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The Occurrence and Distribution of Herbicides in Soil and Irrigation Canals in a High-Input Farming Region of Serbia

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Abstract

This study aims to improve the understanding of, and provide insights into, the environmental fate of herbicides currently used in agriculture, which is addressed through the analysis of the quality of canal water used for irrigation and the agricultural soil in the immediate vicinity. The research was conducted in the main agricultural region of Serbia, characterized by intensive crop production in conventional agriculture. Monitoring was focused on the Danube–Tisza–Danube canal system, specifically the Bogojevo–Bečej section. The presence of 41 currently used herbicides was analyzed in 520 soil samples collected from two depths (0–30 cm and 30–60 cm), as well as in 100 canal water samples. Results showed a high frequency of clopyralid, 2,4-D-methyl ester, terbuthylazine, fenoxaprop-ethyl, and aclonifen, with the highest amountsbeingterbuthylazine and quizalofop-ethyl, which was possibly a consequence of their recent application shortly before sampling. Concentrations of herbicide residues at different depths were closely similar, without the impact of soil mechanical and chemical characteristics on herbicide levels. In canal water characterized as moderately salty and slightly alkaline, herbicide residues were far below the maximum allowable concentrations, suggesting that the canal water is suitable for aquatic life, irrigation, and other uses. The findings suggest that the appropriate use of herbicides in regions under intensive agriculture is important for reducing environmental contamination.

Keywords: soil; water; environment; agriculture; herbicides; residues; pollution; ecology

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1. Introduction

Unlike the period when the synthesis and use of pesticides rapidly developed, today, due to the potentially harmful effects, every compound (before its introduction into production and application) undergoes a strict registration procedure aimed at assessing the risk to human health, animal welfare, and the environmental impact [1]. Considering that intensive crop production has largely relied particularly on the use of herbicides as the dominant plant protection products for decades, their impact on soil and water quality is a priority issue regarding environmental protection and a major cause of global concern [2].

Soil contamination with pesticides may result from their direct application to control harmful organisms, treated seed and combined use with mineral fertilizers. Also, they can indirectly contaminate soil by runoff from treated plants, irrigation with contaminated water, drift during the treatment of surrounding crops, wind, or rain [3,4]. Additional sources of pollution include inappropriate disposal of packaging waste, together with unregulated dumpsites. Pesticide losses in general, depending on the application method and the type of sprayer, range from 22% to 80% [5], so a significant part remains in the environment [6,7]. The behavior of pesticides in the soil is influenced by the physico-chemical properties of pesticides, applied quantity, water solubility, application method, ability of binding to the colloidal particles, soil type and fertility, climatic factors, etc. Adsorption, desorption, diffusion, and degradation processes are directly related to their persistence and leaching into the soil [8]. A particular concern is the occurrence of phytotoxicity in subsequent crops in crop rotation, e.g., residues of certain herbicides applied in the previous crop can cause increased phytotoxicity in the following crop. Similarly, many herbicides, when applied on sandy and highly permeable soils, are quickly leached into the root zone of the cultivated plant and may exhibit phytotoxic effects. Along with the aforementioned, the pesticide application must not disturb the activities of soil microorganisms, which are essential for the cycling of nutrients in the soil. They also play a significant role in the creation and maintenance of soil fertility, influence plant growth and development, and degrade herbicides and other pollutants. Additionally, these microorganisms serve as indicators of changes in the physico-chemical soil properties, which arise under the influence of various external environmental factors [9,10].

Levels of pesticides in environmental samples are measured mostly in micrograms and nanograms [11–13]. Even in small amounts, releases into the environment could result in the long-term accumulation and biomagnification of some pollutants, potentially complicating their negative effects [13]. Pesticides have been reported to affect human health in various ways, which can lead to serious consequences such as endocrine disruption, neurological disruption, and immune and reproductive system effects [13–15]. Consequently, the toxic effects of pesticides on non-target organisms have created great concern worldwide.

A lot of research shows that more than 60% of European soils are considered unhealthy, and around 2.8 million localities within the European Union (EU) have been identified as potentially contaminated. Furthermore, the results suggest that this situation is worsening over time [16]. Despite the occurrence of soil contamination, which is a significant concern, the monitoring of pesticide residues in soil in the EU is not adequately regulated compared to water monitoring. There is also a lack of extensive international studies about pesticide contamination in soil, with most of the existing studies focused on individual active substances or a limited number of them [17]. Some European countries have included reference or maximum levels of pesticides that are no longer in use in their legislation for soil, as their high persistence makes their monitoring necessary, while many currently used pesticides are not yet regulated in this way [17–19]. The Soil Surveillance and Resilience Law could significantly change the existing conditions. In addition, the European Commission has introduced a new EU Soil Strategy for 2030, aiming to ensure that all EU soil ecosystems are in a healthy state by 2050 [20].

Soil, in which pesticides accumulate, represents a serious ecological problem as pesticides, particularly herbicides, are transferred to other ecosystem components, including surface and groundwater. The area of water protection and contamination within the EU has been regulated since 2000 by the Water Framework Directive (WFD) [21]. In recent years certain changes and additions have been introduced, along with proposals for new changes. One of the seventeen goals proposed by the United Nations within the 2030 Agenda for Sustainable Development includes the protection of aquatic ecosystems and the reduction in aquifer pollution [22]. Recently, the European Commission proposed changes to this directive to address the existing shortcomings and adopted new exceptions related to its application, according to which the good status of water bodies is achieved if all parameters are qualified as good. According to the latest updates, all water bodies need to accomplish good status by 2027. The most recent results reveal that at least 35% of European surface waters do not achieve good chemical status and 51% show inadequate ecological status [23].

In parallel, Directive 2000/60/EC [21], amended by Directives 2008/105/EC [24] and 2013/39/EU [25], sets limits for 45 different substances in various water bodies. Among the 45 chemical contaminants currently classified as priority substances, which include pesticides, metals, and industrial chemicals, 21 are categorized as priority hazardous substances regarding their bioaccumulation potential, persistence, and toxicity. Most of these substances are no longer in use [25]. However, there is still an absence of extensive monitoring of pesticide residues that are currently intensively applied. This is of great importance considering the trend of exclusion from using more pesticides and the intensification of applying the remaining current ones.

The particular challenges regarding pesticide residue presence in water are canal network waterways located among arable land under intensive agricultural production. Water bodies near agricultural fields are particularly vulnerable to contamination, as pesticides from treated areas are directly transported into these aquatic systems. These water bodies accumulate significantly higher pesticide concentrations compared to more distant or larger water bodies. When rainfall occurs immediately after pesticide application on crop fields it can lead to the rapid runoff of pesticide molecules. Rainfall or irrigation water facilitates the transport of pesticides, carrying them into nearby surface waters through runoff or into groundwater through leaching.

Crop production uses vast amounts of water, which is often contaminated with substances such as pesticides originating from surrounding arable fields. Contaminated irrigation water can transfer these pollutants to other crops and the environment, affecting the quality of agricultural products and potentially entering the food chain. This study aims to improve the understanding of the environmental fate of currently used herbicides by analyzing canal water used for irrigation and the agricultural soil in the immediate vicinity. Given the existing gaps in their monitoring, special attention is paid to herbicides in use and to watercourses located on arable land. Monitoring was focused on the Danube–Tisza–Danube canal system, located in the main agricultural region of Serbia. The majority of the selected herbicides are commonly applied in crop production, reflecting the dominant agricultural practices in the study area.

2. Materials and Methods

2.1. Study Area

Danube–Tisza–Danube (DTD) is a canal system located in northern Serbia. It is a unique system built for flood control, amelioration, water supply, wastewater management, tourism, and fishing. Situated in the middle of the Pannonian plain, the canal system covers 12.700 km^2, with a total length of 929 km. Part of the system of waterways is the Bogojevo–Bečej canal (Figure 1), which also forms part of the wider Danube–Tisa–Danube canal system. This canal is an important watercourse that connects the Tisza River and the Danube River, and other rivers in the Danube basin. It allows navigation and transport between Bečej and Bogojevo, linking to the Danube, Tisza, and smaller canals. Specific to this canal is that it is situated in the main agricultural region under intensive crop production in conventional agriculture, which implies intensive use of plant protection products.

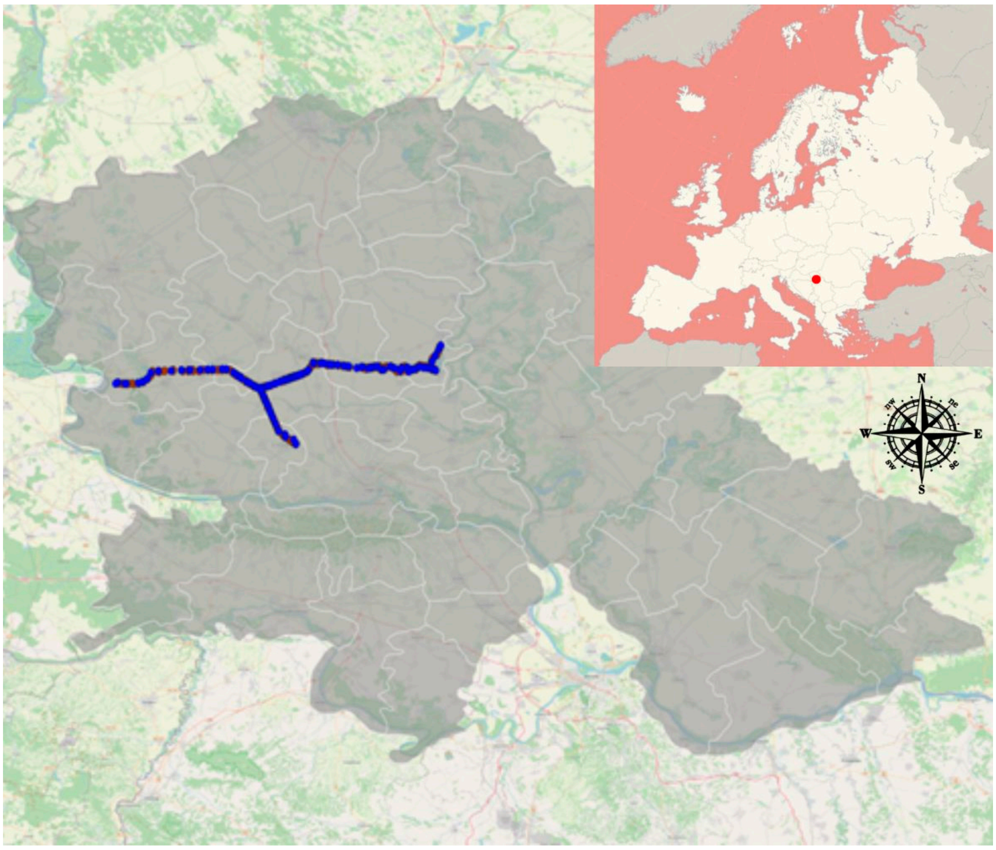

Figure 1. Sampling area—Bogojevo–Bečej canal (Vojvodina, Serbia), marked in blue and brown.

Monitoring was conducted in late spring since this is the time of year when herbicide levels in the environment are expected to reach their peak.

2.2. Chemicals

Certified analytical standards of herbicides with a high purity grade (>98%) were obtained from the manufacturer Dr Ehrenstorfer (Table S1). The solvents used for the extraction and chromatography were obtained from Fisher Scientific (Leicestershire, UK). Individual herbicide stock standard solutions were prepared by dissolving precisely weighed analytical standards in 10 mL of an appropriate solvent (acetonitrile or methanol), after which they were protected from light and stored at −20 °C in dark glass bottles with PTFE closures during the experiment, i.e., 2 months [26]. Through further dilution, working standard solutions of different concentrations were prepared.

2.3. Soil Sampling and Extraction

Soil samples were collected during May and June 2024, at 260 localities, from two depths (0–30 cm and 30–60 cm), along a canal (in total 520 soil samples). From each sampling site approximately 500 g of soil sample was taken by the agrochemical probe. All samples, collected in a cloth bag, were transported to the laboratory. Afterwards, soil samples were air-dried, ground, and sieved to determine the granulometric composition, textural class, and basic chemical properties.

pH values for each sample were determined in water (H_2O) and potassium chloride (KCl) according to the SRPS EN ISO 10390:2022 method [27]. The content of calcium carbonate ($CaCO_3$) was determined according to the SRPS ISO 10693:2005 [28], organic matter content was estimated by the volumetric dichromate method (HRN EN ISO 14235) [29] and defined according to Tyurin, while the base saturation was determined according to Kappen based on the method.

Herbicide extraction from soil samples was performed using the QuEChERS-based method [30]. Previously prepared soil samples (dried and ground) (5 g) were transferred to a polypropylene cuvette (50 mL), then 20 mL of acetonitrile containing 1% HCOOH was added alongside 10 mL of ultrapure water (Fisher Scientific, Leicestershire, UK). Afterwards, the CHROMABOND® QuEChERS (Sigma-Aldrich, Bellefonte, PA, USA) buffer salt mixture (4 g $MgSO_4$, 1 g NaCl, 0.5 g $C_6H_6Na_2O_7 \cdot 1.5\ H_2O$, 1 g $Na_3C_6H_5O_7 \cdot 2\ H_2O$) along with Ceramic Homogenizers were added, and then the samples were hand shaken for 1 min and vortexed for 3 min. After that, the samples were left in an ultrasonic bath for 10 min, followed by centrifugation (Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) for 5 min at 4000 rpm. An aliquot of the supernatant was transferred into a 15 mL cuvette and left in the refrigerator at +4 °C, for 2 h. Afterwards, the CHROMABOND QuEChERS Clean-up salt mixture (900 mg $MgSO_4$, 150 mg Diamino (PSA), 150 mg C18), was added into the cuvettes, which were then hand shaken for 1 min and centrifuged for 5 min at 4000 rpm. The extract was evaporated using a nitrogen stream, dissolved in 1 mL of acetonitrile, filtered through a 0.45 µm membrane filter (Macherey-Nagel GmbH & Co. KG, Duren, Germany), and analyzed.

2.4. Water Sampling and Extraction

Specifically, one hundred water samples were collected using an extendable sampling pole at different points along the canal from Bogojevo to Bečej, during May and June 2024. The samples were collected into glass bottles (volume 1 L) from each sampling site, with the addition of 1 mL of formic acid. Afterwards, the bottles were sealed and transferred to the laboratory. The samples were stored in a refrigerator at +4 °C for approximately 24 to 48 h, until extraction.

Physico-chemical water quality parameters including pH value, electrical conductivity, Ca, Mg, Na presence, and the Na adsorption ratio were analyzed.

Herbicide extraction from water was performed by solid-phase disk extraction using EmporeTM C-18 disks of a diameter of 47 mm (Cat no. 2215 CDC Analytical). Before extraction, the disk was conditioned with 5 mL of methanol and 5 mL of water. Before the disk was dried, the water sample (1000 mL) was passed through the disk at a flow rate of approximately 10 mL/min, using an ENVI 6.1 disk holder manifold (Supelco Cat No 57173 and 57174) that maintained a constant vacuum. Afterwards, the disk was dried under a vacuum for 30 min and the analytes were eluted using a mobile phase (methanol containing 0.05% HCOOH) (2 × 5 mL each). Then the extracts were evaporated in a stream of nitrogen to dryness, and after that reconstituted in the mobile phase (1 mL) and analyzed for the content of 41 herbicides.

2.5. Method Validation

The method was validated by examining the linearity of the detector response, determining the extraction yield, reproducibility of measurement, and limit of detection. The linearity of the detector response for 41 herbicides ranged from 0.9906 to 0.9998. To test the extraction yield of herbicide residues, an appropriate amount of salt was added to 1 L of deionized water to ensure the same ionic strength and conductivity of approximately 388 µS/cm (average value of the tested samples). The water was then spiked in triplicate with a solution of a standard mixture of herbicides of individual concentrations of about 0.1 µg/L, using TPP (triphenylphosphate) as an internal standard. The spiked water samples were conditioned by adding 5 mL of methanol to modify the polarity and extracted in the same way as real water samples from irrigation canals. A control laboratory soil sample, spiked by adding 1 mL of a mixed herbicide standard with individual concentrations of approximately 5 µg/mL to 500 g of soil, was used to determine the soil extraction yield. The spiked soil was then homogenized in a rotary shaker for 24 h, after which the extractions were repeated three times in the same manner as with real samples. The achieved yield was up to 96% for water samples and up to 103% for spiked soil samples [31]. The obtained pesticide residue concentrations were not corrected for the achieved yields of individual pesticides. The limit of detection (LOD) was from 0.1 µg/kg to 1 µg/kg for soil and from 0.0007 µg/L to 0.0139 µg/L for water samples. Average achieved reproducibility (RSD%) was 23.2%.

As control laboratory samples, spiked samples of deionized water and soil were prepared and analyzed in the same manner as described for determining the extraction yield. After each spiked control laboratory sample, pure solvent was passed through the chromatograph as a sample to confirm that no analyte carryover had occurred.

2.6. Herbicide Residues Analysis

The content of herbicide residues in soil and water samples was analyzed using GC-MS/MS and LC-MS/MS due to the different natures of herbicides.

2.6.1. The GC-MS/MS Conditions

Herbicide residue analysis was performed by a Thermo Trace 1300 TSQ 9000 (Thermo Scientific, Austin, TX, USA), operated through X-Calibur software ver. 3.0. Chromatographic separation was achieved using an HP-5-MS column (30 m length × 0.25 mm internal diameter, 0.25 µm film thickness). High-purity helium (99.999 vol%, Linde) served as the carrier gas at a constant flow rate of 1 mL/min. The oven-temperature program started at 60 °C with a 1 min hold, followed by an increase of 10 °C/min up to 180 °C (held for 2 min), and then a ramp of 5 °C/min up to a final temperature of 280 °C, which was maintained for 5 min. The injector was set to 250 °C in the splitless mode, with an injection volume was 1 µL. The ion source temperature was maintained at 230 °C and the interface at 280 °C. Mass spectrometric detection was performed using electron ionization at 70 eV. In selected ion monitoring (SIM) mode, specific target ions were monitored within designated time windows based on their corresponding retention times.

2.6.2. The LC-MS/MS Conditions

The herbicides were quantified using an LC-MS/MS VANQUISH CORE/TSQ Quantis Plus on a Thermo Scientific™ Hypersil GOLD™ aQ C18 Polar Endcapped HPLC Column, 100 mm × 2.1 mm × 1.9 µm (Cat No 25302-102130).

The mobile phase was composed of methanol with 0.1% acetonitrile (solvent A) according to the following program: 0–1 min: 90% B, 10% A; 1–5 min: linear gradient to 50% B, 50% A; 5–10 min: linear gradient to 10% B, 90% A; 10–12 min: hold at 10% B, 90% A; 12–15 min: re-equilibration to initial conditions. The total run analysis was 15 min. Column temperature was set at 35 °C and the flow rate was 0.4 mL/min.

3. Results

3.1. Analysis of Herbicide Residues in Soil Samples

The herbicide residues analyses were performed at 260 localities, where the soil was sampled at two depths of 0–30 cm and 30–60 cm. In the surface soil layer, analysis revealed a high frequency of clopyralid (95%), 2,4-D-methyl ester (88%), terbuthylazine (87%), fenoxaprop-ethyl (81%), and aclonifen (77%). Although concentrations of clopyralid, 2,4-D-methyl ester, fenoxaprop-ethyl, and aclonifen were all below 0.5 µg/kg, terbuthylazine stood out with an average concentration of 58.556 µg/kg, while the maximum value was even 7507.007 µg/kg at one locality. The average content of quizalofop-ethyl, found in only 13% of the samples, was 51.385 µg/kg, resulting in a high value determined at one locality (1303.149 µg/kg). Herbicides metsulfuron-methyl, metamitron, and imazamox (Table 1) in the surface layer of the soil were present in amounts above 10 µg/kg. Out of a total of forty-one analyzed herbicides, three of them (aminopyralid, fluazifop-p-butyl, and iodosulfuron-methyl) were not detected, or their values were below the LOD, while twenty-three of them had a frequency of occurrence below 10% (Table 1, Figure 2).

Table 1. Summary data for herbicide residues in soil samples (0–30 cm)—minimum, maximum, and average concentrations ($\bar{X}$), standard deviation (SD), and relative standard deviation (RSD), with the percentage of positive detections of the target compounds.

Herbicide	Min (µg/kg)	Max (µg/kg)	$\bar{X}$ (µg/kg)	SD (µg/kg)	RSD (%)	Positive Findings (%)
2,4-D-methylester	0.101	2.661	0.475	0.393	82.788	88
Aclonifen	0.101	2.204	0.228	0.181	79.071	77
Amidosulfuron	0.101	2.528	0.243	0.421	173.151	14
Aminopyralid	0.000	0.000	0.000	0.000	0.000	0
Benfluralin	0.115	20.468	1.681	4.423	263.101	8
Bentazon	0.155	0.245	0.193	0.038	19.834	1
Carfentrazone-ethyl	0.101	0.268	0.139	0.052	37.069	5
Clethodim	0.100	0.655	0.146	0.082	55.970	22
Clomazone	0.103	0.643	0.221	0.115	52.251	34
Clopyralid	0.103	1.246	0.399	0.266	66.748	95
Cycloxydim	0.101	0.703	0.202	0.177	87.321	6
Diflufenican	0.101	4.005	0.381	0.619	162.594	36
Ethofumesate	0.101	16.398	0.521	1.980	379.782	37
Fenoxaprop-ethyl	0.100	1.414	0.264	0.181	68.592	81
Fluazifop-P-butyl	0.000	0.000	0.000	0.000	0.000	0
Flufenacet	0.100	61.084	1.140	5.774	506.652	51
Flumioxazin	0.104	1.603	0.297	0.371	125.069	6
Foramsulfuron	0.480	13.703	2.584	3.582	138.620	4
Imazamox	5.496	23.125	13.277	5.828	43.894	2
Iodosulfuron-methyl	0.000	0.000	0.000	0.000	0.000	0
Lenacil	0.920	2.929	2.204	0.273	12.385	29
Mesotrione	0.101	1.596	0.341	0.386	113.217	6
Metamitron	2.681	34.632	17.226	11.633	67.532	4
Metazachlor	1.547	5.272	2.637	1.224	46.417	2
Metobromuron N	0.100	10.402	2.172	4.115	189.486	2
Metribuzin	0.106	4.335	0.905	1.361	150.423	4
Metsulfuron-methyl	0.157	242.025	18.658	62.012	332.364	5
Napropamide	0.102	1.457	0.382	0.430	112.568	5
Nicosulfuron	0.185	2.045	0.932	0.490	52.643	4
Oxyfluorfen	0.102	0.851	0.289	0.259	89.400	3
Pendimethalin	0.105	10.237	1.681	2.503	148.865	6
Phenmedipham	0.100	8.826	5.135	2.259	43.998	27
Propyzamide	0.129	108.603	8.182	26.850	328.145	6
Prosulfocarb	0.113	1.056	0.282	0.235	83.478	5
Quizalofop-ethyl	0.102	1303.149	51.385	222.158	432.340	13
Rimsulfuron	0.105	1.383	0.584	0.479	82.037	4
S-metolachlor	0.109	6.413	1.021	1.692	165.766	5
Terbuthylazine	1.013	7507.007	58.556	503.537	859.918	87
Thifensulfuron-methyl	0.100	1.854	0.347	0.399	115.126	14
Triflusulfuron-methyl	0.105	0.908	0.276	0.263	95.248	3
Tritosulfuron	0.109	0.129	0.119	0.010	8.469	1

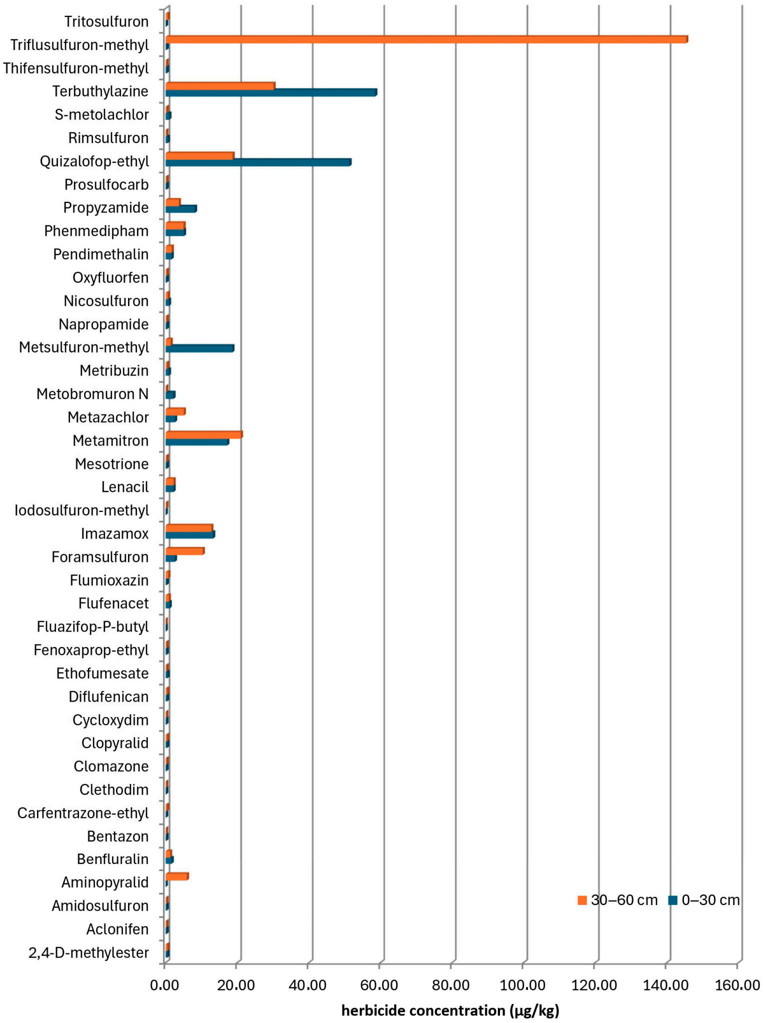

Figure 2. Summarized results of herbicide residues in soil at two depths.

At a depth of 30–60 cm, the residues of clopyralid, 2,4-D-methyl ester, terbuthylazine, fenoxaprop-ethyl, and aclonifen were dominant, with the frequency of occurrence almost identical to that in the surface layer. The occurrence frequency of 21 active substances was below 10%. Residues of bentazon, fluazifop-p-butyl, metazachlor, metobromuron N, and tritosulfuron were not detected or their amounts were below the LOD. Herbicide concentrations in the soil samples ranged from the limit of detection to 145.470 µg/kg, with the highest concentration observed for triflusulfuron-methyl. Furthermore, high concentrations of terbuthylazine, metamitron, quizalofop-ethyl, imazamox, and foramsulfuron were detected (Table 2, Figure 2).

Table 2. Summary data for herbicide residues in soil samples (30–60 cm)—minimum, maximum, and average concentrations ($\bar{X}$), standard deviation (SD), and relative standard deviation (RSD), with the percentage of positive detections of the target compounds.

Herbicide	Min (µg/kg)	Max (µg/kg)	$\bar{X}$ (µg/kg)	SD (µg/kg)	RSD (%)	Positive Findings (%)
2,4-D-methylester	0.101	3.946	0.499	0.487	97.741	89
Aclonifen	0.102	1.020	0.212	0.130	61.391	66
Amidosulfuron	0.100	1.048	0.197	0.196	99.615	14
Aminopyralid	4.490	7.406	5.948	1.458	24.514	1
Benfluralin	0.108	7.117	1.235	2.003	162.122	5

Table 2. *Cont.*

Herbicide	**Min (µg/kg)**	**Max (µg/kg)**	**$\bar{X}$ (µg/kg)**	**SD (µg/kg)**	**RSD (%)**	**Positive Findings (%)**
Bentazon	0.114	0.114	0.114	0.000	0.000	0
Carfentrazone-ethyl	0.100	3.003	0.379	0.744	196.200	6
Clethodim	0.101	0.289	0.139	0.041	29.879	17
Clomazone	0.100	3.314	0.266	0.335	126.337	39
Clopyralid	0.103	4.614	0.414	0.390	94.331	95
Cycloxydim	0.103	0.211	0.148	0.037	24.902	5
Diflufenican	0.102	4.555	0.427	0.733	171.751	26
Ethofumesate	0.100	2.862	0.255	0.362	142.024	25
Fenoxaprop-ethyl	0.101	0.981	0.247	0.155	62.670	79
Fluazifop-P-butyl	0.000	0.000	0.000	0.000	0.000	0
Flufenacet	0.100	67.018	0.884	6.187	699.895	45
Flumioxazin	0.106	5.964	0.777	1.441	185.305	10
Foramsulfuron	0.702	70.962	10.358	22.925	221.316	3
Imazamox	4.206	21.902	12.761	5.585	43.765	3
Iodosulfuron-methyl	0.120	0.240	0.181	0.043	24.035	2
Lenacil	1.602	2.782	2.212	0.241	10.902	30
Mesotrione	0.106	1.532	0.252	0.297	117.835	8
Metamitron	1.939	44.660	21.005	14.417	68.635	6
Metazachlor	5.077	5.077	5.077	0.000	0.000	0
Metobromuron N	0.135	0.135	0.135	0.000	0.000	0
Metribuzin	0.122	1.054	0.413	0.245	59.320	5
Metsulfuron-methyl	0.113	11.330	1.410	2.744	194.560	7
Napropamide	0.101	1.055	0.275	0.317	115.173	5
Nicosulfuron	0.141	1.106	0.605	0.334	55.175	3
Oxyfluorfen	0.105	0.851	0.293	0.322	110.086	2
Pendimethalin	0.117	3.299	1.692	1.118	66.093	2
Phenmedipham	0.105	8.303	5.006	2.196	43.862	28
Propyzamide	0.101	36.442	3.687	9.894	268.383	5
Prosulfocarb	0.104	0.976	0.223	0.253	113.641	4
Quizalofop-ethyl	0.101	329.715	18.710	65.285	348.936	9
Rimsulfuron	0.102	0.438	0.174	0.116	66.462	3
S-metolachlor	0.102	0.851	0.270	0.252	93.434	3
Terbuthylazine	1.046	3185.060	30.173	212.588	704.569	88
Thifensulfuron-methyl	0.101	1.018	0.218	0.223	102.415	13
Triflusulfuron-methyl	0.103	2613.719	145.470	598.638	411.520	7
Tritosulfuron	0.604	0.604	0.604	0.000	0.000	0

The obtained results indicate that the concentrations of herbicide residues in the soil at two depths are very similar, with no significant differences except for aclonifen ($t = 2.325$, $p = 0.021$) and iodosulfuron-methyl ($t = -1.955$, $p = 0.050$) (Table S2).

Table S2, statistics, is available in Supplementary Materials.

Physico-Chemical and Mechanical Properties of Soil Samples

The average pH values of the soil in H_2O and KCl were 8.63 and 7.67, respectively, indicating an alkaline reaction. Due to the average content of $CaCO_3$ (18.92%), the analyzed soils were classified as weakly to strongly carbonated since the content varied from 3.44 to 33.57%. The organic matter of 3.11% indicates that the soil is moderately to well supplied with organic matter, which is a solid value for carbonate soils. However, in some localities the low level of organic matter (0.08%) indicates soils extremely poor in humus.

Base saturation of 99.96% confirms the alkaline character of this soil, considering the extremely high base saturation (Table 3).

Table 3. Physicochemical properties of soil samples (n = 520).

	pH KCl	pH H_2O	$CaCO_3$ (%)	Organic Matter (%)	Base Saturation (%)
$\bar{X}$	7.76	8.63	18.92	3.11	99.96
Min	7.22	7.94	3.44	0.08	99.03
Max	8.75	9.89	33.57	7.5	100
SD	0.27	0.26	6.10	1.51	0.09
RSD	3.52	3.04	32.25	48.59	0.09
LQ	7.61	8.45	14.19	1.93	100
UQ	7.87	8.74	23.42	4.17	100

Mechanical composition of soil (sand 48.18%, silt 29.80%, and clay 22.02%) indicates that, in the majority of localities, the soil is classified as loam soil, which is suitable for growing most crops (Table 4).

Table 4. Mechanical composition of soil samples (n = 520).

	Coarse Sand (%)	Fine Sand (%)	Silt (%)	Clay (%)
$\bar{X}$	3.67	44.51	29.80	22.02
Min	0.20	4.10	0.40	0.10
Max	66.70	93.80	70.80	45.90
SD	7.97	12.98	9.86	7.78
RSD	217.51	29.15	33.09	35.31

Further analysis showed that the soil's mechanical and chemical properties did not influence the herbicide content (p-values ranged between −0.2 and 0.2) (Figure 3). The only exception was metobromuron N, with a p-value of −0.429, where lower levels of this herbicide may be the consequence of high base saturation.

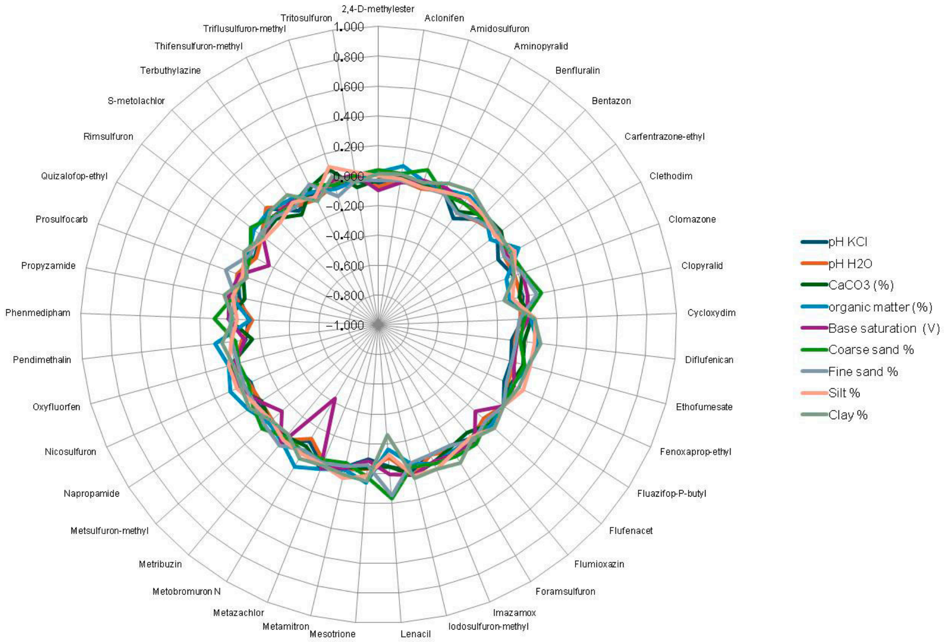

Figure 3. Correlation between soil properties and herbicide active substances.

3.2. Analysis of Herbicide Residues in Water Samples

A total of 100 water samples from the DTD canal network were analyzed for the presence of 41 herbicide active substances. S-metolachlor and terbuthylazine were detected in nearly all samples, with an average concentration of 0.031 μg/L and 0.011 μg/L, respectively. Besides these two herbicides, residues of carfentrazone-ethyl were slightly increased, and the potential explanation is that this herbicide is used as a desiccant, facilitating easier washoff from the treated surfaces and subsequent entry into surface water bodies. Residue concentrations of clopyralid, diflufenican, metazachlor, propyzamide, quizalofop-ethyl, prosulfocarb, cycloxydim, tritosulfuron, mesotrione, aminopyralid, rimsulfuron, bentazon, and metamitron were not found or their amounts were below the LOD values. The occurrence frequency of herbicides imazamox, thifensulfuron-methyl, iodosulfuron-methyl, fluazifop-p-butyl, metsulfuron-methyl, lenacil, triflusulfuron-methyl, pendimethalin, phenmedipham, benfluralin, flumioxazin, fenoxaprop-ethyl, and metribuzin in analyzed canal water samples was below 10%, with concentrations lower than 0.01 μg/L. Moreover, nicosulfuron, clomazone, and amidosulfuron were detected in many samples (Table 5), with average concentrations of 0.009, 0.002, and 0.011 μg/L. The obtained results were expected, considering the intensive use of herbicides based on these active substances for weed control in maize and soybean. Following the banning of many previously used active substances, the application of sulfonylurea herbicides has significantly increased. Ethofumesate, flufenacet, oxyfluorfen, and foramsulfuron, which are used after sowing and before crop emergence, were detected in 26–28% of analyzed water samples, with average values of 0.016, 0.008, 0.003, and 0.004 μg/L. Residues of aclonifen, metobromuron N, 2,4-D-methyl ester, napropamide, and clethodim were found in 10–20% of water samples, with concentrations below 0.01 μg/L.

Table 5. Summary data for herbicide residues in water samples—minimum, maximum, and average concentrations ($\bar{X}$), standard deviation (SD), and relative standard deviation (RSD), with the percentage of positive detections of the target compounds.

Herbicides	min (μg/L)	max (μg/L)	$\bar{X}$ (μg/L)	SD (μg/L)	RSD (%)	Positive Findings (%)
2.4-D-methylester	0.001	0.004	0.002	0.001	28.543	17
Aclonifen	0.001	0.006	0.002	0.001	78.425	19
Amidosulfuron	0.003	0.032	0.011	0.007	67.582	55
Aminopyralid	-	-	-	-	-	0
Benfluralin	0.001	0.001	0.001	0.000	21.657	4
Bentazon	-	-	-	-	-	0
Carfentrazone-ethyl	0.004	0.022	0.011	0.006	51.016	11
Clethodim	0.002	0.005	0.003	0.001	33.533	10
Clomazone	0.001	0.005	0.002	0.001	36.569	67
Clopyralid	-	-	-	-	-	0
Cycloxydim	-	-	-	-	-	0
Diflufenican	-	-	-	-	-	0
Ethofumesate	0.006	0.035	0.016	0.007	40.490	28
Fenoxaprop-ethyl	0.003	0.003	0.003	0.000	0.000	1
Fluazifop-P-butyl	0.002	0.005	0.003	0.001	34.783	8
Flufenacet	0.002	0.020	0.008	0.004	48.194	27
Flumioxazin	0.001	0.003	0.002	0.001	39.973	2
Foramsulfuron	0.002	0.009	0.004	0.002	47.539	26
Imazamox	0.002	0.004	0.003	0.000	11.931	9
Iodosulfuron-methyl	0.006	0.011	0.008	0.002	21.927	8
Lenacil	0.000	0.000	0.000	0.000	12.587	7
Mesotrione	-	-	-	-	-	0
Metamitron	-	-	-	-	-	0
Metazachlor	-	-	-	-	-	0
Metobromuron N	0.003	0.008	0.005	0.001	28.557	18
Metribuzin	0.003	0.003	0.003	0.000	0.000	1

Table 5. *Cont.*

Herbicides	**min (µg/L)**	**max (µg/L)**	**$\bar{x}$ (µg/L)**	**SD (µg/L)**	**RSD (%)**	**Positive Findings (%)**
Metsulfuron-methyl	0.002	0.005	0.004	0.001	25.699	7
Napropamide	0.002	0.013	0.008	0.004	48.699	11
Nicosulfuron	0.002	0.034	0.009	0.010	105.085	73
Oxyfluorfen	0.001	0.014	0.003	0.003	99.885	26
Pendimethalin	0.000	0.001	0.001	0.000	24.295	5
Phenmedipham	0.001	0.002	0.002	0.000	22.751	4
Propyzamide	-	-	-	-	-	0
Prosulfocarb	-	-	-	-	-	0
Quizalofop-ethyl	-	-	-	-	-	0
Rimsulfuron	-	-	-	-	-	0
S-metolachlor	0.006	0.108	0.031	0.030	98.098	100
Terbuthylazine	0.002	0.040	0.011	0.010	93.389	98
Thifensulfuron-methyl	0.002	0.034	0.009	0.010	115.300	8
Triflusulfuron-methyl	0.002	0.007	0.005	0.002	42.236	5
Tritosulfuron	-	-	-	-	-	0

Among all analyzed compounds, s-metolachlor is detected in the highest average concentration. Although plant protection products based on s-metolachlor have been used for decades, they remain widely applied, typically after sowing and before crop emergence in a wide range of crops, either alone or in combination with terbuthylazine. Given that their application coincides with early spring, a period with often intense rainfall, there is a high potential of runoff into surface water. Concentrations above 0.01 µg/L were also determined for terbuthylazine (0.011µg/L), amidosulfuron (0.011 µg/L), ethofumesate (0.016 µg/L), and carfentrazone-ethyl (0.011 µg/L). Overall, herbicide residues in the canal water samples were below the maximum allowable concentration of environmental quality standards (MAC EQS) set by Directive 2013/39/EU [2522] for individual compounds in surface water, and did not exceed the maximum residue level (MRL) of 0.1 µg/L for individual pesticides in drinking water prescribed by Regulation (EC) 98/83/EC [32].

Water Quality

Chemical analysis of DTD canal water samples is provided in the table. The pH values of the analyzed canal water ranged from 7.17 to 7.92 (Table 6), indicating that the water is slightly alkaline. None of the water samples exceeded the permissible limit of 8.5 prescribed by the WHO [33].

Table 6. pH, electrical conductivity (EC), concentration of calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), and Na adsorption ratio (SAR) for water samples.

	pH	**EC (µS/cm)**	**Ca (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**Ca (meq/L)**	**Mg (meq/L)**	**Na (meq/L)**	**SAR**
$\bar{x}$	7.67	387.90	45.40	15.71	21.78	2.27	1.30	0.95	0.71
Min	7.17	120.01	13.07	3.58	5.06	0.65	0.29	0.22	0.30
Max	7.92	720.02	54.92	26.76	32.43	5.48	2.20	1.41	0.99
SD	0.12	75.13	12.10	4.06	6.557	0.60	0.30	0.29	0.18
RSD (%)	1.59	19.37	26.70	25.85	30.11	26.73	26.01	30.10	25.81

Electrical conductivity (EC) is a parameter that depends on the presence of dissolved ions, where high electrical conductivity indicates a greater presence of ions as a consequence of pollution. The average value lies within the range of values characteristic of natural rivers and streams (50–1500 µS/cm) and shows that the water contains a moderate amount of dissolved ions, with a relatively good value. An electrical conductivity of 387.90 µS/cm and a pH value of 7.67 fall within normal ranges, indicating that the canal water is suitable for aquatic life, irrigation, and other uses. Although the water is not entirely free of pollutants, it does not show signs of significant pollution.

Salt concentration in irrigation water can directly affect crop growth and yield [34]. Sodium adsorption ratio (SAR), used to assess Na impact on irrigation water and soil, depends on the concentration of Na, Ca, and Mg (U.S. Salinity Laboratory Staff, 1954), and indicates the suitability of water for use in irrigation. High SAR values indicate a high Na level, contrary to Ca and Mg, which negatively affects soil productivity and plant growth when applied for watering purposes. By analyzing the water of the DTD canal network, the average SAR value of 0.71 (minimum value 0.30 and maximum 0.99) determined that this water is safe for most soils (SAR < 3) [35]. However, particular caution is required when using this water for the surrounding land irrigation as the soil is predominantly alkaline, which may increase the risk of sodicity.

Guidelines for evaluating the sodicity risk of irrigation water take into account both salinity, measured by EC and sodicity, assessedthrough (SAR), which reflects the balancing role of calcium (Ca) and magnesium (Mg) in mitigating the detrimental impact of sodium (Na) on soil permeability [34].

A diagram relating to the classification of irrigation water, EC, and other parameters such as SAR, the US Salinity Laboratory Diagram [35], is given in Figure 4.

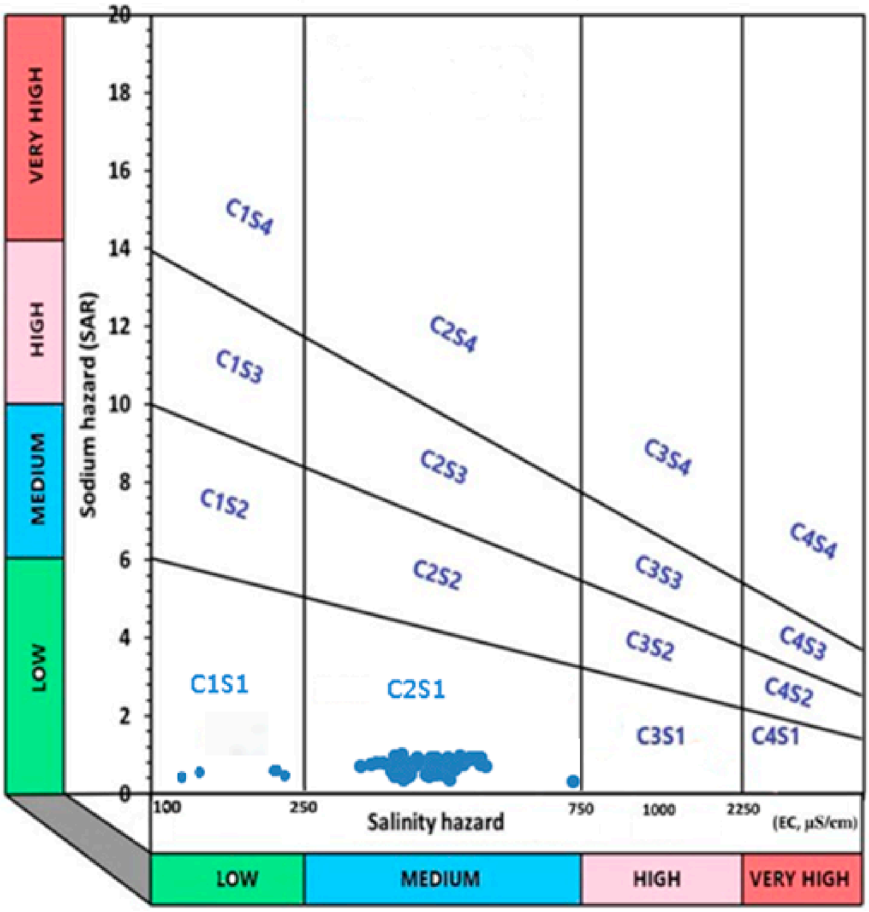

Figure 4. Water samples classification diagram [36].

The water included in this research mostly belongs to the C2S1 category, and represents moderately salty water, considering the EC. Such water is suitable for watering most crops since the risk of salt accumulation is moderate. On the other hand, S1 water belongs to the class with low Na hazard, taking into account its low content in opposition to Ca and Mg, and it can be applied to most types of soil without a significant risk of compaction or degradation of its structure. The water classification diagram shown in Figure 4 confirms these statements [37].

The influence of chemical characteristics of water (pH, SAR, and EC) on herbicide residues is shown in Figure 5. For most of the analyzed herbicides, no significant correlation was found between water properties and the presence of herbicide residues, with *p*-values between −0.2 and 0.2. However, increasing the Na content in water leads to a decrease in the concentration of thifensulfuron-methyl, nicosulfuron, metobromuron N, flufenacet, ethofumesate, and terbuthylazine in water (*p*-values −0.5 to −0.7). On the other hand, increasing the level of Na ions affects the increase in the content of the herbicide clomazone.

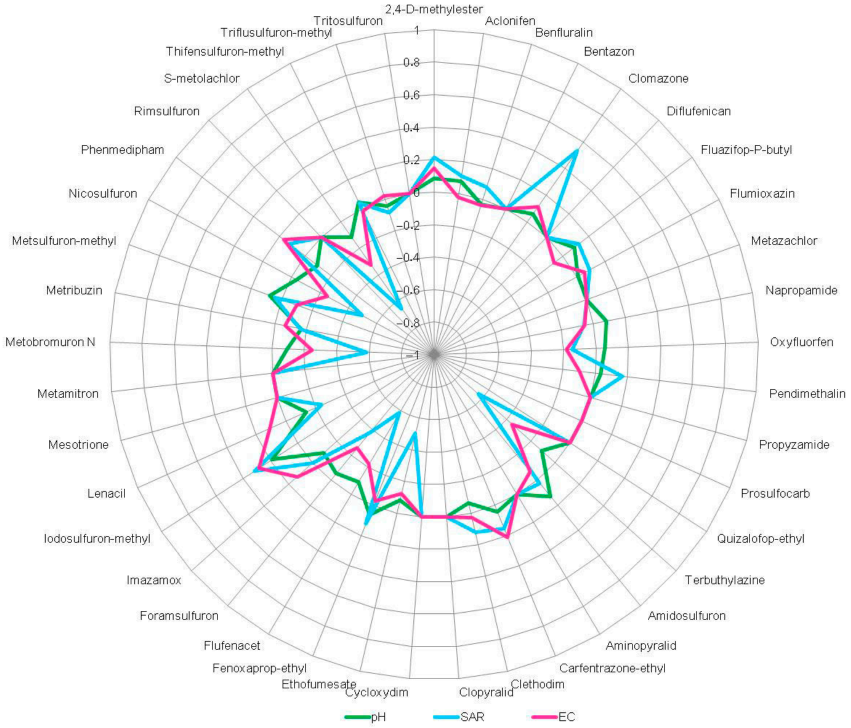

Figure 5. Correlation between water properties and herbicide active substances.

4. Discussion

Global pesticide use in agriculture reached 3.7 million tons of active substances in 2022, marking a 4% increase from 2021, a 13% rise over the past decade, and was twice the amount used in 1990. Compared to the 1990s, the last decade saw a 121% increase in herbicide use, 54% in fungicides and bactericides, and 48% in insecticides. During this time, the composition of pesticides used also shifted—herbicides increased from 40% to 50% of total use, while the shares of insecticides and fungicides/bactericides declined to 22% each from 26% and 25%, respectively [38]. Bearing in mind all of the above, there is a growing concern about the presence of herbicides in the environment, particularly in waters and soils that are directly exposed to anthropogenic influences through agricultural production. The issue of herbicide-related pollution needs more attention in certain agricultural regions, putting a heavy strain on the environment. Watercourses near arable areas are particularly exposed due to the intensive application of plant protection products, mainly herbicides. Also, irrigation canals are especially exposed to contamination. One good example is the

Vojvodina region (Serbia) through which the Danube–Tisza–Danube canal network passes. In this region, agriculture plays a vital role in the economy, and to maintain the production levels, large amounts of herbicides per hectare are required. Therefore, constant monitoring of the impact of these activities on the environment is necessary, and to identify potential risks for aquatic ecosystems and soils, extensive studies are crucial to check the presence of pollutants, with a special emphasis on currently used herbicides [19].

Pesticides often find their way into surface water through various natural processes, including surface and subsurface runoff and leaching through soil layers [39]. They can also be drifted by wind and soil erosion during their application [40,41] on agricultural areas. Highly soluble herbicides in water are more likely to be transported during rain or irrigation [42]. It is shown that the amount and type of pesticide residues found in surface waters also depend on several factors, such as application technique, soil management, crops, and climate conditions [43].

At the same time, this water is used for irrigation and is an irreplaceable resource in the production of a wide range of crops. Therefore, in addition to the occurrence of phytotoxicity, there is a danger of food contamination and a possibility of harmful effects on the aquatic biocenosis. For this reason, it is important to control the quality of the environment in terms of herbicide residues. In line with the goals of sustainable agriculture and environmental protection, herbicide residues in surface watercourses have become a major focus of research in recent years [2,42–46]. Pesticides drifting from fields intonearby protected areas represents a serious risk to the stability of these sensitive ecosystems. The growing use of pesticides in soybean and sugarcane cultivation has contributed to the degradation of soil and water quality, putting the rich biodiversity at risk [47].

Beyond their effects on human health, pesticides threaten aquatic environments by polluting ecosystems and potentially entering the food chain. They also have a strong impact on flora and fauna by altering microbial diversity, reducing fertility, and disrupting essential ecosystem processes [48].

Out of the 41 active substances analyzed in the canal water of the DTD network, 28 compounds were identified, with s-metolachlor and terbuthylazine having the highest frequency of occurrence. These herbicides were applied after sowing and before the emergence of maize, which is the dominant crop in this area. Due to the atmospheric precipitation, they were easily washed off from the treated surfaces and subsequently reached watercourses. However, the total herbicide residues in canal water samples were below the maximum allowed concentrations prescribed in Directive 2013/39/EC [25] for surface water, as well as below the limit values for pesticides in drinking water according to 98/83/EC [32].

In contrast, a study examining pesticide contamination in river waters within an agricultural zone identified quizalofop-ethyl, trifluralin, and pendimethalin. Additionally, the insecticide tebufenpyrad was detected at a concentration of 0.330 mg/L [2]. A separate investigation involving 287 surface water samples, including rainwater, streams, ponds, springs, and rivers, collected from 20 agricultural sites in a sub-basin area revealed the frequent presence of herbicides such as atrazine, clomazone, haloxyfop-methyl, and glyphosate. Conversely, no detectable levels were found for clethodim, chlorimuron-ethyl, diuron, fluazifop-p-butyl, imazamox, mesotrione, metsulfuron, nicosulfuron, or pendimethalin. During the rainy season, nearly all samples (about 99%) tested positive for residues of at least one of the monitored herbicides [49]. Since water and soil are deeply interconnected in agricultural landscapes, especially in lowland regions such as Vojvodina, herbicide residues detected in surface water are often mirrored by their presence in the surrounding soil. Therefore, it is equally important to research how these compounds behave in both parts of the environment. Soil and sediments serve as primary reservoirs for herbicides as these substances tend to accumulate there, influencing their subsequent distribution to other environmental compartments. Studies that examine these issues are carried out worldwide [19,50–55]. Herbicides' persistence in the environment largely depends on how well they bind to the soil. This process is influenced not only by the weather, especially rainfall, but also by the soil's characteristics, such as its organic matter and clay content, mineral composition, pH level, and temperature [56,57].

In this study, the dominant herbicides present in the surface soil layer were clopyralid, 2,4-D-methyl ester, terbuthylazine, fenoxaprop-ethyl, and aclonifen, which are intensively applied in the production of sugar beet, sunflower, soybean, wheat, and oilseed rape to control a wide range of weeds. A potential scenario for the high concentrations of terbuthylazine and quizalofop-ethyl residues in the soil on individual sites could be its application shortly before sampling. As a pre-emergence herbicide, terbuthylazine tends to remain concentrated near the soil surface, resulting in high residue levels in the upper soil layer. On the other side, in soil depths of 30–60 cm, with the frequency of occurrence identical to that in the surface layer, the same herbicides were present. However, the presence of herbicides from the sulfonylurea group (triflusulfuron-methyl) in the concentration of 145.470 μg/kg is a consequence of its application on the field under the sugar beet, slightly before sampling [58]. Considering that the soils are alkaline and only a small amount of sulfonylurea herbicides can be adsorbed and remain in soil samples [8], the persistence of these herbicides is expected to be short. Herbicide residues monitoring in agricultural soil in the Republic of Serbia, in 2023, showed higher concentrations of s-metolachlor and clopyralid in the soil samples [19].

The analyzed soil is characterized by an alkaline reaction and a high $CaCO_3$ content, classifying it as weakly to strongly calcareous. The average organic matter content indicates moderate to good humus supply, which is considered typically adequate for calcareous soils. However, extremely low values at certain localities point to humus-poor soils, which are unsuitable for agricultural production. The very high base saturation reflects the soil's strong alkaline nature. Soil with these characteristics generally shows a reduced mobility of pesticides, which can explain the low level of herbicides in canal water compared to land in the immediate vicinity.

5. Conclusions

The increased use of herbicides in agriculture has led to growing concerns about their environmental impact. The issue of herbicide-related pollution needs more attention in certain agricultural regions where the watercourses are in intensive production areas. Special attention should be paid to currently used herbicides, since there are gaps in their monitoring. This research represents the determination of currently used herbicides in irrigation canal water and soil near those watercourses within the main agricultural region of Serbia, as a model for an area under intensive crop production in conventional agriculture.

Analysis of the canal water showed that although the water samples contained at least one active substance, the amounts of herbicide residues were below the maximum allowable concentrations of environmental quality standards, even for drinking water.

The soil's mechanical and chemical properties were also analyzed. The average pH values of the analyzed soil samples indicated an alkaline reaction, while according to the average content of $CaCO_3$ the soils were classified as weakly to strongly carbonated but moderately to well supplied with organic matter. The most abundant herbicides in the soil samples were clopyralid, 2,4-D-methyl ester, terbuthylazine, fenoxaprop-ethyl, and aclonifen. Terbuthylazine and quizalofop-ethyl were detected in the highest amounts, suggesting their possible recent application shortly before sampling. Moreover, the concentrations of herbicide residues in the soil at two depths were highly similar, without a significant difference. These results emphasize the importance of introducing regulations to control soil pollution, including the setting of MRL values.

Due to their indispensable role, herbicides are still an important element in agricultural production. However, in order to maintain the appropriate quality of the complete ecosystem, it is necessary to carry out long-term monitoring programs of currently used herbicides in soils and waters, especially in regions with intensive agricultural activities.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/environments12070246/s1, Table S1: List of Certified analytical standards of herbicides; Table S2: Statistics.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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

Abbreviations

The following abbreviations are used in this manuscript:

DTD	Danube–Tisza–Danube Canal System
EU	European Union
WFD	Water Framework Directive
EC	Electrical Conductivity
SAR	Sodium Adsorption Ratio

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