, the residence period of water in the critical zone is dramatically decreased by preferential flow, which minimizes the probability that dissolved compounds will bind to soil particles, leading to low adsorption [40].

A significant factor involved in the breakdown of pesticides in the soil is microorganisms. The activity of aerobic microorganisms is reduced when the soil water capacity approaches saturation, resulting in an anoxic and nearly saturated soil–water system with a slower degradation rate and a longer half-life [45]. Throughout the experiment, the average soil moisture ranged from 33.6% to 62.9%. Consequently, although S-metolachlor and benfluralin could adversely impact soil microbial communities [33,46], the dissipation of herbicides was probably affected by biodegradation. Pesticide biodegradation, however,

depends on a wide range of environmental conditions and is not just dependent on the existence of bacteria with the appropriate degrading enzymes [47].



**Figure 5.** Preferential flow channels created by (a) roots and earthworms and (b) cracks (personal file).

The physical and chemical characteristics of a pesticide, as well as its interactions with the soil, plant microbiome, water, and other compounds of various types in the rhizosphere, determine how the pesticide behaves inside a plant through numerous mechanisms (such as uptake and translocation). The octanol/water partition coefficients ( $\text{LogK}_{\text{ow}}$ ) of pesticides have a significant impact on their fate in plant tissues with regard to phytoaccumulation and pesticide transport within the plant. Pesticides with  $\text{LogK}_{\text{ow}}$  values between 3.0 and 4.0 are more easily absorbed and translocated in plant tissues [48,49]. S-metolachlor and benfluralin have  $\text{LogK}_{\text{ow}}$  values of 3.05 and 5.19, respectively [16,20]. Also, Gikas et al. [50] investigated the uptake and translocation of S-metolachlor within constructed wetland vegetation. The results showed that S-metolachlor was detected in different plant parts (roots, stems, and leaves) of *Typha latifolia* and *Phragmites australis*, with concentrations ranging from 1.67  $\mu\text{g/g}$  to 6.18  $\mu\text{g/g}$ . Benfluralin residue studies in primary crops were conducted on leafy crops (lettuces), pulses, and oilseeds (alfalfa and peanuts) after soil application and cereals (wheat) after foliar application. Low levels of benfluralin (1.3%) were observed in lettuces; the majority of residues were recovered as aqueous and organo-soluble fractions (46% and 16%, respectively), while up to 47% of the residues remained unextracted, of which 17.7% was detected to be incorporated into the plants' natural components. Alfalfa and peanuts showed a similar trend, with the extracted fractions including a large number of unknown metabolites that together accounted for less than 3% of the total [51]. Therefore, chickpea accumulated a higher amount of S-metolachlor than benfluralin, which is clarified by their different hydrophobicity levels. This is probably

another parameter that led to different half-life values for S-metolachlor and benfluralin in the top 0–20 cm of the soil profile.

In the present study, the half-life was calculated for S-metolachlor in soil by the equation  $DT_{50} = \ln 2/k$ . The half-life for the first-order kinetics was 21.66 days (Table 5). Numerous studies have recorded  $DT_{50}$  values for S-metolachlor in soils collected from fields with various crops and tillage practices. Previously, the first-order kinetics  $DT_{50}$  value for S-metolachlor dissipation in soil was lower (12 days) than that reported by Caracciolo et al. [52]. Similarly, Wołejko et al. [12] reported that the estimated value of  $DT_{50}$  for S-metolachlor was 11.1–14.7 days in soil. On the other hand, the  $DT_{50}$  values in experiments by Long et al. [53] ranged from 26.3 to 40.1 days for five different soils, and were higher than in the findings of the current study. Also, the estimated half-life for S-metolachlor was in the same range as reported by Shaner et al. [54], which ranged from 18 to 27 days. There is a lack of dissipation studies for benfluralin in soil. Vischetti et al. [33] reported the same range of  $DT_{50}$  as the current study for benfluralin in three different soils, ranging from 11.4 to 37.9 days. In the current study, the half-life value of benfluralin was 30.13 days (Table 6).

### 3.3. Soil Risk Assessment

An LOQ of 0.1  $\mu\text{g/g}$  was chosen for soil risk assessment given the fact that LOQ values have been reported to range from  $1.58 \times 10^{-3}$  to 1.63 [55]. According to Ockleford et al. [56] and Silva et al. [57], predicted environmental concentrations (PEC) of authorized pesticides are frequently used to interpret their concentrations in soil. These PEC values are utilized in the evaluation of certain active substances and are determined using worst-case scenarios. PECs are determined for the primary crops to which the substance is applied, taking into account tillage depths of 5 cm for permanent crops and 20 cm for annual crops. Chickpea is an annual crop. Therefore, we believe that the depth of 20 cm is appropriate for risk assessment. The ecological risk based on TER under the worst-case scenario (ws) and the dissipation scenario (ds) is demonstrated in Table 10. In general, for the two herbicides and four soil organisms, benfluralin showed the highest risk under both scenarios for *F. candida*, because of its higher half-life and initial concentration. Also, the higher risk could be due to its higher initial concentration and lower NOEC [9]. More specifically, the TERws of benfluralin was equal to 2.08, exhibiting an acute risk for *F. candida*, while the TERds was 9.01, showing a chronic risk. In the cases of *E. fetida* and *H. aculeifer*, the TER values were greater than 10, which means a negligible risk. The high TER values for S-metolachlor ( $TER > 10$ ) indicate a negligible risk in soil. Consequently, benfluralin is riskier than S-metolachlor for soil organisms.

**Table 10.** Toxicity–exposure ratios (TERws and TERds) for soil organisms at a 0–20 cm depth.

Pesticide	MPCws <sup>1</sup>	MPCds <sup>2</sup>	<i>E. fetida</i>		<i>F. candida</i>		<i>E. crypticus</i>		<i>H. aculeifer</i>	
			TERws	TERds	TERws	TERds	TERws	TERds	TERws	TERds
S-metolachlor	1.0	0.13	26.57	25	na <sup>3</sup>	na	na	na	na	na
Benfluralin	2.64	0.61	11.66	50.49	2.08	9.01	na	an	378.78	1639.34

<sup>1</sup> Mean pesticide concentration for the worst-case scenario ( $\mu\text{g/g}$ ). <sup>2</sup> Mean pesticide concentration for the dissipation scenario ( $\mu\text{g/g}$ ). <sup>3</sup> Not applicable.

The risk quotient (RQ) values under the ws scenario and ds scenario for the studied herbicides are shown in Table 11. Our study presented higher risks ( $RQs > 1$ ) for both herbicides for the WS scenarios, indicating higher risk for soil organisms. For the ds scenario, the RQ value for S-metolachlor was 0.48, presenting medium risk, while the RQ value for benfluralin was 1.11. Therefore, benfluralin remains highly risky for soil organisms, even 60 days after pesticide application. The higher risk of benfluralin could be due to its higher initial concentration and half-life [9].

**Table 11.** Risk quotients for the most sensitive species at a 0–20 cm depth.

Pesticide	MPCws <sup>1</sup>	MPCds <sup>2</sup>	RQws	RQds
S-metolachlor	1.00	0.13	3,76	0.48
Benfluralin	2.64	0.61	4.80	1.11

<sup>1</sup> Mean pesticide concentration for the worst-case scenario (µg/g). <sup>2</sup> Mean pesticide concentration for the dissipation scenario (µg/g).

#### 4. Conclusions

Our study aimed to assess the soil ecological risks of S-metolachlor and benfluralin in soil. In the present study, a sensitive and efficient GC-ECD method was developed and validated for the determination of S-metolachlor and benfluralin residues in soil. The dissipation kinetics of S-metolachlor and benfluralin in soil (0–20 cm) followed first-order kinetics with half-lives of 21.66 and 30.13 days, respectively, indicating that benfluralin is more persistent than S-metolachlor in soil. The results for samples obtained from the 20–80 cm soil profile showed that both S-metolachlor and benfluralin present high leaching following preferential flow, which significantly contributed to the dissipation of these pesticides. Also, a soil ecological risk assessment was conducted in the top 0–20 cm of the soil profile, indicating the TERs for four soil organisms and the RQ. In all cases, both the TER and RQ values showed that benfluralin is riskier than S-metolachlor for soil organisms.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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