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*Soil Chemistry*

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# CHANGES IN SOIL CONTAMINATION BY SELECTED HERBICIDES USED IN PROTECTION OF CEREALS**

*Abstract*. The aim of the studies was to evaluate the herbicidal contaminations in soil. Monitoring tests were carried out in two periods: 2002–2008 and 2010–2013, on cereal plantations located in south-western Poland. The samples of soil were collected at harvest time. The determination of 2,4-D, MCPA, diflufenican, dicamba, chlortoluron, fluroxypyr, isoproturon, clopyralid residues were conducted using the chromatography GC/ECD and HPLC/UV. Comparing the research results from both periods, a decrease of several percent in the number of the samples with residues was observed. In the years 2010–2013, the average residues of herbicide determined in 27% of samples ranged from 0.0012 to 0.0052 mg $kg^{-1}$.

Cereals constitute the main crop in Poland. A wide range of species and cultivars enables the cultivation of these plants on nearly all types of soils. Wheat is a dominant crop. Therefore, chemical control of weed infestation in cereals is of a high significance in the scale of the entire country, both due to economic reasons and the effect on the environment. In cereals, the compounds containing single active substances, as well as their mixtures are used. Taking into account a wide range of herbicides, the preparations based on derivatives of phenoxy acids, derivatives of phenylurea, are most often used. In recent years, the group of sulfonylurea derivatives has become more and more important [4, 5].

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The first synthetic pesticides became available during the 1940s, generating large benefits in terms of increased food production. The concern about the adverse impact of pesticides on the environment and on human health started being voiced in the early 1960s. Since then, the debate on the risks and benefits of pesticides has not ceased and a large amount of research has been conducted on the impact of pesticides on the environment [14].

The information on the residue and degradation rate of herbicides in soils allows evaluating the behavior of herbicides in the environment. Persistence in topsoil is one of the criteria for pesticide registration at the European Union level. The $DT_{50}$ [dissipation time (days) for 50% of the initial residue to be lost] in field conditions should be less than 3 months, unless there are unacceptable effects on terrestrial organisms [1]. In soil, the activity of herbicides may be reduced by chemical or biological degradation of its active ingredients. Adsorption by soil colloids, absorption by plants or leaching to lower layers of the soil profile also influences the biological activity of herbicides in the soil [3]. In plants, the biological activity of herbicides may be reduced by low retention and washing-off of the herbicide from leaf surface by rain, dew and irrigation to the soil [9].

New EU regulations (Directive 2009/128/EC) [2] in plant protection are aimed at national reduction in pesticide use. New strategies include developing methods suitable to local conditions. The use of chemicals is to be reduced while safeguarding the desired effectiveness.

Research on pesticide residues assesses the effect of applied chemicals on the environment and human health [7, 10]. Moreover, long–term monitoring allows for the analysis of the consequences of the introduced changes, and for choosing the best methods minimizing the risk resulting from the use of chemical plant protection.

The aim of this study was the analysis of herbicide contamination in the soil on the basis of monitoring research on cereal plantations (winter and spring crops) cultivated in the fields of south–western Poland.

## MATERIALS AND METHODS

Monitoring research was conducted in two periods (2002–2008 and 2010–2013) on fields of winter and spring cereals. In each growing season, shortly before harvest, the samples of soil were collected from cultivated fields (1196 soil samples in the years 2002–2008 and 671 in 2010–2013). Interviews were conducted among the field owners, who stated that, in most cases, the previous crops were cereals, winter oilseed rape and pea. The fields were established on different soils (pH = 5.4–6.8, $C_{org}$ = 0.7–1.9%). The size of the controlled cereal fields was diverse and ranged from 2 to 12 hectares. On selected fields, the farmers applied herbicides containing 2,4-D, MCPA, diflufenican, dicamba, chlorto-

luron, fluroxypyr, isoproturon, clopyralid and others. Herbicide treatments and introduced amounts were done according to instructions regarding the terms and the doses set up by herbicide producers. Herbicides were applied *postemergence* at the turn of March to April. The harvest took place from the middle of July to the first days of the third decade of August.

The soil samples were taken from the middle of each plot to avoid interference and side effects from the neighbouring fields. The soil samples were taken at the top soil layer (0–20cm of depth). Soils were collected as five random subsamples from each field. The five subsamples of each field were pooled to obtain one composite sample and they were stored in polyethylene bags and kept frozen (-20°C) until the analysis. The analytical procedure consisted of three crucial steps:

*Extraction of the analyzed substance from the matrix*

Soil samples were homogenized and then passed through a 2-mm sieve. Soil portions (3 x 10g) were mixed with 3 x 2.5g of Diatomaceous Earth (Dionex® ASE® Prep DE) and transferred into stainless steel cells. Extraction was done using accelerated solvent extraction on fully automated Dionex ASE 350 extractor (Dionex®, CA, USA) [extraction solvent – acetone, acetonitrile or methanol (33mL per cell for two cycles of extraction), temp. 40°C, extraction time – 20min. and pressure – 0.2MPa)]. The combined extracts (from three cells) were then slowly evaporated under a nitrogen stream until dry.

*Extract cleaning*

Dry residues were dissolved in 30mL of water and subjected to SPE (Solid Phase Extraction). 3mL-capacity cartridges and sorbent bed – 0.5g of octadecyl, 40µm particle size (Bakerbond®, J.T.Baker®, Philipsburg, NJ, USA) were used. Sorbent was preconditioned with water (3mL) and then methanol (3mL). 30mL of extract solution was loaded with small portions onto the cartridge and the eluate was discarded. Analytes were eluted with 3mL of acetone. For 2,4-D, MCPA, dicamba, fluroxypyr and clopyralid, additionally collected extract was evaporated to dryness. Next, dry residue was dissolved in methanol (2mL) and esterified with diazomethane (injection solvent).

*Final determination*

A gas chromatograph Varian CP 3800 equipped with Varian GCMS 2000 software and an electron capture detector (Varian®, CA, USA) was used to carry out the final determination. Throughout the entire experiment, a VF-5ms capillary column (30m x 0.25mm x 0.25µm film thickness) (Varian®, CA, USA) was

used. Nitrogen was used as carrier gas at a flow rate of 1.5mL $min^{-1}$. Chromatographic separation was performed at the column oven where the initial temperature was held at 120˚C for 7min. Then, the temperature ramped at a rate of 10˚C $min^{-1}$. to 200˚C and was held for 2 minutes. Finally, the second ramp was continued at 5˚C $min^{-1}$. to 230˚C, which was held for 20min. Injector and detector temperatures were set at 230 and 300˚C, respectively. Aliquots of 1µl of the samples were injected.

Chlortoluron and isoproturon samples were analysed using high performance liquid chromatography (Shimadzu® HPLC measuring set) with UV-detection. The separation of compounds was performed using a DuPont® ZORBAX SIL (4.6 x 25mm) column and 5% of isopropanol + 95% of heksane (V/V) as mobile phase at a flow rate of 0.4 $mLmin^{-1}$. The injection volume was 20µL and detection was performed at 254nm.

The recovery of tested substances from soil was determined by analyzing fortified samples. Analysis was carried out at four concentration levels in three replicates. The obtained results (average recovery and quantification limit of the method) are detailed in Table 1.

TABLE. 1. LIMIT OF QUANTIFICATION AND AVERAGE RECOVERY IN SOIL

| Substance | Limit of quantification [mg $kg^{-1}$] | Average recovery [%] |
|---|---|---|
| 2,4-D | 0.0012 | 89.6 |
| MCPA | 0.0015 | 91.3 |
| Dicamba | 0.0015 | 92.5 |
| Chlortoluron | 0.0008 | 88.4 |
| Isoproturon | 0.0010 | 94.2 |
| Diflufenican | 0.0009 | 93.8 |
| Fluroxypyr | 0.0008 | 85.7 |
| Clopyralid | 0.0010 | 97.2 |

Each soil sample was analyzed three times. Repeatability of the analytical results was satisfactory, with relative standard deviation (RSD) not exceeding 9.6% of the mean values. All experimental data was calculated using the statistical program Statgraphics Centurion, version XV and Excel (MS Office 2010).

## RESULTS AND DISCUSSION

In the whole period of monitoring research, 1867 samples were subjected to analysis. In the soil samples originating from crop plantations situated in the fields of south–western Poland, the residue of the analyzed herbicides was

detected. The data regarding the number of samples, percentage share of the samples with residue, as well as mean values of detected residue in soil samples are shown in Table 2.

TABLE 2. HERBICIDE RESIDUES IN SOIL

| Active substance | Monitoring period | Nomber of samples | Samples with residue | % of samples with residues | Residues* [mg·kg$^{-1}$] |
|---|---|---|---|---|---|
| 2,4-D | 2002–2008 | 272 | 112 | 41.2 | 0.0087 |
| | 2010–2013 | 178 | 62 | 34.8 | 0.0052 |
| | | | | | |
| MCPA | 2002–2008 | 196 | 72 | 36.7 | 0.0074 |
| | 2010–2013 | 102 | 31 | 30.5 | 0.0046 |
| | | | | | |
| Dicamba | 2002–2008 | 121 | 27 | 22.3 | 0.0030 |
| | 2010–2013 | 74 | 12 | 16.2 | 0.0024 |
| | | | | | |
| Chlortoluron | 2002–2008 | 176 | 58 | 33.0 | 0.0062 |
| | 2010–2013 | 98 | 28 | 28.6 | 0.0028 |
| | | | | | |
| Isoproturon | 2002–2008 | 159 | 47 | 29.6 | 0.0056 |
| | 2010–2013 | 82 | 14 | 17.1 | 0.0038 |
| | | | | | |
| Diflufenican | 2002–2008 | 104 | 26 | 25.0 | 0.0024 |
| | 2010–2013 | 46 | 8 | 17.4 | 0.0019 |
| | | | | | |
| Fluroxypyr | 2002–2008 | 96 | 20 | 20.8 | 0.0021 |
| | 2010–2013 | 52 | 8 | 15.4 | 0.0018 |
| | | | | | |
| Clopyralid | 2002–2008 | 72 | 8 | 11.1 | 0.0016 |
| | 2010–2013 | 39 | 3 | 7.7 | 0.0012 |

*average concentration of residues (only for samples with residues).

Considering the particular active substances and the number of samples in which these compounds were used, it is possible to state that the residue of 2,4-D, MCPA, chlortoluron and isoproturon belonged to the most often detected compounds. These results confirm the fact that just these substances were most commonly applied in crop protection. Comparing the results from the years 2010–2013 and the earlier period (2002–2008), it is possible to observe that the mean percentage share of the samples with residue did decrease. In particular periods, it amounted to 27% and 31% respectively. The most considerable differences,

exceeding 6%, were recorded for 2,4-D, MCPA and dicamba. Similar tendency was observed for the assessment of mean values of residue concentrations. In the research carried out in the years 2010–2013, the range of concentrations was between 0.0012–0.0052 mg $kg^{-1}$, while in the earlier period, residue values ranged from 0.0016 to 0.0087 mg $kg^{-1}$.

Monitoring research on pesticide residue in the environment involves mainly plant material (grain, seed, fruits and vegetables). In the mentioned investigation it is also possible to notice steady decrease in the number of the samples with residue, as well as lower values of residue concentration [6, 8, 11, 15]. In the case of plant material, the results of monitoring research are comparable to the standards – Maximum Residue Level (MRL) [12]. For soils, similar standards have not been introduced. To assess the results obtained, it can be assumed that mean MRL value for herbicides (plant material) equals 0.1 mg $kg^{-1}$. Assuming this value, it should be stated that in the examined soil samples no residue, whose value exceeded MRL standard, was found.

The research results involving the tested herbicide residues in soil prove that the use of herbicides could not result as a threat to humans or the agricultural environment. Nevertheless, it should be stressed that all the samples originated from the fields corresponded with the requirements where herbicide application was controlled and the instructions given by the producer were followed. It is not possible to exclude sporadic incidents exceeding permissible values. Such cases are usually caused by a lack of farmers' knowledge, bad condition of the spraying devices, exceeding the recommended dosage, the use of fake herbicides or a situation where the farmer purposely damages his/her field, because they are counting on being compensated [13].

## CONCLUSION

Comparing the research results from both periods (2002–2008 and 2010–2013), a decrease of several percent in terms of the number of the samples with residue, as well as diminished mean values of detected residue concentration are possible to notice. This indicates a positive effect of the changes introduced in technology and the way of herbicide application. Moreover, MRL values exceeding permissible ones (set for plant products) were not stated in any of the analyzed soil samples.

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## ZMIANY W ZANIECZYSZCZENIU GLEB WYBRANYMI HERBICYDAMI STOSOWANYMI W OCHRONIE ZBÓŻ

Celem badań była ocean zanieczyszczeń herbicydowych gleb. Badania monitoringowe prowadzono w dwóch okresach 2002–2008 i 2010–2013 na plantacjach roślin zbożowych z terenu południowo-zachodniej Polski. Próbki gleb pobierano w czasie zbioru rośliny uprawnej. Pozostałości 2,4-D, MCPA, diflufenikanu, dikamby, chlorotoluronu, fluroksypyru, izoproturonu, klopyralidu oznaczano techniką chromatografii GC/ECD i HPLC/UV. Porównując wyniki badań z obu okresów stwierdzono kilku procentowy spadek liczby próbek z pozostałościami. W latach 2010–2013, średnie stężenie pozostałości wykrytych w 27% próbek gleby wynosiło 0.0012–0.0052 mg $kg^{-1}$.