PESTICIDE RESIDUES IN AGRICULTURAL SOILS: EMPHASIZING THE NEED FOR NATIONAL-LEVEL MONITORING

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Abstract
This study emphasizes the importance of establishing a comprehensive national monitoring program for pesticide residues in agricultural soils, especially in regions with intensive crop production. Due to widespread use, herbicides pose significant environmental and health risks, with soil being particularly vulnerable to contamination. Monitoring was conducted in agricultural soil in Vojvodina (Serbia) in 2023 and 2024. Samples were collected from surface layer and analyzed using LC-MS/MS and GC-MS/MS techniques for 41 herbicidal active substances. The 2023 analysis revealed that all samples contained multiple herbicide residues, with up to 19 active substances detected in a single sample. In 2024, high detection frequencies were noted for clopyralid, 2,4-D-methyl ester, terbuthylazine, fenoxaprop-ethyl, and aclonifen, although most were found at low concentrations. These findings confirm the persistence and accumulation of herbicide residues in agricultural soils, underscoring the urgent need for more effective regulation, improved agricultural practices, and sustainable weed management strategies to protect soil health and the environment.

Introduction
In order to protect crops from a wide range of pests and ensure optimal yields, contemporary plant protection relies almost completely on the use of chemical agents, mostly herbicides. Nowadays, the risks associated with pesticide use have outweighed their benefits [1]. Pesticides are regarded as particularly important for the environment due to their potential toxicity and the physicochemical characteristics of certain active ingredients, which enable them to interact with the environment, resulting in high mobility and/or persistence [2]. Thus, as a consequence of their intensive use, the growing trend of environmental protection and food safety, monitoring of the presence of pesticide residues is crucial.
The soil is particularly vulnerable. Although a non-renewable resource with a possible high degradation rate, soil represents the foundation for agricultural production. The land is most threatened by anthropogenic factors through activities related to agricultural production.
Pollution caused by pesticide use in agriculture requires particular attention, especially in regions with intensive crop production. In these areas, the economy heavily depends on agriculture, and high pesticide use per hectare is common to ensure adequate yields [2].
Much research demonstrated that pollution of surface soil leads to pesticide contamination of both groundwater and surface freshwater [3]. Therefore, controlling pesticide levels in surface soil is crucial for protecting public health [4].
However, extensive surveys of pesticide residues in agricultural soils are surprisingly scarce [5-8], nor is the monitoring of pesticide residues in soil regulated appropriately. Healthy soils form the basis for 95% of the food, support over 25% of the world's biodiversity, and represent the largest terrestrial carbon reservoir. However, soil is a limited resource, and more than 60% of

soils in the EU are not in good condition. Significant change of the existing conditions in this area, aiming to ensure that all EU soil ecosystems are in a healthy state, could be done by the Soil Surveillance and Resilience Law, as well as a new EU Soil Strategy for 2030 [9].
This study aims to highlight the importance of establishing and maintaining a comprehensive national-level monitoring program for pesticides in agricultural soil, which is essential for assessing environmental impact, ensuring food safety, and promoting sustainable farming practices.

Experimental

Sampling area.
Sampling area covered region under intensive agricultural production, located in the northern part of Serbia (Vojvodina) (Figure 1). In two monitoring programs of pesticide residues in agricultural soil, analysis was done at 128 localities in 2023 and 260 localities in 2024.
Soil was sampled at the surface layer (0-30 cm) by collecting 20 sub-samples at various points diagonally in the plots within the production area, using a soil sampling probe or shovel. Covered with chernozem as the most widespread type of soil, this region is recognized for its intensive agricultural production of maize, soybean, sugar beet, and sunflower.

Figure 1. Sampling area

Extraction and analysis.
Certified analytical standards of herbicides with a purity greater than 98% were sourced from Dr. Ehrenstorfer. The solvents used for the extraction and chromatography were supplied by Fisher Scientific (Leicestershire, UK). Individual stock standard solutions of herbicides were prepared by accurately dissolving the analytical standards in a suitable solvent. These solutions were then protected from light and stored at -20 °C in dark glass bottles. Working standard solutions of different concentrations were subsequently prepared by appropriate dilution.
For the extraction of herbicide residues from soil, a modified QuEChERS-based method was applied. The extraction was preceded by sample preparation, which included air-drying, grinding, and sieving of soil samples. Afterward, a 10 g sample was weighed and transferred to a 50 mL polypropylene cuvette with 3 mL of deionized water and 10 mL of acetonitrile acidified with 2% formic acid.
The mixture was shaken for 1 min, vortexed for 1 min, and after which, a salt buffer mixture was added (4 g of magnesium salt, 1 g of sodium chloride, 1 g of Na citrate, and 0.5 g of disodium citrate sesquihydrate). The prepared samples were shaken for 1 min, vortexed for 1 min, left for 10 min in an ultrasonic bath, and centrifuged for 5 min at 4000 rpm. In the next step, the aliquot was evaporated to dryness, dissolved in acetonitrile or acetone, filtered through

a 0.45 µm membrane filter, transferred to a vial, and analyzed. Depending on the herbicide nature, residues were analyzed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) and chromatography–tandem mass spectrometry (GC-MS/MS). Analysis covered 41 herbicide active substances.

Results and discussion

In the 2023 analysis (Figure 2), herbicide residues were found in all soil samples, with the minimum number of detected residues being 6, while the maximum number of active substances per location increased to 19. The most frequently detected herbicides were prosulfocarb, napropamide, and bentazon. Additionally, 2,4-D methyl ester, flumioxazine, metazachlor, oxyfluorfen, and propyzamide were present in a significant number of soil samples (50-90%). The highest concentration found was 18.90 µg/kg for terbuthylazine [10]. The monitoring program was carried out in 2024 to assess the current situation (Figure 2). Herbicide residue analyses revealed a high frequency of clopyralid, 2,4-D-methyl ester, terbuthylazine, fenoxaprop-ethyl, and aclonifen. While the concentrations of clopyralid, fenoxaprop-ethyl, and aclonifen were all below 0.5 µg/kg, clomazone, ethofumesate, metsulfuron-methyl and s-metolachlor stood out with a concentration of 11.856, 24.335, 26.137 and 29.878 µg/kg, respectively. Among the 41 herbicides analyzed, three were either not detected or were below the limit of detection (LOD), while twenty-three had occurrence frequencies below 10% [11].

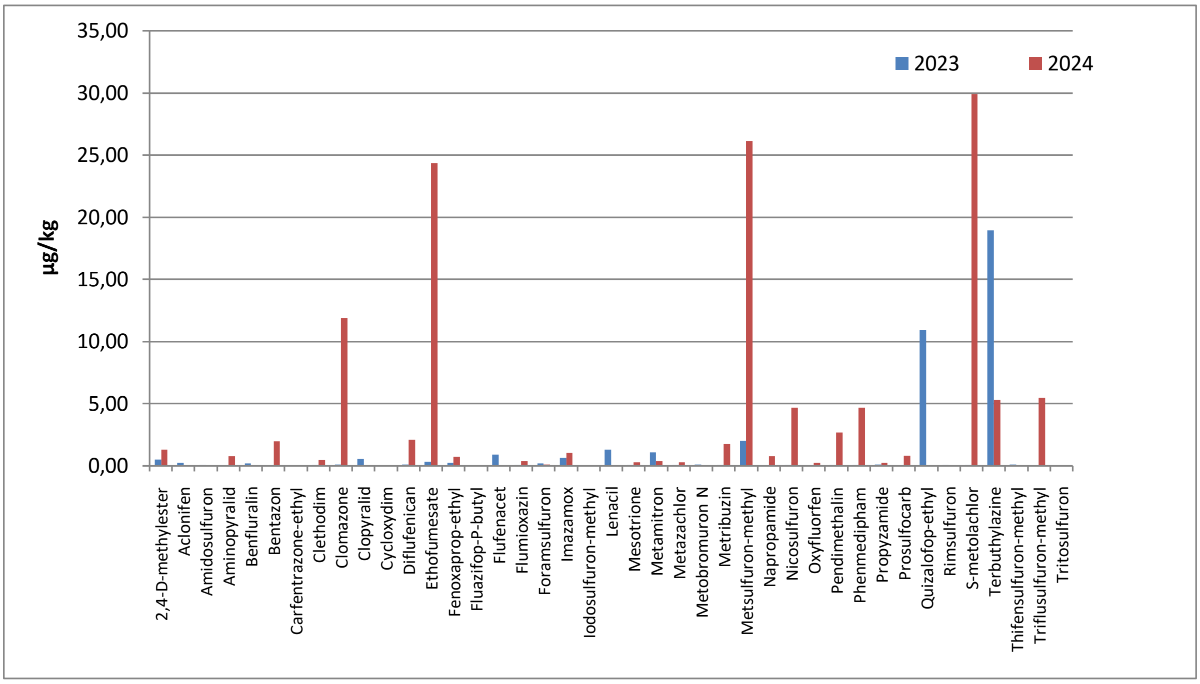

Figure 2. Herbicide residues in soil samples.

The monitoring results from 2023 and 2024 indicate a persistent and complex presence of herbicide residues in agricultural soils. In 2023, all soil samples contained herbicide residues, with up to 19 active substances detected in a single sample, reflecting a high level of chemical diversity and accumulation. Particularly concerning was the exceptionally high concentration of terbuthylazine.

In 2024, although the concentrations of the most frequently detected herbicides were generally low, the consistently high detection rates suggest widespread use and environmental persistence. S-metolachlor emerged as a compound of particular concern due to its notably high concentration at one location, despite its moderate average value.

Conclusion

The data from both years underscore ongoing and intensive herbicide application, leading to cumulative contamination and potential ecological risks. These findings highlight the need for more stringent monitoring, responsible herbicide management, and consideration of alternative weed control strategies to mitigate long-term impacts on soil health and the broader environment.

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