

Article

Monitoring of Herbicide Residues in Agricultural Soils in Vojvodina Province (Northern Serbia)

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Abstract: Pesticides in soils raise concerns about the biodiversity, food safety, and contamination of watercourses, contributing to unsustainable land management practices. Monitoring the residue levels in agricultural soils is essential, as this offers valuable insights into the current extent of soil contamination and potential environmental risks attributed to their application. This study aimed to address the occurrence of the currently used herbicides in soil under intensive crop production, comparing the results of monitoring at two depths (0–30 and 30–60 cm) in 2013 and 2023. The research concerned the main agricultural area in Vojvodina Province (Serbia) and evaluated the presence of 41 herbicides in 128 localities. Pesticides were found in all samples, finding even more than six different herbicides per sample. The significant concentrations of s-metolachlor, etofumesate, clomazone, diflufenican, pendimethalin, and terbutylazine found can be attributed to application practices, as they are typically applied pre-emergence, either through direct soil treatment with or without incorporation. Moreover, the correlation between different depths, herbicide residues, and soil properties was not significant. The decrease in the herbicide residues found in 2023 compared to the residues found in 2013 can be attributed to the implementation of good agricultural practices, which promote sustainable agricultural strategies through controlled pesticide application.

Keywords: soil; herbicides; pesticides; residues; monitoring; environment; plant protection products; sustainability; organic agriculture; Balkans



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1. Introduction

Soil, an essential foundation for agricultural production, serves as a vital source of energy, minerals, microelements, and nutrients for plants. These elements, transferred through the food chain, represent a source of life for all living organisms. The soil is a non-renewable resource with a possible high degradation rate, which can be reflected in the partial or complete impairment of one or more of its functions [1]. Agriculture, in particular, plays a significant role in soil degradation, keeping in mind that it is a primary anthropogenic factor contributing to this issue [2].

At the same time, according to United Nations data, the population is predicted to increase significantly over the next 30 years, requiring a corresponding increase in food

production [3]. Meeting this need will rely on sustainable agricultural practices that are based on minimizing environmental degradation and conserving natural resources with the aim of achieving the highest possible yields. The achievement of the aforementioned goals depends on the rational use of pesticides. However, contemporary agricultural practices demand the extensive use of diverse plant protection products.

The use of chemical pesticides in contemporary agricultural production has effectively reduced crop losses caused by various pests, thereby meeting the escalating global food demands. Approximately one-third of agricultural commodities are produced with the help of chemical plant protection products [4]. Globally, the overall use of pesticides in agriculture is stable, with 2.7 million tons of active ingredients used in 2020. The application rate of pesticides per unit area of cropland on a global scale stood at 1.8 kg/ha; the total trade volume of pesticides in formulated products reached around 7.2 Mt and a corresponding market value of USD 41.1 billion. The use of pesticides in European agriculture has increased by 3% from the 1990s to the present decade, possibly attributed to the strict regulations of the European Common Agricultural Policy, which controls and regulates pesticide use. In 2020, the region's pesticide application per unit of cropland stood at around 1.6 kg/ha, which is below the global average [5].

Despite their numerous benefits, as well as their importance for the economy, the extensive and ongoing use of pesticides has raised significant concerns regarding their impact on the environment and human health. Diffuse pollution by agrochemicals poses a significant risk to soil health [6], since the soil is the initial recipient of pesticides following their application. These compounds bind to the soil, forming permanent residues, while water-soluble pesticides are washed away, posing a risk of contaminating surface and underground waters [7]. The introduction and presence of pesticides in the soil not only impact its functions, biodiversity, and food safety, but also facilitate the movement of pollutants through deeper soil layers to groundwater, increasing the potential risks to humans and other non-target organisms. The intensive and/or unsuitable application of plant protection products, especially herbicides, also leads to the development of resistant biotypes. Additionally, persistent herbicides can cause damage to subsequent crops in crop rotation systems [8].

Even though agricultural soil serves as a primary sink and essential reservoir for pesticides, extensive surveys of agricultural soils for current-use pesticides (CUPs) are surprisingly scarce, with significant studies only published in Spain, Portugal, the Netherlands [9], Czech Republic [7], France [10], and the USA [11]. Pesticide residues have been detected in various types of non-agricultural [10] and agricultural lands [12–14], including those under organic agricultural systems [9,15]. Moreover, the impacts of pesticide residue mixtures on non-target soil organisms remain poorly understood. Research indicates that combinations of pesticides have had negative effects on earthworms [16] and soil microbiota [17]. This is concerning, as earthworms and microorganisms are vital for maintaining soil fertility. However, the consequences of multiple pesticides contaminating the soil remain unclear, as pesticide mixtures in soils are typically assessed only at the case study level due to high analytical costs and the absence of a mandatory post-approval pesticide-monitoring system [9].

Despite the occurrence of soil contamination, which presents a significant concern, the monitoring of pesticide residues in soil in the European Union (EU) is not regulated appropriately, compared to the area of water monitoring, which is regulated by the EU Water Framework Directive [18]. Additionally, there is a lack of extensive international studies on soil pesticide contamination, with most studies focusing on individual pesticides or a limited number of compounds [13]. Some European countries have incorporated into their legislation the reference or maximum levels in soils for no-longer approved and highly persistent pesticides [19]. However, there are currently no established thresholds for currently used pesticides in this legislation [20]. The adoption of the Soil Monitoring and Resilience Law could significantly alter the current conditions. According to recent scientific findings, a concerning trend has emerged regarding the health of European soils.

Research indicates that over 60% of European soils are currently deemed unhealthy, with approximately 2.8 million sites within the EU being identified as potentially contaminated. Moreover, empirical evidence suggests that this situation is deteriorating over time. Recently, the European Commission adopted the proposal of a document aiming to establish a level of protection for soil equivalent to that currently in place for water within the EU. This legislative framework, known as the Soil Monitoring Law, is designed to support the attainment of healthy soils by 2050, aligning with the EU's Zero Pollution objective. Under this directive, Member States will be required to conduct the monitoring and assessment of soil health across their territories. Subsequently, authorities and landowners can implement appropriate measures based on the findings to safeguard soil quality [21].

Thus, knowledge regarding the fate and behavior of pesticides in soils is still limited. Due to the lack of regulations, large-scale monitoring programs for pesticide residues in soil are essential to achieve sustainable production while minimizing health and environmental risks. The monitoring of these residue levels in agricultural soils is highly important, since it provides valuable information on the actual levels of soil contamination and environmental risks resulting from pesticide application [12]. Therefore, this study aimed to analyze the presence of residues of currently used herbicides in arable soils, concerning the main agricultural area of Vojvodina Province (Serbia). The production in Vojvodina mostly takes place within high-input modern agriculture systems that include frequent applications of synthetic pesticides and fertilizers, requiring the comprehensive monitoring of pesticide residues. The selected sites included arable lands under intensive crop production, while the targeted herbicides were currently used substances. The monitoring was carried out in 2013 and 2023 at two depths to provide insights into the state of agricultural land contamination and assess the differences in the applied agricultural practices.

2. Materials and Methods

2.1. Studied Area and Soil Sampling

The monitoring covered the region of Vojvodina, located in the northern part of Serbia, in the Panonian Basin (Figure 1), with chernozem as the most widespread type of soil, covering 41% of the area. This northern region of Serbia stretches to the Pannonian Plain and almost all of the Vojvodina area lies within central Europe, serving as the primary agricultural area with 1.78 million hectares of arable land. Agriculture is one of the most important economic activities of Serbia, with approximately 70% of the country's total land area, or 4,867,000 hectares, designated as agricultural land [22]. In open-field conventional agricultural systems, cereals, maize, wheat, sugar beet, and oilseeds, or at a smaller scale, vegetables, fruits, and vine, are grown. The region is recognized for its intensive agricultural practices, focusing on maize, soybean, sugar beet, and sunflower as dominant crops in the conventional system of production. In this production system, to protect crops from a wide range of pests and ensure optimal yields, intensive plant protection measures are implemented, and the use of chemical agents for plant protection is a standard practice. Compared to other types of plant protection products (PPPs), herbicides are predominantly utilized. Therefore, considering their decades of intensive use, as well as the growing trend of environmental protection and food safety, monitoring the presence of herbicide residues is essential.

The initial sampling took place during the growing season in 2013, at two depths (0–30 cm and 30–60 cm) in fields with crops, comprising 128 localities. Sampling was repeated at the same localities during 2023, resulting in a total number of 512 soil samples. From each field, one composite sample was collected, formed by collecting 20 sub-samples at various points diagonally in the plots within the production area, using a soil sampling probe or shovel. These sub-samples were combined to create an average sample mass of 500 g for further analysis. All samples were transported to the laboratory, stored, and frozen. Prior to the herbicide residue analysis, the samples were thawed and homogenized.

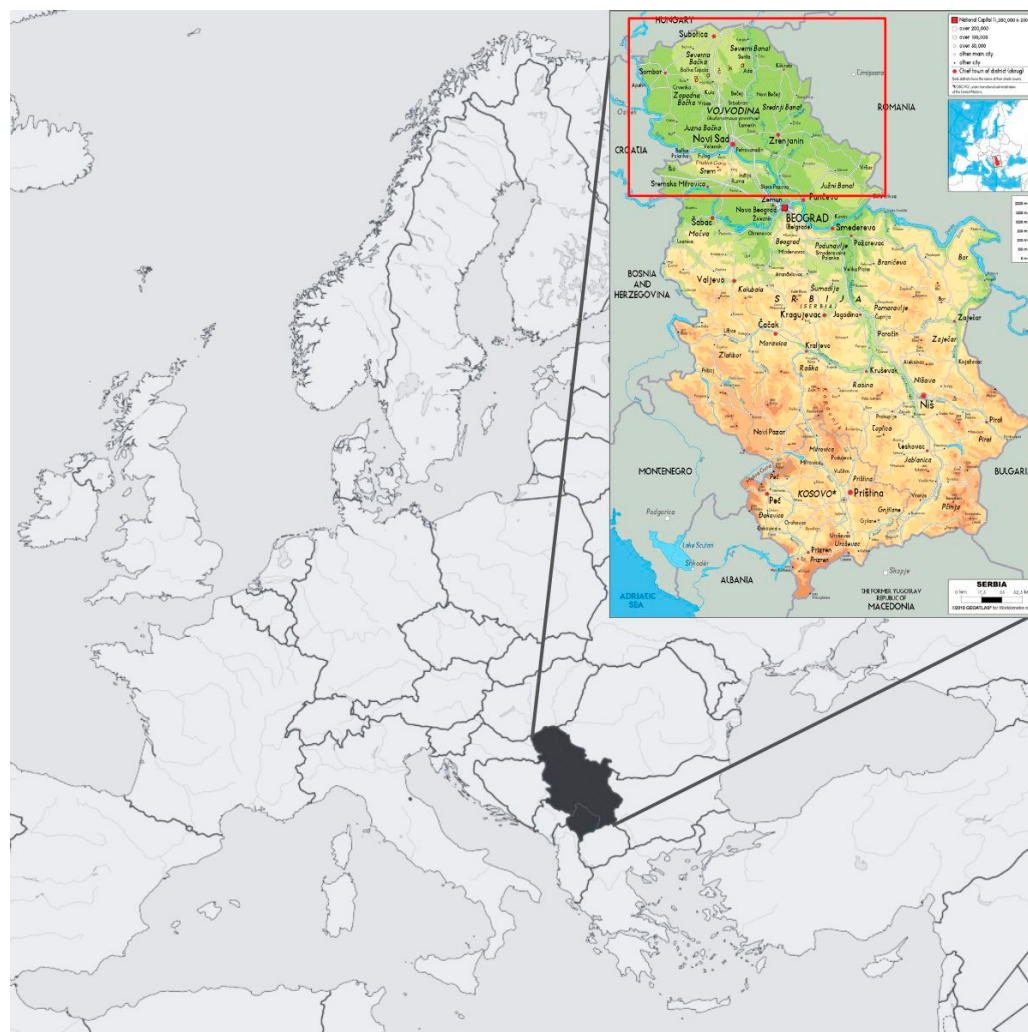


Figure 1. Study area (Vojvodina Province) [23,24].

2.2. Determination of Soil Property

Before further analysis, the soil samples were air-dried, ground, and sieved through a 2 mm mesh. The soil texture was determined using the traditional method with 0.1 mol/L of Na-pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$). The pH values of the soil samples were measured in water (H_2O) and potassium chloride (KCl) following the ISO 10390 method [25]. The organic matter content was assessed using the dichromate method [26] and defined according to Gračanin [27]. The calcium carbonate (CaCO_3) content was determined according to HRN ISO 10693 [28]. The Cation Exchange Capacity (CEC) was determined using the standard method with ammonium acetate ($\text{CH}_3\text{COONH}_4$), and is expressed in mmol/100 g of soil.

2.3. Pesticide Residue Analyses

For the analysis, approved and currently used herbicide active substances were chosen—amidosulfuron, aminopyralid, carfentrazone-ethyl, clethodim, clopyralid, cycloxydim, ethofumesate, fenoxaprop-ethyl, flufenacet, foramsulfuron, imazamox, iodosulfuron-methyl, lenacil, mesotrione, metamitron, metobromuron n, metribuzin, metsulfuron-methyl, nicosulfuron, phenmedipham, rimsulfuron, s-metolachlor, thifensulfuron-methyl, triflurosulfuron-methyl, tritosulfuron, 2,4-d-methylester, acclonifen, benfluralin, bentazon, clomazone, diflufenican, fluazifop-p-butyl, flumioxazin, metazachlor, napropamide, oxyfluorfen, pendimethalin, propyzamide, prosulfocarb, quizalofop-ethyl, and terbutylazin (Appendix A). In total, we analyzed 41 active substances belonging to Class III, suggesting significant toxicity [29], with bio-concentration factors mostly far above 1. The purities

of the herbicides' analytical standards used in this study ranged from 96% to 99.9%. All analytical standards were sourced from LGC Standards, Augsburg, Germany.

The extraction of pesticides from the soil was performed using the modified QuEChERS method EN15662 [30–32]. Prior to analysis, the soil samples were air-dried, ground, and sieved through a 2.0 mm sieve. Afterward, a 10 g sample was weighed and transferred in a 50 mL polypropylene cuvette. Deionized water purchased from Fisher Scientific Loughborough, UK, (3 mL) was added to the sample, followed by vigorous shaking. Then, 10 mL of acetonitrile (Fisher Scientific, Loughborough, UK) with 2% Formic acid (CH_2O_2) purchased from Merck KGaA, Darmstadt, Germany, was added and shaken for 1 min, then vortexed for 1 min, after which, a salt buffer mixture (Agilent Technologies, Folsom, CA, USA) was added (QuEChERS extraction kits—4 g of magnesium salt (MgSO_4), 1 g of sodium chloride (NaCl), 1 g Na of Citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), and 0.5 g of disodium citrate sesquihydrate ($\text{C}_{12}\text{H}_{18}\text{Na}_4\text{O}_{17}$)). The prepared samples were shaken for 1 min, vortexed for 1 min, left for 10 min in an ultrasonic bath, and centrifuged (Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) for 5 min at 4000 rpm. Following this, the solid and liquid acetonitrile phases were separated. The aliquot was evaporated (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) to a dry residue and dissolved in acetonitrile or acetone (Fisher Scientific Loughborough, UK). The extract was filtered through a 0.45 μm membrane filter (Macherey-Nagel GmbH & Co. KG, Duren, Germany), transferred to a vial, and analyzed. In order to avoid the salt's impact on the extraction yield of the polar pesticides, the purification procedure was not carried out.

Considering the different natures of herbicides, the analysis was carried out by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) and gas chromatography–mass spectrometry (GC-MS) in 2013, and by gas chromatography–tandem mass spectrometry (GC-MS/MS) and liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in 2023 [31,32].

2.4. Data Analysis

Statistical software Statistica version 14.0.0.15. (Tibco Software Inc., Palo Alto, CA, USA, 2021) was used for the statistical analysis of data in this study. The data analysis also employed the method of descriptive statistics. To test the differences between herbicide concentrations at different soil depths, the two-sample *t*-test was applied ($p < 0.05$).

3. Results

The research conducted focused on currently used herbicides. While modern herbicides, and pesticides in general, are designed to be highly effective at the smallest possible doses, with low persistence and toxicity towards non-target organisms, many currently utilized pesticides remain persistent and harmful [7,33]. Also, some currently used herbicides are on the list of priority water pollutants [34]. Therefore, research must focus on monitoring the presence of residues of these currently used herbicides to influence their management and good agricultural practice over time.

3.1. Monitoring of Herbicide Residues in 2013

The 2008 ban on the use of herbicides based on atrazine, simazine, and certain chloroacetanilides led to a significant increase in the use of sulfonylureas [35] and the remaining herbicides from the triazine and chloroacetamide groups, specifically terbuthylazine and s-metolachlor. In light of these changes, a study was conducted to assess the condition of the residues of currently used herbicides in soil in intensively farmed agricultural regions. The results from 2013 revealed the presence of herbicide residues in samples from all sites and at both depths, with each sample containing at least six different herbicide substances. The analysis revealed that 47 out of 128 soil samples contained 6–10 herbicides, while 81 samples contained 11–16 herbicides. In 28 samples, 8 different herbicide residues were found, with the highest number of detected active substances (16) observed in 2 samples (Figure 2).

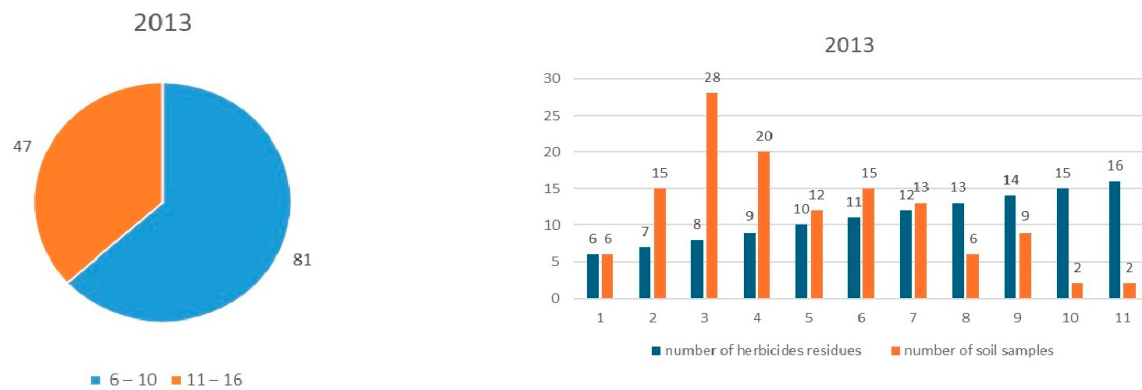


Figure 2. Presence of herbicides in soil samples—2013.

In a comprehensive analysis of 128 agricultural soil samples for the presence of 35 herbicide active substances, the presence of 26 herbicides at a depth of 0–30 cm and 25 herbicides at a depth of 30–60 cm was determined. Residues from the thiocarbamates, acetamides, benzothiadiazinone, and phenoxy-carboxylates groups were found most frequently (Table 1). Specifically, prosulfocarb, napropamide, and bentazon were present in nearly all samples (97–100%). Herbicides such as 2,4-D methyl ester, flumioxazine, metazachlor, and propyzamide were detected in 50–90% of samples, while nicosulfuron, s-metolachlor, clomazone, oxyfluorfen, pendimethalin, and terbutylazine were found in 20–50% of samples. In contrast, the occurrence of other analyzed herbicides was below 20% (Figure 2). Notably, no residues of some sulfonyleurea herbicides (amidosulfuron, iodosulfuron-methyl, rimsulfuron, thifensulfuron-methyl, and tritosulfuron), clopyralid, cycloxydim, fluazifop-P-butyl, and quizalofop-P-ethyl were detected, or their concentrations were below the limit of detection (LOD). These findings highlight the widespread occurrence and heterogeneous presence of herbicide residues in the soil.

Table 1. Frequency and min/max concentrations of individual herbicides detected in 128 soil samples at two depths.

Active Substance	Depth (cm)	2013			2023		
		Frequency (%)	Min (mg/kg)	Max (mg/kg)	Frequency (%)	Min (mg/kg)	Max (mg/kg)
2,4-D-methyl ester	0–30	89.06	<LOD	5.65	85.16	<LOD	4.37
	30–60	88.28	<LOD	7.73	10.94	<LOD	6.77
Aclonifen	0–30	0.00	na	na	91.41	<LOD	9.42
	30–60	0.00	na	na	92.19	<LOD	6.83
Amidosulfuron	0–30	0.00	<LOD	<LOD	0.78	<LOD	0.20
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
Aminopyralid	0–30	0.78	<LOD	0.76	2.34	<LOD	1.28
	30–60	2.34	<LOD	2.65	0.00	<LOD	<LOD
Benfluralin	0–30	0.00	na	na	0.00	<LOD	<LOD
	30–60	0.00	na	na	0.00	<LOD	<LOD
Bentazon	0–30	100.00	0.126	5.27	99.22	<LOD	7.70
	30–60	99.22	<LOD	5.68	99.22	<LOD	9.02
Carfentrazone-ethyl	0–30	0.00	na	na	0.00	<LOD	<LOD
	30–60	0.00	na	na	0.00	<LOD	<LOD
Clethodim	0–30	2.34	<LOD	0.45	1.56	<LOD	0.21
	30–60	2.34	<LOD	0.19	0.00	<LOD	<LOD
Clomazone	0–30	32.03	<LOD	229.40	29.69	<LOD	22.62
	30–60	27.34	<LOD	72.03	26.56	<LOD	25.98
Clopyralid	0–30	0.00	<LOD	0	0.00	<LOD	<LOD
	30–60	0.00	<LOD	0	1.56	<LOD	179.80

Table 1. Cont.

Active Substance	Depth (cm)	2013			2023		
		Frequency (%)	Min (mg/kg)	Max (mg/kg)	Frequency (%)	Min (mg/kg)	Max (mg/kg)
Cycloxydim	0–30	0.00	<LOD	0	0.78	<LOD	0.12
	30–60	0.00	<LOD	0	0.78	<LOD	0.13
Diflufenican	0–30	0.78	<LOD	2.07	1.56	<LOD	3.81
	30–60	1.56	<LOD	4.22	1.56	<LOD	3.27
Ethofumesate	0–30	0.78	<LOD	24.34	2.34	<LOD	8.96
	30–60	0.78	<LOD	6.29	2.34	<LOD	1.88
Fenoxaprop-ethyl	0–30	5.47	<LOD	1.67	3.13	<LOD	2.09
	30–60	2.34	<LOD	0.39	3.13	<LOD	3.99
Fluazifop-P-butyl	0–30	0.00	<LOD	<LOD	0.00	<LOD	<LOD
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
Flufenacet	0–30	0.00	na	na	0.00	<LOD	<LOD
	30–60	0.00	na	na	0.00	<LOD	<LOD
Flumioxazin	0–30	67.97	<LOD	1.83	72.66	<LOD	1.10
	30–60	71.09	<LOD	0.86	79.69	<LOD	0.72
Foramsulfuron	0–30	0.78	<LOD	0.11	4.69	<LOD	0.39
	30–60	3.13	<LOD	0.19	0.00	<LOD	<LOD
Imazamox	0–30	5.47	<LOD	3.69	3.91	<LOD	8.53
	30–60	3.91	<LOD	1.89	0.00	<LOD	<LOD
Iodosulfuron-methyl	0–30	0.00	<LOD	<LOD	0.00	<LOD	<LOD
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
Lenacil	0–30	0.00	na	na	2.34	<LOD	21.84
	30–60	0.00	na	na	0.00	<LOD	<LOD
Mesotrione	0–30	3.13	<LOD	0.37	3.91	<LOD	24.06
	30–60	0.78	<LOD	0.27	2.34	<LOD	1.87
Metamitron	0–30	3.13	<LOD	0.72	1.56	<LOD	4.05
	30–60	3.91	<LOD	3.94	1.56	<LOD	3.38
Metazachlor	0–30	78.91	<LOD	1.44	75.78	<LOD	1.16
	30–60	68.75	<LOD	1.29	78.13	<LOD	0.67
Metobromuron N	0–30	0.00	na	na	8.59	<LOD	4.33
	30–60	0.00	na	na	1.56	<LOD	3.21
Metribuzin	0–30	12.50	<LOD	10.36	12.50	<LOD	14.44
	30–60	10.94	<LOD	5.19	16.41	<LOD	9.74
Metsulfuron-methyl	0–30	0.78	<LOD	26.14	12.8	<LOD	3.18
	30–60	0.78	<LOD	12.64	3.13	<LOD	65.01
Napropamide	0–30	99.22	<LOD	2.21	98.44	<LOD	2.74
	30–60	97.66	<LOD	3.17	97.66	<LOD	2.72
Nicosulfuron	0–30	24.22	<LOD	40.19	25.00	<LOD	76.57
	30–60	22.66	<LOD	21.7	21.88	<LOD	46.39
Oxyfluorfen	0–30	52.34	<LOD	0.70	60.16	<LOD	1.04
	30–60	48.44	<LOD	0.69	53.91	<LOD	0.63
Pendimethalin	0–30	28.13	<LOD	37.62	35.16	<LOD	50.78
	30–60	27.34	<LOD	11.04	28.91	<LOD	30.69
Phenmedipham	0–30	0.78	<LOD	4.66	0.00	<LOD	<LOD
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
Propyzamide	0–30	61.72	<LOD	0.71	67.19	<LOD	3.47
	30–60	69.53	<LOD	1.19	71.09	<LOD	2.34
Prosulfocarb	0–30	100.00	0.109	5.58	98.44	<LOD	5.86
	30–60	97.66	<LOD	2.93	98.44	<LOD	5.97
Quizalofop-ethyl	0–30	0.00	<LOD	<LOD	0.00	<LOD	<LOD
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
Rimsulfuron	0–30	0.00	<LOD	<LOD	0.00	<LOD	<LOD
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
s-metolachlor	0–30	38.28	<LOD	670.20	35.16	<LOD	114.70
	30–60	30.47	<LOD	329.90	31.25	<LOD	80.95

Table 1. Cont.

Active Substance	Depth (cm)	2013			2023		
		Frequency (%)	Min (mg/kg)	Max (mg/kg)	Frequency (%)	Min (mg/kg)	Max (mg/kg)
Thifensulfuron-methyl	0–30	0.00	<LOD	<LOD	0.00	<LOD	<LOD
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
Triflusulfuron-methyl	0–30	1.56	<LOD	10.07	3.91	<LOD	16.08
	30–60	3.13	<LOD	2.14	0.00	<LOD	<LOD
Tritosulfuron	0–30	0.00	<LOD	<LOD	0.00	<LOD	<LOD
	30–60	0.00	<LOD	<LOD	0.00	<LOD	<LOD
Terbutylazine	0–30	42.97	<LOD	37.85	41.41	<LOD	99.03
	30–60	35.16	<LOD	32.03	32.03	<LOD	36.14

na—not analyzed; LOD = 0.001 mg/kg for all analytes.

The individual herbicide concentrations in the soil samples ranged from the limit of detection (LOD) to 670.2 mg/kg, with the highest concentration observed for s-metolachlor. Additionally, high concentrations of etofumesate, metsulfuron-methyl, nicosulfuron, clomazone, diflufenican, pendimethalin, and terbutylazine were detected (Table 1). These elevated levels can be attributed to application practices, as herbicides based on s-metolachlor, etofumesate, clomazone, diflufenican, pendimethalin, and terbutylazine are typically applied after sowing and before crop emergence, either through direct soil treatment with or without incorporation. Conversely, the high residual values of sulfonylurea herbicides were likely due to their intensive application immediately before soil sampling.

In the surface soil layer, the most frequently detected substances were prosulfocarb, ranging from 0.109 to 5.575 mg/kg, napropamide, ranging from the LOD to 2.214 mg/kg, and bentazon, ranging from 0.126 to 5.267 mg/kg (Table 1). At a depth of 30–60 cm, higher concentrations of prosulfocarb, napropamide, and bentazon were observed, while the levels of terbutylazine decreased.

The analysis of herbicide residues was conducted at two soil depths: 0–30 cm and 30–60 cm. Statistical analysis revealed that, for most herbicides, the concentrations in the surface layer (0–30 cm) were similar to those in the deeper layer (30–60 cm). The differences in the concentrations of residues found for all tested compounds in the two analyzed layers were not statistically significant. The exception was clethodim, for which a significant difference was noted ($t = 6.577$, $p = 0.022$). The average concentration of clethodim was 0.453 mg/kg in the 0–30 cm layer, whereas it decreased to an average of 0.139 mg/kg at the 30–60 cm depth (Table 2).

Table 2. Number of positive samples and average concentrations of herbicide residues by depth—2013.

Active Substances	Depth of Soil Sample		<i>t</i> -Test for Independent Samples
	0–30 cm $\bar{x} \pm \text{SD mg a.s./kg Soil}$	30–60 cm $\bar{x} \pm \text{SD mg a.s./kg Soil}$	
2,4-D-methylester	1.305 ± 1.058	1.477 ± 1.351	$t = 1.065^{\text{NS}}$; $p = 0.288$; d.f. = 225
Amidosulfuron	—	—	—
Aminopyralid	0.758	1.479 ± 1.014	$t = 0.615^{\text{NS}}$; $p = 0.601$; d.f. = 2
Bentazon	1.939 ± 1.061	1.918 ± 1.081	$t = 0.160^{\text{NS}}$; $p = 0.873$; d.f. = 253
Clethodim	0.453	0.139 ± 0.041	$t = 6.577^*$; $p = 0.022$; d.f. = 2
Clomazone	11.856 ± 6.213	4.763 ± 2.176	$t = 1.010^{\text{NS}}$; $p = 0.316$; d.f. = 74
Clopyralid	—	—	—
Cycloxydim	—	—	—
Diflufenican	2.068	2.315 ± 2.697	$t = 0.075^{\text{NS}}$; $p = 0.953$; d.f. = 1
Ethofumesate	24.335	6.288	—

Table 2. Cont.

Active Substances	Depth of Soil Sample		<i>t</i> -Test for Independent Samples
	0–30 cm $\bar{x} \pm SD$ mg a.s./kg Soil	30–60 cm $\bar{x} \pm SD$ mg a.s./kg Soil	
Fenoxaprop-ethyl	0.711 $\pm$ 0.464	0.234 $\pm$ 0.145	$t = 1.696^{NS}$; $p = 0.128$; d.f. = 8
Fluazifop-P-butyl	–	–	–
Flumioxazin	0.336 $\pm$ 0.209	0.331 $\pm$ 0.184	$t = 0.149^{NS}$; $p = 0.882$; d.f. = 177
Foramsulfuron	0.110	0.150 $\pm$ 0.028	$t = 1.289^{NS}$; $p = 0.288$; d.f. = 3
Imazamox	1.037 $\pm$ 1.349	0.817 $\pm$ 0.741	$t = 0.328^{NS}$; $p = 0.750$; d.f. = 10
Iodosulfuron-methyl	–	–	–
Mesotrione	0.251 $\pm$ 0.111	0.273	$t = 0.175^{NS}$; $p = 0.872$; d.f. = 3
Metamitron	0.371 $\pm$ 0.266	1.109 $\pm$ 1.586	$t = 0.908^{NS}$; $p = 0.394$; d.f. = 7
Metazachlor	0.278 $\pm$ 0.202	0.259 $\pm$ 0.164	$t = 0.692^{NS}$; $p = 0.489$; d.f. = 187
Metribuzin	1.724 $\pm$ 2.511	1.074 $\pm$ 1.357	$t = 0.864^{NS}$; $p = 0.395$; d.f. = 28
Metsulfuron-methyl	26.139	12.648	–
Napropamide	0.775 $\pm$ 0.416	0.811 $\pm$ 0.477	$t = 0.657^{NS}$; $p = 0.511$; d.f. = 250
Nicosulfuron	4.669 $\pm$ 8.209	2.648 $\pm$ 4.444	$t = 1.174^{NS}$; $p = 0.245$; d.f. = 58
Oxyfluorfen	0.207 $\pm$ 0.106	0.213 $\pm$ 0.121	$t = 0.324^{NS}$; $p = 0.746$; d.f. = 127
Pendimethalin	2.658 $\pm$ 6.980	1.201 $\pm$ 2.558	$t = 1.161^{NS}$; $p = 0.250$; d.f. = 69
Phenmedipham	4.657 $\pm$ 0.934	–	–
Propyzamide	0.215 $\pm$ 0.107	0.228 $\pm$ 0.202	$t = 0.522^{NS}$; $p = 0.602$; d.f. = 166
Prosulfocarb	0.789 $\pm$ 0.650	0.772 $\pm$ 0.595	$t = 0.219^{NS}$; $p = 0.827$; d.f. = 251
Quizalofop-ethyl	–	–	–
Rimsulfuron	–	–	–
s-metolachlor	29.878 $\pm$ 99.076	21.781 $\pm$ 54.520	$t = 0.458^{NS}$; $p = 0.648$; d.f. = 86
Terbutylazine	5.301 $\pm$ 7.459	4.527 $\pm$ 5.516	$t = 0.578^{NS}$; $p = 0.565$; d.f. = 98
Thifensulfuron-methyl	–	–	–
Triflurosulfuron-methyl	5.481 $\pm$ 6.488	1.489 $\pm$ 0.662	$t = 1.399^{NS}$; $p = 0.234$; d.f. = 4
Tritosulfuron	–	–	–

Legend: $\bar{x}$ SD = Arithmetic mean $\pm$ Standard deviation; Σ = total number of samples; Found = number of samples with herbicides found; NS = non-significant; d.f. = degrees of freedom; * = levels of statistical significance.

3.2. Monitoring of Herbicide Residues in 2023

Given the ten-year gap since the previous study, the research was repeated to assess the current levels of herbicide residues in agricultural land and gain insights into the level of pollution.

In the 2023 analysis conducted at the same locations, herbicide residues were detected in all soil samples. Similar to the findings in 2013, the minimum number of detected residues was 6, while the maximum number of active substances per location increased to 19. Among the arable soil samples analyzed, 52.3% contained 6–10 active substances, 44.5% contained 11–16 active substances, and 3.1% contained more than 16 active substances (Figure 3).

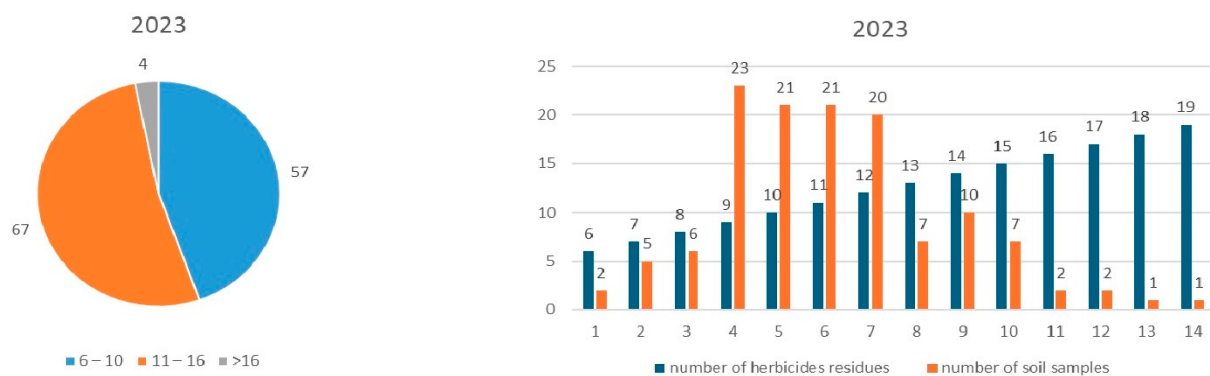


Figure 3. Presence of herbicides in soil samples—2023.

Prosulfocarb, napropamide, and bentazon were again the most commonly detected herbicides, with the same frequency of occurrence as in 2013. Additionally, the herbicide aclonifen was identified with a very high frequency (above 91%) at both soil depths. This compound was registered for use on the market of the Republic of Serbia in 2020 [36]. In addition to prosulfocarb, napropamide, and bentazon, the presence of 2,4-D methyl ester, flumioxazine, metazachlor, oxyfluorfen, and propyzamide was detected in a significant number of soil samples (50–90%). However, the overall content of analyzed herbicides in the soil samples was lower compared to the 2013 monitoring results. The maximum concentration was reached by clopyralid (179.8 mg/kg) at a depth of 30–60 cm, while in the surface layer, residues of this herbicide at the same locality were not determined (Table 1). The concentration of s-metolachlor in the 2023 soil samples was also notably reduced, with a maximum concentration of 114.7 mg/kg. In 23 soil samples, 9 different herbicide residues were found, and the highest number of detected active substances (19) was found in only 1 soil sample (Figure 3). Statistical analysis showed that, for most herbicides, the concentrations in the surface layer (0–30 cm) were similar to those in the deeper layer (30–60 cm). A significant difference in the average content for depths was observed for diflufenican, flumioxazin, metabromuron, metamitron, metribuzin, napropamide, and terbutylazine (Table 3).

Table 3. Number of positive samples, average concentrations of herbicide residues by depth—2023.

Active Substances	Depth of Soil Sample		<i>t</i> -Test for Independent Samples
	0–30 cm	30–60 cm	
	$\bar{x} \pm SD$ mg a.s./kg Soil	$\bar{x} \pm SD$ mg a.s./kg Soil	
2,4-D-methylester	1.163 ± 1.114	0.966 ± 0.837	$t = 1.4605^{NS}$; $p = 0.146$; d.f. = 221
Aclonifen	0.765 ± 1.098	0.588 ± 0.856	$t = 1.372^{NS}$; $p = 0.171$; d.f. = 233
Amidosulfuron	0.200	—	—
Aminopyralid	0.338 ± 0.386	—	—
Benfluralin	—	—	—
Bentazon	2.137 ± 1.387	1.832 ± 1.105	$t = 1.944^{NS}$; $p = 0.053$; d.f. = 252
Carfentrazone-ethyl	—	—	—
Clethodim	0.180 ± 0.039	—	—
Clomazone	2.672 ± 5.708	0.983 ± 1.260	$t = 1.616^{NS}$; $p = 0.111$; d.f. = 70
Clopyralid	—	98.976 ± 114.292	—
Cycloxydim	0.129	0.119	—
Diflufenican	3.538 ± 0.382	0.208 ± 0.082	$t = 12.049^*$; $p = 0.0068$; d.f. = 2
Ethofumesate	4.451 ± 3.370	4.451 ± 3.370	$t = 1.345^{NS}$; $p = 0.250$; d.f. = 4
Fenoxaprop-ethyl	1.325 ± 1.302	1.134	$t = 0.137^{NS}$; $p = 0.895$; d.f. = 6
Flufenacet	—	—	—
Fluazifop-P-butyl	—	—	—
Flumioxazin	0.361 ± 0.264	0.264 ± 0.176	$t = 3.924^{**}$; $p = 0.0001$; d.f. = 193
Foramsulfuron	0.273 ± 0.137	—	—
Imazamox	2.292 ± 2.942	—	—
Iodosulfuron-methyl	—	—	—
Lenacil	4.138 ± 7.828	—	—
Mesotrione	4.549 ± 9.579	0.303 ± 0.127	$t = 0.595^{NS}$; $p = 0.574$; d.f. = 6
Metabromuron	1.177 ± 1.345	3.283 ± 0.729	$t = 3.588^{**}$; $p = 0.0043$; d.f. = 11
Metamitron	4.276 ± 4.126	0.893 ± 1.063	$t = 3.546^{**}$; $p = 0.0011^*$; d.f. = 37
Metazachlor	0.264 ± 0.131	0.238 ± 0.140	$t = 1.317^{NS}$; $p = 0.189$; d.f. = 198
Metribuzin	4.694 ± 4.169	0.893 ± 1.063	$t = 3.934^{***}$; $p = 0.0004$; d.f. = 35
Metsulfuron-methyl	3.182	25.205 ± 34.489	$t = 0.553^{NS}$; $p = 0.636$; d.f. = 2
Napropamide	0.746 ± 0.462	0.903 ± 0.491	$t = 2.602^{**}$; $p = 0.009$; d.f. = 249
Nicosulfuron	6.042 ± 14.914	0.429 ± 0.439	$t = 1.676^{NS}$; $p = 0.099$; d.f. = 40
Oxyfluorfen	0.226 ± 0.127	0.258 ± 0.167	$t = 1.318^{NS}$; $p = 0.190$; d.f. = 144
Pendimethalin	3.319 ± 8.637	4.078 ± 9.020	$t = 0.377^{NS}$; $p = 0.707$; d.f. = 80

Table 3. Cont.

Active Substances	Depth of Soil Sample		<i>t</i> -Test for Independent Samples
	0–30 cm $\bar{x} \pm SD$ mg a.s./kg Soil	30–60 cm $\bar{x} \pm SD$ mg a.s./kg Soil	
Phenmedipham	–	–	–
Propyzamide	0.376 $\pm$ 0.553	0.290 $\pm$ 0.320	$t = 1.285^{NS}$; $p = 0.200$; d.f. = 175
Prosulfocarb	0.742 $\pm$ 0.484	0.843 $\pm$ 0.812	$t = 1.197^{NS}$; $p = 0.232$; d.f. = 250
Quizalofop-ethyl	–	–	–
Rimsulfuron	–	–	–
s-metolachlor	17.928 $\pm$ 26.503	14.306 $\pm$ 14.539	$t = 0.511^{NS}$; $p = 0.610$; d.f. = 83
Terbutylazine	8.666 $\pm$ 14.685	2.981 $\pm$ 2.452	$t = 2.202^*$; $p = 0.030$; d.f. = 93
Thifensulfuron-methyl	–	–	–
Triflurosulfuron-methyl	4.901 $\pm$ 6.065	–	–
Tritosulfuron	–	–	–

Legend: $\bar{x} \pm SD$ = Arithmetic mean $\pm$ Standard deviation; Σ = total number of samples; Found = number of samples with herbicides found; NS = non-significant; d.f. = degrees of freedom; *, **, *** = levels of statistical significance.

By summarizing the results of the herbicide residues in the agricultural land of the Republic of Serbia, it can be stated that good agricultural practices were applied and good management tools for plant protection were implemented (Figure 4).



Figure 4. Determined values of herbicides in the soil according to the specified categories, jointly for both years (2013 and 2023).

3.3. Soil Properties

The obtained results indicate minor variations in the mechanical composition and chemical properties of the tested soil samples (Table 4). Most samples were dominated by the fine sand fraction, with slightly smaller proportions of powder and clay. Based on mechanical composition, the samples were primarily classified as sandy loam. The humus content ranged from low to high according to the Scheffer–Schachtschabel classification. The average pH values of the soil in H₂O and KCl remained consistent across both years. The analyzed soils were classified as weakly to strongly carbonated. The Cation Exchange Capacity (CEC) values varied from 1.5 to 68.5 in the 2013 samples, and from 1 to 56.75 in the 2023 samples, depending on the type of clay, soil pH, and organic matter content.

Table 4. Physicochemical properties of soil samples (n = 128).

Soil Properties 2013	Max	Min	Average $\pm$ SD	CoV	LQ	UQ
pH in KCl	8.53	4.78	7.29 $\pm$ 0.6	0.09	7.27	7.57
pH in water	9.79	5.80	8.23 $\pm$ 0.51	0.06	8.13	8.41
CaCO ₃ (%)	31.98	0.27	11.86 $\pm$ 7.85	0.66	5.01	17.89
Organic matter (%)	8.41	0.29	3.32 $\pm$ 1.11	0.34	2.64	4.00
CEC (T)	68.50	1.50	24.82 $\pm$ 7.46	0.30	20.75	28.44
Mechanical composition						
Coarse sand	37.0	0.10	1.99 $\pm$ 3.71	1.87	0.50	2.00
Fine sand	84.20	8.60	36.42 $\pm$ 11.55	0.32	28.53	41.78
Powder	55.60	5.00	31.73 $\pm$ 7.62	0.24	28.63	36.00
Clay	59.10	6.50	29.86 $\pm$ 8.52	0.29	24.53	35.33
Soil Properties 2023	Max	Min	Average $\pm$ SD	CoV	LQ	UQ
pH in KCl	8.28	4.46	7.26 $\pm$ 0.68	0.09	7.23	7.62
pH in water	9.27	6.06	8.18 $\pm$ 0.54	0.07	8.14	8.43
CaCO ₃ (%)	39.86	0.09	12.37 $\pm$ 8.36	0.68	3.94	18.23
Organic matter (%)	7.98	0.84	3.38 $\pm$ 1.18	0.35	2.55	3.96
CEC (T)	56.75	1.00	24.55 $\pm$ 8.13	0.33	19.44	29.19
Mechanical composition						
Coarse sand	23.20	0.10	1.72 $\pm$ 2.69	1.56	0.50	1.70
Fine sand	81.40	9.60	37.42 $\pm$ 12.86	0.34	29.65	44.88
Powder	63.20	6.10	31.86 $\pm$ 7.90	0.25	28.18	36.43
Clay	56.00	5.40	29.01 $\pm$ 8.93	0.31	23.40	33.63

CoV: coefficient of variation; LQ: lower quartiles; UQ: upper quartiles.

Additionally, the influence of soil characteristics on the occurrence of pesticide residues was examined (Figure 5). Overall, there was no significant correlation between soil properties and the presence of herbicide residues, with *p*-values ranging from -0.1 to 0.1 for the largest number of samples.

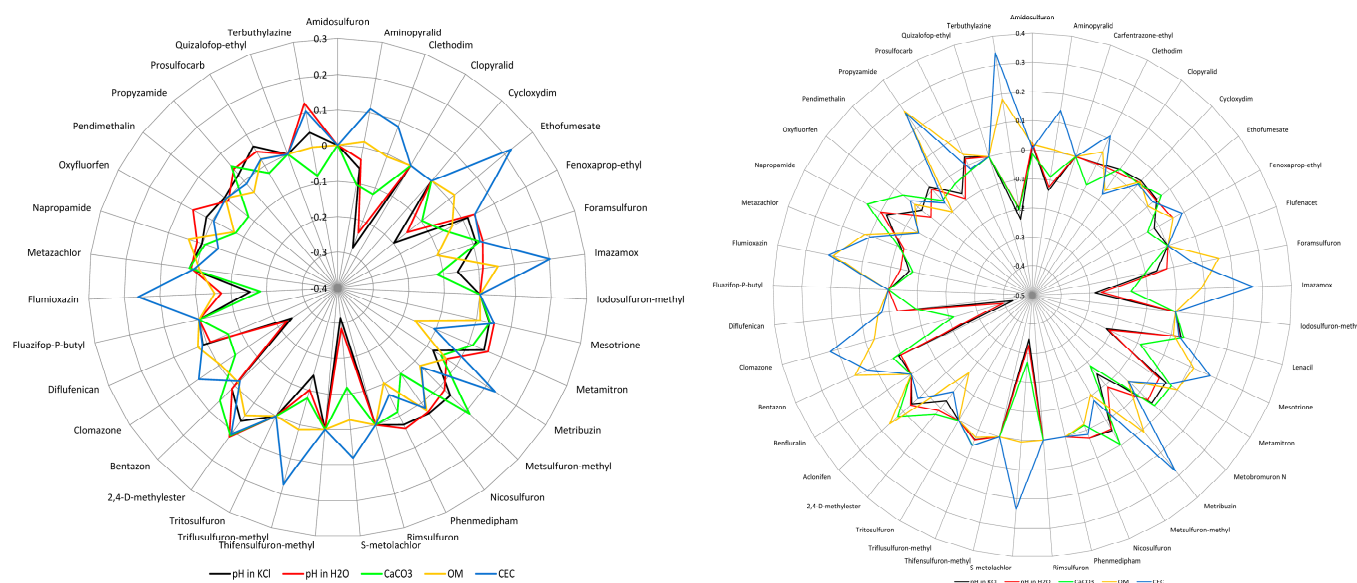


Figure 5. Graphical illustration of the correlation between soil properties and herbicide active substances 2013 and 2023.

4. Discussion

Despite agricultural soil being a primary sink and key reservoir for pesticides, extensive surveys that examine numerous sites and a wide range of current-use pesticides in agricultural soils are very rare [7]. The accumulation of pesticides in agricultural lands is a consequence of intensive plant protection [15]. The findings of these studies showed the presence of herbicide residues in all analyzed soil samples in 2013, but also 2023. This outcome was expected, considering the current global usage of approximately two million tons of pesticides annually, with herbicides accounting for over 50% of this total [20].

As part of the Green Deal, the European Commission adopted a proposal in June 2022 to reduce the use and risk of chemical pesticides and the use of the more hazardous pesticides by 50% by 2030, aiming to build a more sustainable and healthy food production system under the Farm to Fork Strategy [37]. It is basically the Regulation on the Sustainable Use of Plant Protection Products, which, beyond setting quantitative use reductions, implements integrated pest management (IPM) and prioritizes non-chemical alternatives.

In accordance with our research, monitoring across the European Union has revealed the presence of pesticide residues in all agricultural soil samples [7,10,15,20], with 83% containing more than three active pesticide substances. In France, an analysis of 47 soil samples across different land uses revealed the presence of 111 pesticides. It was found that nearly all soil samples from arable land contained the residues of at least seven active substances [10].

Prosulfocarb, napropamide, bentazon, and acetonifene were detected in almost all samples. However, the most used herbicide, glyphosate, was not included in our study, given that it is a total herbicide that is not used to protect field crops. The highest values of pesticides in arable lands in Europe are mainly attributed to glyphosate, diflufenican, azoxystrobin, epoxiconazole, tebuconazole, and boscalid, and were determined in areas of Switzerland and France [15,38]. In contrast to this, the lowest values, below 500 ng/g, were found in agricultural lands in the Czech Republic [13] and Spain [39]. The results of the analysis showed large amounts of s-metolachlor and clopyralid in the soil samples. Those higher values may be attributed to the soil sampling immediately after herbicide treatment. However, due to the low sorption in slightly to moderately alkaline soils, only a small amount of sulfonylurea herbicides was adsorbed and remained in soil samples [40].

Although organic farming prohibits the use of chemical agents for plant protection, pesticide residues have been detected in soil samples from fields cultivated under organic systems for over 20 years. The predominant herbicides identified were linuron, napropamide, chloridazon, and atrazine, including its degradation products. Considering that the plots under organic production were not exposed to the direct application of pesticides, the presence of these residues could be attributed to their unexpectedly long persistence or indirect contamination from nearby conventional fields through processes such as drift, aeolian erosion, or runoff [15].

A large study conducted in the EU between 2015 and 2018 covered three countries (Spain, Portugal, and the Netherlands) and four of the main EU crops (vegetable, orange, grape, and potato), amounting to 340 soil samples. The residues with the highest frequency of detection and the highest content in soil were the herbicide glyphosate and its main metabolite AMPA, and pendimethalin. The results suggested the intense use of glyphosate-based herbicides in some farms in this area, while the presence of pendimethalin was relatively expected, considering that it is a pre-emergence herbicide with application in vegetable production [9].

Furthermore, within the European Union, regular land surveys are conducted as part of the LUCAS Survey framework to gather information on land-related matters. Established by the European Commission, LUCAS is the periodic Land Use/Land Cover Area Frame Survey conducted in EU Member States. Starting in 2009, large-scale monitoring has been undertaken, specifically targeting the surface layer of the soil (0–20 cm). These initiatives have primarily concentrated on assessing physical and chemical properties, as well as the presence of heavy metals. In 2015, a similar study was carried out, and in the 2018 LUCAS Soil survey, the evaluation of residues of plant protection products (PPPs) was included as an additional component. An analysis was conducted on the presence of 118 active substances, including plant protection products (PPPs) and their metabolites, with 70 of these substances being approved, at a total of 3473 sites. The research showed the presence of pesticides in 74.5% of agricultural soils, 57.1% of which were samples with more than two active substances [41,42].

The pH level of the soil is a crucial factor that can impact the movement and degradation of pesticides [43]. This may be due to the higher capacity of these soils to absorb pesticides, leading to heightened persistence [44]. In this study, according to the results from 2013, it was determined that, with a decrease in soil pH, the content of cletodime ($p = -0.25$), etofumesate ($p = -0.17$), s-metolachlor ($p = -0.29$), and clomazon ($p = -0.24$) increased, while for 2023, a weak to moderate negative correlation was obtained for s-metolachlor ($p = -0.34$), clomazone ($p = -0.41$), imazamox ($p = -0.27$), and mesotrione ($p = -0.21$). In the study reported by Riedo et al. [15], atrazine and its TPs showed a negative correlation with soil pH.

On the other hand, the content of CaCO_3 and organic matter did not significantly affect the amount of herbicides in the soil in both years. With an increase in the Cation Exchange Capacity, the concentrations of etofumesate, imazamox, s-metolachlor, flumioxazin, terbutylazine, clomazone, and propizamide increased. The CEC in soil can significantly impact herbicide residues. CEC is a measure of the soil's ability to hold positively charged ions (cations). Soils with a high CEC can adsorb more herbicide molecules, which can reduce their availability for plant uptake or movement through the soil. While this may diminish the immediate efficacy of herbicides, it could lead to prolonged residual effects as the herbicides are slowly released back into the soil solution. Overall, soils with a higher CEC tend to retain herbicide residues longer, which can have implications for both the efficacy of the herbicides and their environmental impacts. Understanding the CEC of a given soil can help in predicting the behavior and management of herbicide applications [45].

In the study reported by Froger et al. [10], the occurrence of pesticides could not be attributed to soil characteristics or the sampling period. The sampling period did not affect the number of pesticide residues or their cumulative concentration. Moreover, there were no correlations between pesticide detection and soil properties in either “cultivated soils” (arable lands, vineyards, and orchards) or “uncultivated lands or grasslands” (such as forests, brownfields, and permanent grasslands), which are partially observed in our study, since the correlation between herbicide residues and soil properties was not significant.

In view of the above, the presence of herbicides in agricultural land is predominantly influenced by the chemical properties of the active ingredients, the timing of their application, and the climatic conditions in the specific area of monitoring.

5. Conclusions

Based on the monitoring results of agricultural land under intensive crop production, it can be concluded that, in 2023, more samples with numerous herbicide residues (>16) were found. Still, the amount of herbicide residues found in 2023 decreased compared to the residues from 2013. No significant correlation was obtained between soil properties and the presence of herbicide residues for the largest samples. This reduction can be attributed to the implementation of good agricultural practices, which promote sustainable agricultural strategies through controlled pesticide application. In addition, all the herbicides analyzed during the initial monitoring were still used after ten years. This continued use is justified from toxicological and ecotoxicological perspectives and from the standpoint of reduced or delayed resistance in weed populations. There is still insufficient knowledge regarding the fate and behavior of pesticides in soils, especially the currently used ones, besides those that have been extensively used and are highly persistent. Due to the lack of regulation, large-scale monitoring programs for each year are crucial for accomplishing production sustainability and lowering health and environmental risks. Future monitoring programs should include sampling at the end of the vegetation period, after harvesting, to obtain more reliable results.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Table A1. Properties of analyzed herbicides [46].

Herbicide	Chemical Group	Application Time	Molecular Formula	Molecular Weight (g/mol)	Water Solubility (mg/L) pH 7	log K _{OW} at pH 7 and 20 °C	Vapor Pressure (mPa) (at 20 °C)	Soil Degradation, DT ₅₀ in Field (day)	Bioconcentration Factor (l L/kg [−])	Threshold of Toxicological Concern (Cramer Class)
2,4-D-methyl ester	Phenoxy-carboxylates	post em	C ₉ H ₈ Cl ₂ O	235.064	/	/	/	/	/	High (class III)
Aclonifen	Diphenyl-ether	post em	C ₁₂ H ₉ ClN ₂ O ₃	264.66	1.4	4.37	0.016	80.4	2896	High (class III)
Amidosulfuron	Sulfonylureas	post em	C ₉ H ₁₅ N ₅ O ₇ S ₂	369.4	5600	−1.56	1.3 × 10 ^{−3}	21 (typical)	4.85	High (class III)
Aminopyralid	6-Chloropicolinates	post em	C ₆ H ₄ Cl ₂ N ₂ O ₂	207.02	2480	−2.87	2.59 × 10 ^{−5}	12.1	100	High (class III)
Benfluralin	Dinitroanilines	post em	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	335.28	0.064	5.27	1.8	39.9	/	High (class III)
Bentazon	Benzothiadiazinone	post em	C ₁₀ H ₁₂ N ₂ O ₃ S	240.3	7112	−0.46	0.17	7.5	21	High (class III)
Carfentrazone-ethyl	N-Phenyl-triazolinones	post em	C ₁₅ H ₁₄ Cl ₂ F ₃ N ₃ O ₃	412.2	29.3	3.7	7.2 × 10 ^{−3}	8.2	176	High (class III)
Clethodim	Cyclohexanediones (DIMs)	post em	C ₁₇ H ₂₆ ClNO ₃ S	359.92	5450	1.50	2.68 × 10 ^{−2}	3	3.5	High (class III)
Clomazone	Isoxazolidinone	post em	C ₁₂ H ₁₄ ClNO ₂	239.7	1212	2.58	27	27.3	40	High (class III)
Clopyralid	6-Chloropicolinates	post em	C ₆ H ₃ Cl ₂ NO ₂	192.0	7850	−2.63	1.36	8.2	1	High (class III)
Cycloxydim	Cyclohexanediones (DIMs)	post em	C ₁₇ H ₂₇ NO ₃ S	325.47	53	1.36	0.01	5	low risk	High (class III)
Diflufenican	Phenyl ethers	pre/post em	C ₁₉ H ₁₁ F ₅ N ₂ O ₂	394.3	0.05	4.2	4.25 × 10 ^{−3}	64.6	1276	High (class III)
Ethofumesate	Benzofurans	pre/post em	C ₁₃ H ₁₈ O ₅ S	286.35	50	2.7	0.65	37.8	144	High (class III)
Fenoxaprop-ethyl	Aryloxyphenoxy-propionates (FOPs)	post em	C ₁₈ H ₁₆ ClNO ₅	361.77	0.9	4.28	1.87 × 10 ^{−4}	4	4.9	High (class III)
Fluazifop-P-butyl	Aryloxyphenoxy-propionates	post em	C ₁₉ H ₂₀ F ₃ NO ₄	383.4	0.93	4.5	0.12	8.2	320	High (class III)
Flufenacet	α-Oxyacetamides	post em	C ₁₄ H ₁₃ F ₄ N ₃ O ₂ S	363.33	51	3.5	0.09	39	71.4	High (class III)

Table A1. Cont.

Herbicide	Chemical Group	Application Time	Molecular Formula	Molecular Weight (g/mol)	Water Solubility (mg/L) pH 7	log K _{OW} at pH 7 and 20 °C	Vapor Pressure (mPa) (at 20 °C)	Soil Degradation, DT ₅₀ in Field (day)	Bioconcentration Factor (l L/kg [−])	Threshold of Toxicological Concern (Cramer Class)
Flumioxazin	N-Phenyl-imides	pre em	C ₁₉ H ₁₅ FN ₂ O ₄	354.3	0.786	2.55	0.32	17.6	low risk	High (class III)
Foramsulfuron	Sulfonylureas	post em	C ₁₇ H ₂₀ N ₆ O ₇ S	452.4	3293	−0.78	4.20 × 10 ^{−8}	25.4 (typical)	low risk	High (class III)
Imazamox	Imidazolinones	post em	C ₁₅ H ₁₉ N ₃ O ₄	305.33	626,000	−2.9	6.3 × 10 ^{−8}	16.7	0.1	High (class III)
Iodosulfuron-methyl	Sulfonylureas	post em	C ₁₄ H ₁₄ IN ₅ O ₆ S	507.26	25,000	−0.7	2.6 × 10 ^{−6}	3.2	low risk	High (class III)
Lenacil	Uracils	post em	C ₁₃ H ₁₈ N ₂ O ₂	234.29	2.9	1.69	1.7 × 10 ^{−6}	39.8	18	High (class III)
Mesotrione	Triketones	pre/post em	C ₁₄ H ₁₃ NO ₇ S	339.32	1500	0.11	5.7 × 10 ^{−3}	5	low risk	High (class III)
Metamitron	Triazinones	post em	C ₁₀ H ₁₀ N ₄ O	202.21	1770	0.85	7.44 × 10 ^{−4}	11.1	75	High (class III)
Metazachlor	α-Chloroacetamides	pre/post em	C ₁₄ H ₁₆ ClN ₃ O	277.75	450	2.49	0.089	6.8	low risk	High (class III)
Metobromuron N	Phenylureas	post em	C ₉ H ₁₁ BrN ₂ O ₂	259.1	328	2.48	0.144	22.4	low risk	High (class III)
Metribuzin	Triazines	pre/post em	C ₈ H ₁₄ N ₄ OS	214.29	10,700	1.7	0.121	19	10	High (class III)
Metsulfuron-methyl	Sulfonylureas	post em	C ₁₄ H ₁₅ N ₅ O ₆ S	381.37	2790	−1.87	1 × 10 ^{−6}	13.3	1	High (class III)
Napropamide	Acetamides	pre em	C ₁₇ H ₂₁ NO ₂	271.35	74	3.3	2.2 × 10 ^{−2}	72	98	High (class III)
Nicosulfuron	Sulfonylureas	post em	C ₁₅ H ₁₈ N ₆ O ₆ S	410.4	90,700	−2.16	6 × 10 ^{−3}	13.5	low risk	High (class III)
Oxyfluorfen	Diphenyl ethers	pre/post em	C ₁₅ H ₁₁ ClF ₃ NO ₄	361.7	0.116	4.86	0.026	73	1637	High (class III)
Pendimethalin	Dinitroanilines	pre em	C ₁₃ H ₁₉ N ₃ O ₄	281.312	0.33	5.4	3.34	100.6	5100	High (class III)
Phenmedipham	Phenlcarbamates	post em	C ₁₆ H ₁₆ N ₂ O ₄	300.31	1.8	2.7	7 × 10 ^{−7}	16.7	165	High (class III)
Propyzamide	Benzamides	post em	C ₁₂ H ₁₁ Cl ₂ NO	256.12	9	3.27	0.058	50.5 (typical)	49	High (class III)
Prosulfocarb	Thiocarbamates	post em	C ₁₄ H ₂₁ NOS	251.39	13.2	4.48	0.79	9.8	700	High (class III)

Table A1. Cont.

Herbicide	Chemical Group	Application Time	Molecular Formula	Molecular Weight (g/mol)	Water Solubility (mg/L) pH 7	log K _{OW} at pH 7 and 20 °C	Vapor Pressure (mPa) (at 20 °C)	Soil Degradation, DT ₅₀ in Field (day)	Bioconcentration Factor (l L/kg [−])	Threshold of Toxicological Concern (Cramer Class)
Quizalofop-ethyl	Aryloxyphenoxy-propionates (FOPs))	post em	C ₁₉ H ₁₇ ClN ₂ O ₄	372.8	0.31	4.28	0.04	60	867	High (class III)
Rimsulfuron	Sulfonylureas	post em	C ₁₄ H ₁₇ N ₅ O ₇ S ₂	431.4	7300	−1.46	8.9 × 10 ^{−4}	10.8	low risk	High (class III)
s-metolachor	Chloroacetamide	pre em	C ₁₅ H ₂₂ ClNO ₂	283.79	480	3.05	3.7	23.17	68.8	High (class III)
Thifensulfuron-methyl	Sulfonylureas	post em	C ₁₂ H ₁₃ N ₅ O ₆ S ₂	387.4	54.1	−1.65	5.19 × 10 ^{−6}	10	0.8	High (class III)
Triflusaluron-methyl	Sulfonylureas	post em	C ₁₇ H ₁₉ F ₃ N ₆ O ₆ S	492.43	260	0.94	1.01 × 10 ^{−2}	4.5	1.3	High (class III)
Tritosulfuron	Sulfonylureas	post em	C ₁₃ H ₉ F ₆ N ₅ O ₄ S	445.3	78.3	0.62	9.3 × 10 ^{−5}	8.2	low risk	High (class III)
Terbuthylazine	Triazines	pre/post em	C ₉ H ₁₆ ClN ₅	229.81	6.6	3.4	0.152	21.8	34	High (class III)

Pre em: Pre-emergence; Post em: Post-emergence.

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