

MONITORING OF HERBICIDAL POLLUTION IN GROUND AND SURFACE WATER ON ARABLE LAND OF SOUTH-WEST POLAND

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Abstract: Some active ingredient of herbicides, after application, can create a risk for ground and surface water. The aim of investigations was monitoring of herbicidal pollution in ground and surface water on arable areas.

The investigations were conducted in the years 2000–2002. The samples were collected (from stationary points located in the south-west Poland) twice a year (in spring and autumn about 3–6 weeks after nominal term of herbicide application). Surface water was sampled in 27 points and ground water in 18 wells.

The residues of herbicide active ingredients (triazine and phenoxy acids) were determined using HPLC methods with UV detection and GLC method with ECD detection.

The residues of active compounds in surface water (in spring and autumn) were detected. Residues at concentrations exceeding the EU safety standards were detected most frequently in springtime. The contamination levels in excess admissible limits were found in ca. 15% of surface water samples. In ground water (from wells) residues were detected sporadically and its level was very low (ca. 0.01–0.1 mg*dm⁻³).

Key words: water contaminations, herbicide, water monitoring, residue, HPLC, triazine, phenoxy acid derivatives

INTRODUCTION

Some active ingredient of herbicides, after application, can create a risk for ground and surface water (Sadowski and Kucharski 1997; Dąbrowski et al. 1997). Studies conducted in the USA and Canada (Cavalier et al. 1989; Frank et al. 1991; Spalding and Burbach 1989), and in Western Europe (Buser 1990; Readman et al. 1993; Zozaneas et al. 1993) confirmed the ground and surface water contamination. Monitoring of herbicidal pollution in water is very important to analysis of environmental hazard.

The aim of investigations was monitoring of herbicidal pollution in ground and surface water on arable land.

MATERIALS AND METHODS

The investigations were conducted in the years 2000–2002. Samples of water collected in the network stationary points in the south-west Poland were the material for this study. The samples were collected twice a year (in spring and autumn about 3–6 weeks after nominal time of herbicide application). Surface water (melioration ditches, infield water-courses) was collected in 27 points and ground water in 18 wells.

The residues of herbicide active ingredients (triazine and phenoxy acids) from 1 liter of water were extracted using dichloromethane and determined using HPLC methods with UV detection. For the verification of the results (especially in the cases of detection of “large” residues) the sample was analysed in parallel using the GLC method with ECD detection.

RESULTS AND DISCUSSION

In the years 2000–2002 the fluctuations of the frequency of the residues' occurrence were observed. In the surface water the derivatives of phenoxy acids were detected in 21.6%–44.0% of samples collected in spring and in 6%–12% of samples collected in autumn (Fig. 1). The residues exceeding $0.001 \text{ mg} \cdot \text{dm}^{-3}$ were detected in 5.7% of samples. The triazines (Fig. 3) were detected in 9.4%–27% of the samples collected in spring and 10.5%–27% of the samples collected in autumn, where 2% of samples contained the residues exceeding $0.001 \text{ mg} \cdot \text{dm}^{-3}$.

In ground (wells) water the frequency of residues' occurrence amounted respectively to: 17.8%–20% in spring and 0.2%–14% in autumn for phenoxy derivatives

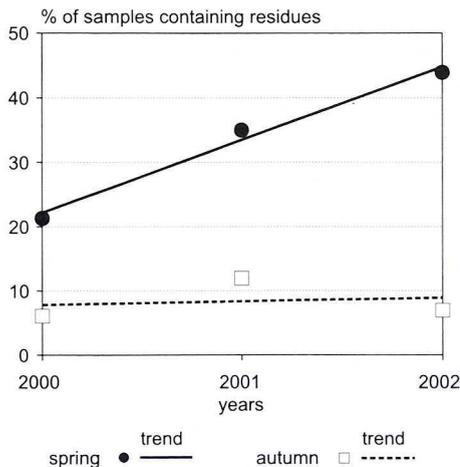


Fig. 1. Residue of phenoxy acid derivatives in surface water – % of samples containing residues

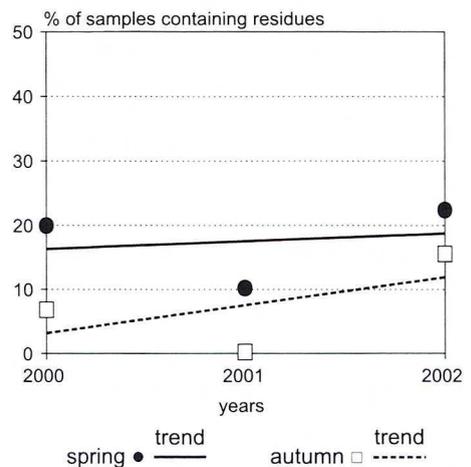


Fig. 2. Residue of phenoxy acid derivatives in ground water – % of samples containing residues

(Fig. 2) and 16%–27% (spring) and 14.4%–30.2% (autumn) for triazines (Fig. 4). Similar results obtained Spalding et al. (1989), where about 22% of ground water samples taken from wells (Nebraska State) contained residues of atrazine in concentration to $0.003 \text{ mg} \cdot \text{dm}^{-3}$. In the years 1985–1987 Cavalier et al. (1989) detected 18 active ingredients of herbicides (triazine, phenoxy acid and phenylurea derivatives) in surface and ground water samples (Arkansas State).

The experiments, which were conducted in the longer time scope (Sadowski and Kucharski 1999; 2002) show that the frequency of triazines' occurrence has been decreasing systematically, whilst the occurrence of the phenoxy compounds has been increasing.

The most frequently detected active ingredients are presented in table 1. Among the phenoxy derivatives, the most frequently detected ones occurred to be 2,4-D, MCPA and dicamba. Among the triazines – atrazine and simazine were the most frequently detected ones. The remaining substances were detected occasionally. In many samples the residues of several active ingredients were detected simultaneously (about 64% of the samples in which the residues were detected). In the majority of the samples (above 90% of the samples) the amount of detected residues did not exceed $0.0001 \text{ mg} \cdot \text{dm}^{-3}$ (for multi-residues). Only in about 4% of the samples the level of the residues exceeded those numbers.

Variation in the frequency of the residues occurrence in particular years was closely connected with the changes in the application intensity of triazine and phenoxy herbicides in the investigated area. Additionally, in the last ten years the use of triazine herbicides was restricted in Poland by law (the maximum dose was lowered to $1.5 \text{ kg a.i.} \cdot \text{ha}^{-1}$) and they were partly replaced by other herbicides.

The residues of herbicides at concentrations exceeding the EU safety standards were detected most frequently in spring (in surface water). The restrictions of the

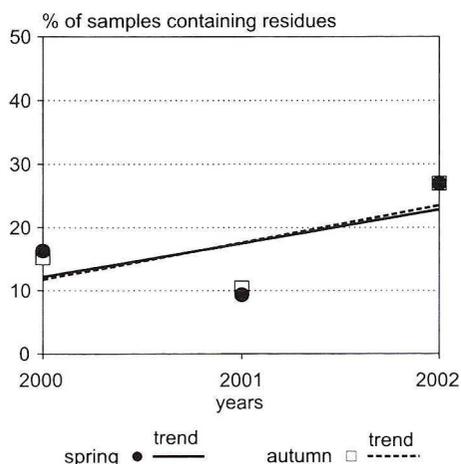


Fig. 3. Residue of triazine derivatives in surface water – % of samples containing residues

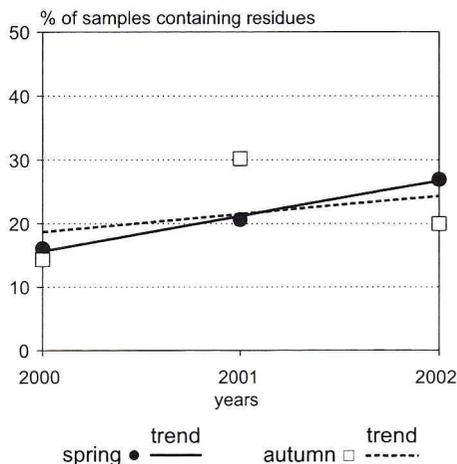


Fig. 4. Residue of triazine derivatives in ground water – % of samples containing residues

Table 1. Active substances detected in water samples

Substance	% of samples containing residues	
	surface water	ground (well) water
2,4 -D	93	94
MCPA	92	93
dicamba	12	15
dichloroprop	3	1
clopyralid	8	2
atrazine	96	99
simazine	60	54
cyanazine	6	2
metribuzin	3	1
metamitron	3	1
prometryne	1	0

use of triazine herbicides apparently contributed to the systematic decrease of water pollution caused by this group of substances. Similar observations described Croll (1991) for detected in ground and surface water phenylurea derivatives (isoproturon and chlortoluron).

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POLISH SUMMARY

MONITORING ZANIECZYSZCZEŃ HERBYCIDOWYCH WÓD
GRUNTOWYCH I POWIERZCHNIOWYCH NA TERENACH ROLNICZYCH
POŁUDNIOWO-ZACHODNIEJ POLSKI

Niektóre substancje aktywne herbicydów charakteryzują się wysoką persystencją w środowisku. Związki takie, po aplikacji mogą stwarzać ryzyko zanieczyszczenia wód powierzchniowych i gruntowych.

W latach 2000–2003 prowadzono badania monitoringowe wód gruntowych i powierzchniowych. Próbkę wody pochodziły z sieci stałych punktów bierzych (27 ujęć wody powierzchniowej i 18 studni gospodarskich) zlokalizowanych na terenach rolniczych Dolnego Śląska. Próby wody pobierano wiosną i jesienią, około 3–6 tygodni po nominalnym okresie aplikacji herbicydów. Pozostałości substancji aktywnych herbicydów (triazyny i pochodne fenoksykwasów) analizowano techniką chromatografii cieczowej HPLC z detekcją UV oraz chromatografii gazowej GLC z detekcją ECD.

Badania monitoringowe wskazują na obecność wykrywalnych pozostałości substancji aktywnych badanych herbicydów w kilku do kilkudziesięciu procentach przebadanych prób wody. Wyższe stężenia pozostałości, jak również procentowy wzrost liczby próbek z wykrytymi zanieczyszczeniami herbicydowymi odnotowano wiosną. Ze względu na jakościowe i ilościowe ograniczenie stosowania herbicydów z grupy triazyn następuje powolne zmniejszanie liczby prób wody, w których stwierdzono obecność triazyn.