

Determination of sulfonylurea herbicide residues in agricultural soil

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Abstract As the consequence of triazines and some chloroacetanilide herbicides ban, the use of sulfonylureas has significantly increased. With the aim of establishing the impact of agriculture to the environment and quality of agricultural product, a monitoring program has been carried out in order to evaluate presence of SUs in agricultural soil. Of the 68 analyzed soil samples (0-30 cm) under intensive agricultural production, SUs were present in 20 samples. Extraction was performed by modified QuEChERS method. For the determination of SUs residues HPLC-DAD and Zorbax Eclipse XDB C18 column were used. Mobile phase composed of 0.1% CH₃COOH and acetonitrile; gradient (52-47% acetonitrile); flow rate 0.9 ml/min; wavelength 230 nm. The results obtained for the validation parameters completely fulfill SANCO/825/00 rev. 8.1 16/11/2010 criteria. In the most of the analyzed soil samples, residues of thifensulfuron-methyl, nicosulfuron, oxasulfuron and rimsulfuron were found. Iodosulfuron-methyl-sodium and prosulfuron have been established in only 3.9% of samples, while residues of metsulfuron-methyl, amidosulfuron and tritosulfuron have not been found, or their content was below the limit of detection. **Keywords: soil, sulfonylurea herbicides, residues**

1. Introduction

The fate of pesticides in soil is influenced by the physico-chemical properties of pesticide, the properties of the soil (presence of clay materials, organic matter, pH), climate, biology, and other factors (Singh, 2001). The increased use of pesticides, and especially herbicides, has caused pollution of soils worldwide. Some herbicides can remain active in the soil for weeks, months or year. This can be an advantage, as it ensures long-term weed control and at the same time, if the herbicide stays in the soil longer than intended, it may damage sensitive crops sown in subsequent years. E.g. chlorsulfuron is used in wheat and barley, but can remain active in the soil for a long period and damage legumes and oilseeds.

A real problem represents the difficulty in identifying herbicide residues before they cause a problem. Once the crop has emerged, diagnosis is difficult because the symptoms of residual herbicide damage can often be confused with and/or make the crop vulnerable to other stresses, such as nutrient deficiency or disease.

The phytotoxic effect of nicosulfuron and its metabolites on dicotyledonous plants leads to a self-limitation in the re-planting period. After sowing, in 27-30 days interval since pesticide application, phytotoxic effects are obvious on cereals, sugar beet, canola and clover. The listed crops should not be sown on land previously treated by nicosulfuron before next spring, when the expected level of herbicide residues and their degradation products is <0.001 mg/kg (Lazić *et al.*, 2015; Lazić *et al.*, 2016).

The trace determination of herbicide residues, generally in environmental samples, presents a challenging analytical problem. The low dosage used requires the application of highly sensitive analytical techniques to detect trace concentrations of residues in soil (Ye *et al.*, 2006). Due to the low level of compounds and complexity of sample, clean-up and enrichment before analysis is necessary and become a crucial step for the determination of herbicides in environmental samples. Developing analytical methods for SUs has been particularly problematic, due to their polarity and the chemical instability of these compounds (Grahovac *et al.*, 2013). Methods based on reversed-phase and normal phase liquid chromatographic (LC) techniques with the adequate sensitivity of detectors have been widely used (Liu *et al.*, 2003; Grahovac *et al.*, 2016).

In order to evaluate the presence of sulfonylurea herbicide residues in soil under intensive agricultural production, this study was conducted.

2. Material and Methods

2.1. Extraction procedure

Analysis was carried out on 68 soil samples from conventional agricultural production (0-30 cm). The samples were mixed and the average sample of 500 g was formed, packed into polyethylene bags and marked with the accurate data about the location and date of sampling. Samples were transported to the laboratory and kept in the freezer at 20 °C until the analysis (Carter and Gregorich, 2006).

For the extraction of herbicides from soil, the multi-residue method was applied and validated according to the documents SANCO/825/00 rev. 8.1 16/11/2010 and OECD Environmental Health and Safety Publications, Series on testing and assessment. Validation parameters such as specificity, the linearity of detector response, the accuracy of the method, precision and limits of detection and quantification were evaluated.

Herbicides were extracted from soil by modified QuEChERS method EN15662. Prior to the analysis samples were air-dried, ground, and sieved through the sieve of 2 mm. The sample of 10 g was measured into a polypropylene cuvette of 50 ml with addition of 3 ml of deionized water and vigorously shaken. Afterward, 10 ml of 2% HCOOH acetonitrile were added and shaken 1 min, homogenized in vortex for 1 min, after which a mixture of buffering salts was added (Agilent QuEChERS extraction kits, Cat. No. 5982-5650-4 g MgSO₄, 1 g NaCl, 1 g NaCitrat, 0.5 g disodium citrate sesquihydrate).

In this manner prepared samples were repeatedly shaken 1 min, then additionally shaken on vortex for 1 min, left in ultrasonic bath for 10 min and centrifuged 5 minutes at 400 rpm. After this procedure, solid and fluid acetonitrile phase separated. The corresponding volume was evaporated until dry and diluted in 1 ml of acetonitrile. The extract was filtered through 0.45 µm membrane filter, transferred in vial and analysed (Lazić *et al.*, 2014).

2.2. HPLC analysis

Chromatographic analysis and extraction procedure were described in our previous publication (Lazić *et al.*, 2014). For the chromatographic analysis, an Agilent 1100 Series system with DAD detector and Zorbax SB-C18 column (5 µm, 250mm × 3 mm internal diameter) were used. The mobile phase was acetonitrile (A) and 0.1% (V/V) acetic acid in water (B). The following gradient profile was 0–10 min linear from 52% to 47% (A). Flow rate was 0.9 ml/min and wavelength was 230 nm. The external standard and matrix match calibration on five levels were used.

3. Results and Discussion

The multi-residue method for the determination of sulfonylurea herbicide residues in soil samples was validated in accordance with SANCO and OECD criteria. The achieved values completely fulfilled the required criteria (Lazić *et al.*, 2014).

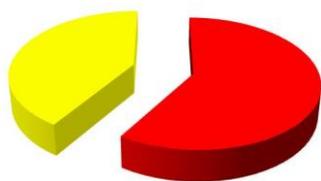


Figure 1. Samples with positive findings of sulfonylurea herbicide residues

In total of 68 analyzed soil (0-30 cm) samples under intensive agricultural production, SUs were present in 20 samples. Residues of sulfonylurea herbicides were detected in 62.5% samples, while in 37.5% their content was under the limit of detection, i.e. samples did not contain residues of these compounds (Figure 1).

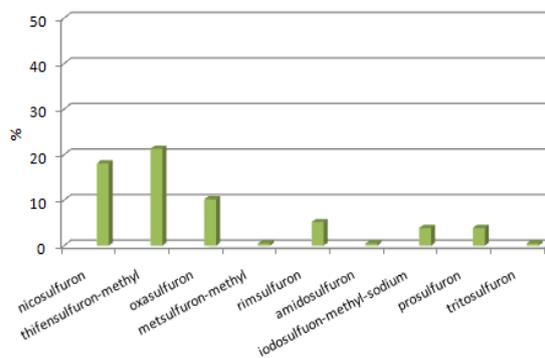


Figure 2. Sulfonylurea herbicide residues in the analysed soil samples

In regard to representation of sulfonylurea herbicide residues in analysed soil samples, residues of thifensulfuron-methyl, the herbicide that is used for control of broad-leaved weeds in maize and soybean, have been established in the greatest number of soil samples (21.3%) (Figure 2). Thifensulfuron ester and acid are potentially mobile in all soil types and degrade rapidly to carbon dioxide, which reduces soil contamination by these compounds to the minimum if used at recommended rates. Residues of oxasulfuron which is used in soybean were detected in 10.2% of the analysed samples of agricultural soil under soybean. Residues of nicosulfuron, herbicide used in maize were also found in a significant percentage (18.1%). Content of rimsulfuron residues in top soil samples was 5.2%. Residues of herbicides that are used in combination with other compounds such as iodosulfuron-methyl-sodium, and prosulfuron were found in only 3.9% of samples, while residues of metsulfuron-methyl, amidosulfuron and tritosulfuron have not been found, or their content was below the limit of detection. Generally speaking, residues of herbicides that are used in wheat and barley crops were detected in significantly lower percentage, or their content was below the limit of detection.

In regard to the time of the sampling, in 94.87% of the analysed samples, level of sulfonylurea herbicides residues exceeded the value of 0.05 mg/kg for which it is established that it can cause fitotoxicity in susceptible crops (Figure 3).

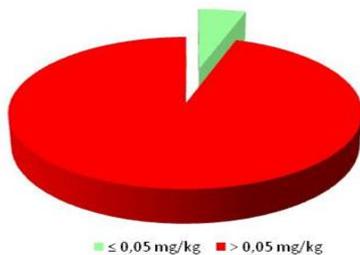


Figure 3. Level of sulfonyleureas residues in the analysed soil samples

Sulfonyleureas have been used in wheat, maize and soybean crops, and their intensive use is reflected in efficient control of wide spectrum of weeds, capability to stop or repress weeds with low concentrations of use and low toxicity to mammals. These herbicides release the residues in soil, which may become available to subsequent crops and can affect phytotoxic symptoms in susceptible plants.

4. Conclusions

In the most of the analyzed soil samples, residues of thifensulfuron-methyl, nicosulfuron, oxasulfuron and rimsulfuron were found. Iodosulfuron-methyl-sodium and prosulfuron have been established in only 3.9% of samples, while residues of metsulfuron-methyl, amidosulfuron and tritosulfuron have not been found, or their content was below the limit of detection. The comparison of the detected herbicide residues in the analysed soil samples under certain crops, with the list of registered plant protection products in the Republic of Serbia and their purpose, showed that in most cases farmers complied with GAP related to pesticide application.

5. Acknowledgement

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