COMPARISON OF PHENYLUREA PESTICIDES RECOVERY FROM DIFFERENT SOIL TYPES

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Abstract

The subject of this research work is to determine the recoveries of the studied analytes from the chemical group of phenylurea: isoproturon, diuron and linuron, depending on the physical-chemical soil properties within the validation of multi-residual method for the determination of the herbicide residues in soil by (LC-MS/MS) after QuEChERS extraction of spiked soil samples. The factorial ANOVA did not show any statistical significances regarding the influence of the paired values of different pesticides and soil types. The same result was obtained by the one-way ANOVA calculated for different soil types (p_s=0.151060 for $p<0.05$) and different pesticides (p_p=0.165207 for $p<0.05$) regarding the values of average recoveries. Fishers LSD post hoc test emphasized the homogenity and similarity among average recovery values in both cases.

Keywords: phenylurea, QuEChERS, recovery, soil, LC-MS/MS

Introduction

The use of herbicides in agriculture is a significant factor responsible for the mass production of food. The low degradability of pesticides has led to their presence in water, soil and food. Chemical characteristics of pesticides, such as low solubility in water and high in fats, stability to photo-oxidation and low vapor pressure are the main elements that determine not only the efficiency but also the persistence of pesticides in the environment [1].

The compounds of herbicides can be very persistent in the environment and if they are stable and persist for a long time in soil or water, their application is gradually discontinued or limited in dosage. Phenylurea herbicides are a group of pesticides used to control harmful weeds on agricultural land.

These herbicides are produced and distributed under different names, some of which are: diuron, isoproturon, linuron, buturon, chlortoluron, methiuron, tebuthiuron... These compounds have the ability to inhibit photosynthesis and thus successfully suppress harmful weeds that cause problems on agricultural land. The decomposition of these herbicides in soil can be a slow and problematic process. The decomposition of phenylurea herbicides can be performed under acidic or alkaline conditions and also UV irradiation. Although a large number of phenylureas can be found in agricultural production, little is known about their toxicity, which they can cause with prolonged use. Diuron is a widely used herbicide of all phenylurea herbicides in the whole world. The acute toxicity potential for all phenylureas appears to be low, with oral LD_{50} values typically greater than 1 g/kg [2].

In the normal pH range these herbicides are stable when exposed to hydrolysis and exist as the undissociated form in natural waters. The photochemical degradation of these compounds caused by sunlight is of very little importance. The herbicides from the phenylurea group the plants adopt via the root and they are quickly translocated to the stems and leaves via xylem. In addition to diurons, linuron and isoproturon have also been widely used in agricultural production for surface application on the leaves of the treated plants.

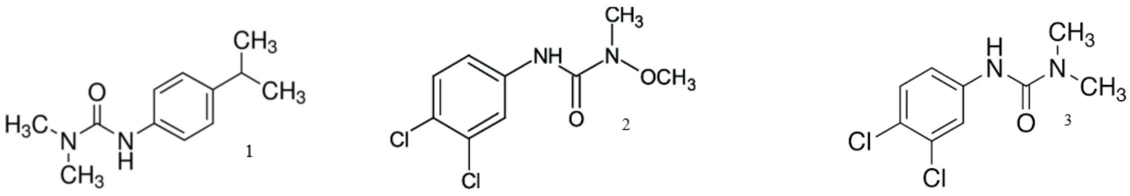

Figure 1. Structural formula of isoproturon (1), linuron (2) and diuron (3)

These compounds inhibit enzymes involved in the Hill reaction and because of that they interrupt the process of photosynthesis. Lewis and Gardiner (1996) have reviewed data on the use and fate and behaviour of these herbicides [3].

The release of linuron into the environment is mainly through machine washing after application, drainage, and accidental spillage as it is widely used in agriculture [4].

The pesticide-soil sorption interaction can include mineral or organic components, and sometimes both of them [5]. The physical and chemical characteristics of the herbicide define the movement of the herbicide towards the target location, the persistence, soil mobility and photostability. Therefore, it is possible to predict which compounds can cause potential problems in the environment [6]. In general, measuring of the trace compounds such as pesticide residues is highly difficult due to time consumption, while the long procedure causes losses of the analytes [7, 8]. The aim of this study was to determine the recoveries of investigated herbicides depending on the physicochemical properties of three different soils. For the extraction of the isoproturon, diuron and linuron, the QuEChERS method was used, followed by liquid chromatography tandem mass spectrometry (LC-MS/MS).

Material and method

The experimental part of the research work, which included the enrichment of the soil samples by the tested pesticides with their extraction, was done at the Department of Phytomedicine and Environmental Protection, Faculty of Agriculture in Novi Sad. The chromatographic separation on LC-MS/MS was performed at the Public Health Institute in Belgrade. The samples of three soil types with different physicochemical characteristics were used (Table 1), in which the presence of pesticide residues (blank samples) was not detected. In order to set the validation parameters, the blank samples were enriched with a certain amount of tested pesticides.

The analytical standards of diuron, linuron and isoproturon were parched from dr. Ehrenstorfer. The stock (≈ 1.0 mg/mL) and working solutions (10 µg/mL) were prepared in acetonitrile (HPLC purity, J.T. Baker). As an internal standards the following were used: (10 µg/mL) carbofuran-D3, atrazine-D5 and isoproturon-D6.

LC-MS/MS analysis. The 6410 Agilent Technologies LC-MS/MS with electrospray ionization was used. The separation was performed using a Zorbax Eclipse XDBC18 column (50 mmx4.6mm id 1.8 µm.) at 25 ºC. The mobile phase (0.4 mL/min): methanol with 0.1% formic acid and 0.1% formic acid in water in the gradient mode. Total run was 30 min. The injection volume was 5 µL. The target ion transition with highest intensity (primary ion transition) was used for the quantitation, whereas the second target ion transition was used for the confirmation.

Table 1. Soil characteristics

Soil	pH (H_2O)	$CaCO_3$ %	Organic matter %	Send 2-0.2 mm %	Send 0.2-0.02 mm %	Powder 0.02-0.002 mm %	Clay <0.002 mm %
1.	8.71	30.6	0.11	1.58	91.7	3.4	3.32
2.	8.16	7.45	3.76	10.25	22.45	25.03	42.27
3.	7.65	1.02	0.88	0. 53	21. 39	29.04	49.04

The instrument uses MassHunter software version B.06.00 for the quantitation and confirmation.

Method validation - recovery was determined according to SANTE/12682/2019 [9]. Recovery was obtained by spiking soil samples in the concentrations 1.0 and 10.0 mg/kg. The limit of detection (LOD) was estimated in the MRM mode analysis as the lowest concentration level that yielded S/N ratio of five.

The pesticides extraction from spiked soil samples was carried out using a modified QuEChERS method [10].

Statistical analyses. In order to determine the statistical differences among the obtained recovery values as the dependent variables and the pesticides and soil types as the independent variables the factorial and one-way factor analysis of variance (ANOVA) were applied using Statistica 13.2 (TIBCO Software Inc. University license).

The calculated differences were tested by Fisher’s LSD post-hoc test.

Results and discussions

Before accessing qualitative analysis or the quantification of pesticides it is necessary to set the acquisition parameters of the mass spectrometer - to set the multiple reaction monitoring mode (MRM). MRM-MS sensitivity is dependent upon the appropriate tuning of instrument parameters such as collision energy (CE) and energy of fragmentation (Frag) in order to generate maximal transmission of the pesticide product ions (Table 2).

Table 2. Soil characteristics

Pesticide	Rt (min)	Precursor ion (*m/z*)	Product ion (*m/z*)	Frag (V)	CE (V)
Isoproturon	21.77	207 207	169 72	70 70	15 17
Diuron	22.03	233 233	160 72	70 70	18 25
Linuron	23.56	249 249	182.1 160	120 120	10 20

The obtained recoveries with RSD (%) values are given in the table 3. The obtained RSD values represent the precision of the method.

Table 3. Average recoveries (%)

Pesticide	**Soil 1**	**Soil 2**	**Soil 3**
Isoproturon	97,2 (12,43)	93,3 (4,7)	91,9 (7,45)
Diuron	103,7 (11,72)	99,8 (3,05)	97,2 (7,44)
Linuron	99,7 (12,43)	90,5 (7,23)	86,7 (5,68)

The factorial ANOVA did not show any statistical significances regarding the influence of the paired values of different pesticides and soil types. The same result was obtained by the one-way ANOVA calculated for different soil types (p_s=0.151060 for $p<0.05$) and different pesticides (p_P=0.165207 for $p<0.05$) regarding the values of average recoveries. Fishers LSD post hoc test emphasized the homogenity and similarity among average recovery values in both cases.

Conclusions

The influence of main physicochemical properties of three soils on isoproturon, diuron and linuron recoveries in this matrix were studied applying QuEChERS soil sample preparation followed by the LC-MS/MS determination.

The organic matter and clay content affected the recovery of the studied pesticides. The obtained dependence indicates that with increasing organic matter and clay content (soil 2 and 3), the recoveries were lower than in soil 1.

The applied statistical analyses did not emphasize any statistical differences among pesticides, soil types and obtained recoveries, pointing out the homogenitiy and similarity among obtained data.

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