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The Occurrence of Acid Herbicides Concentrations in some Environmental Samples from Romania

INSTITUTUL NAȚIONAL DE CERCETARE-DEZVOLTARE PENTRU ECOLOGIE INDUSTRIALĂ
ECOIND
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Diana Puiu, Roxana Scutariu, Vasile Iancu, Alina Tatarus, Nicoleta Vasilache

National Research and Development Institute for Industrial Ecology ECOIND, 71-73, Drumul Podul Dambovitei Street, code 060652, Bucharest, Romania

This paper deals with the screening of the 4 acidic herbicides (triclopyr, fluroxypyr, dicamba and clopyralid) occurrence in a wine-growing area and near some WWTPs. The soil samples were prevailed over Romania's Tarnava river bank, above and below the main cities to assess a possible herbicides occurrence through runoff, while surface water samples were collected upstream and downstream the WWTP's located near big cities (Tg. Jiu, Craiova, Cluj Napoca, Bucharest) and major rivers (Jiu, Somes, Dambovita). Besides the potential existence of diffuse contamination, the possible loading of surface water with herbicides from treatment plants can also be highlighted. Despite of intensive use of the herbicides in agriculture, urban green areas and households, the European authorities are not concerned by compounds toxicity for aquatic life in order to establish a reference value for environmental samples monitoring. On the same note, Romania's law sets a common herbicide limit concentration for potable and underground water, but not for surface water, wastewater effluents or soil.

Experimental Part

A volume of 100 mL of each liquid sample was filtered and acidified to pH 2. The selected compounds were determined by gas chromatography coupled with mass spectrometry method (GC-MS/MS Thermo TSQ 8000Evo, TG-5SilMS 60 m x 0.25 mm x 0.25 µm, inlet 260 °C, flow rate 1.2 mL/min) after solid phase extraction (SPE Dionex AutoTrace 280, 6 mL ethyl acetate) and derivatisation with MTBSTFA. In addition to the water samples, soils were first extracted with methanol, then centrifuged. Ethyl acetate solvent was used for all steps: GC extraction, derivatization and analysis; the SPE cartridge was Strata-C18-E.

RESULTS AND DISCUSSIONS

The residues quantified in the soil samples taken in October indicate a reduced herbicide contamination over time. As shown in table 1, only small concentrations of fluroxypyr and dicamba were detected, probably due to moderate persistence, and none of clopyralid and triclopyr. Unfortunately, these analytes have a great potential in leaching into groundwater.

Otherwise, the analyzed surface waters contain all 4 synthetic auxins, where the highest concentration was for fluroxypyr (526 ng/L). However, according to the Shapiro-Wilk p-values test results (table 2) for the quantified data, the distribution is normal, which means that there are no significant outlier concentrations, except of triclopyr (305 ng/L). Skeness and Kurtosis error standards show the tendency of the data to vary to higher values.

Applying the univariate analysis as ANOVA and Kruskal-Wallis tests, no statistically significant difference was found between the city samples at the 95.0% confidence level. There is also no strong difference between city-related data and upstream and downstream water data, which were selected as MANOVA factors in multivariate analysis. However, a decrease in residues was observed after the discharge of effluents from the treatment plant near Tg. Jiu and Cluj (fig. 1). One possible explanation is that the effluents do not contain selected herbicides or the volume of water discharged substantially dilutes the analyte concentration. However, the results obtained are estimated and a more specific analysis should be made.

A correlation between the water half-life (t ½) of clopyralid, dicamba, fluroxypyr and triclopyr (261, 40, 10.5 and 24.8 days) and the data obtained shows that, in addition to high concentrations of fluroxypyr in surface water, the contamination is also elevated due to its low half life (t ½ = 10.5 days) (fig 2) for the tested samples. This suggests a recent and also frequent contamination with fluroxypyr, being possible by the slow desorption of the contaminated agricultural land. On the other hand, the biodegradation of herbicides in water does not follow a linear pattern, so these values could represent initial residues with higher concentrations.

With the exception of triclopyr, these herbicides are used in Romanian agriculture. But these auxins are not include by Water Framework Directive in the list of priority substances for surface waters.

Table 1 Summary characterization of herbicides concentrations from analysed water and soil samples

	Surface water				River bank soil			
	frequency	min	max	mean	frequency	min	max	mean
	%	ng/L	ng/L	ng/L	%	µg/kg	µg/kg	µg/kg
Clopyralid	62.5	< 10	137	78.1	0	< 0.25	< 0.25	-
Dicamba	100	104	217	155	100	2.14	2.91	2.44
Fluroxypyr	100	89.5	526	258	100	2.37	4.19	3.09
Triclopyr	75.0	< 10	305	105	0	< 0.25	< 0.25	-

Table 2 Short descriptive statistics of the results quantified in water samples

	CLOPYRALID	DICAMBA	FLUROXYPYR	TRICLOPYR
Minimum	29.36	104.4	89.26	18.48
Maximum	137.0	216.7	525.9	305.2
Median	81.6	153.2	228.6	56.18
95.0% Lower Confidence Limit	28.06	124.4	126.8	-8.082
95.0% Upper Confidence Limit	128.1	185.2	389.7	218.5
Variance	1,624	1,322	24,738	11,658
Coefficient of Variation	0.516	0.235	0.609	1.026
Standard Error of Skewness	0.913	0.752	0.752	0.845
Standard Error of Kurtosis	2.000	1.481	1.481	1.741
Shapiro-Wilk Statistic	0.973	0.976	0.882	0.799
Shapiro-Wilk p-value	0.897	0.941	0.198	0.058

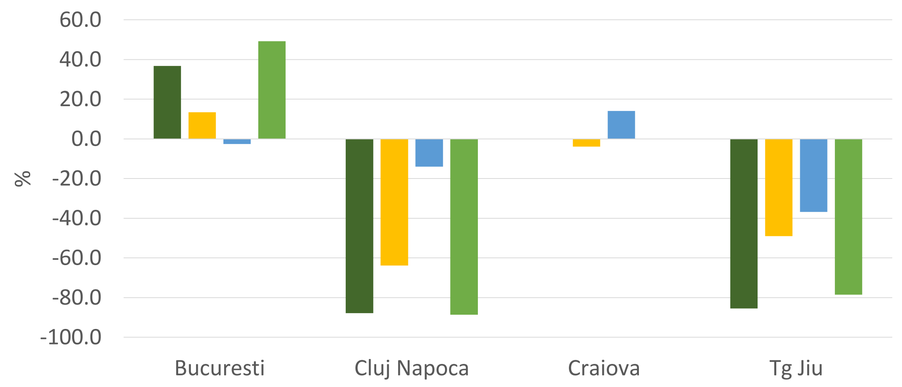

Fig. 1 Surface water herbicides concentrations percentage difference between the upstream and downstream of the wastewater treatment stations

In this case, the results were evaluated with the maximum concentration limits (100 ng / L) established by the current European directives and the Romanian legislation for groundwater and drinking water. As shown in fig. 3, the concentrations exceed the limit for 12.5-100% of the analyzed samples, the dicamba results being the highest. Compared to the legislation of other non-EU countries, the quality criteria are much lower, at the level of µg/L, for both drinking water and surface water. Noteworthy from Europe, Canada and Australia pays special attention to these compounds (Table 3).

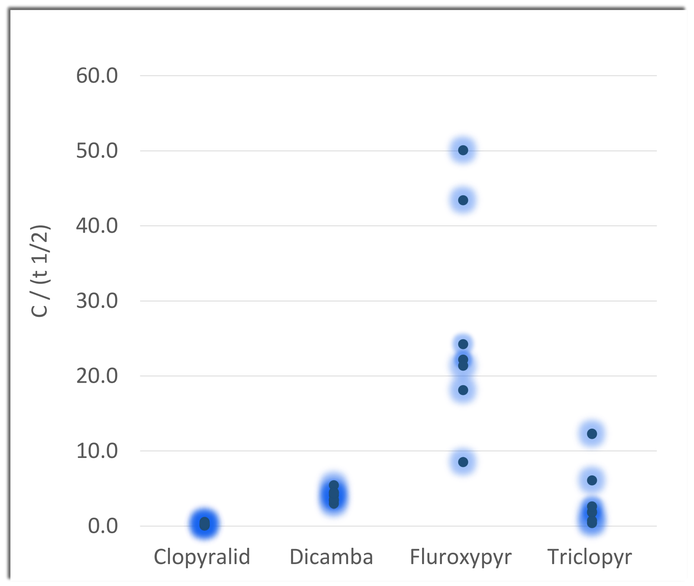

Fig. 2 The herbicides variation concentrations reported to the half life time (t ½) graphs

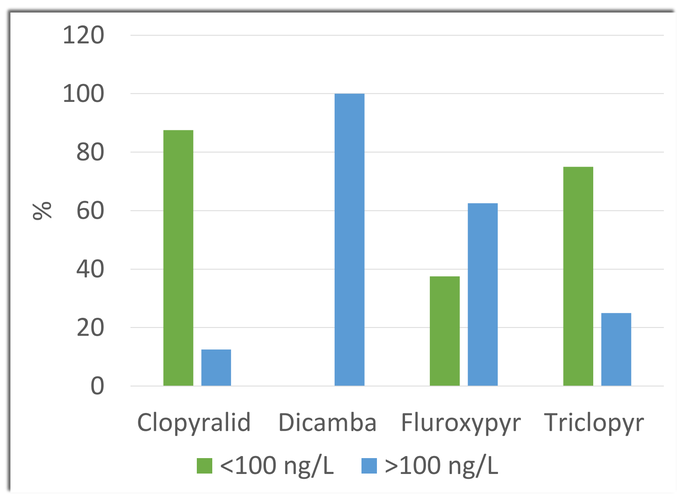

Fig. 3 Samples percentage with herbicides concentrations above 100 ng/L

Table 3 Representative maximum allowable concentration of auxin herbicides in some countries

	EU	Canada	Australia	Canada
	drinking water			surface water
	µg/L	µg/L	µg/L	µg/L
Triclopyr	-	-	-	-
Fluroxypyr	-	-	-	-
Dicamba	-	120	100	10
Clopyralid	-	90	1000	-
Herbicides	0.1	-	-	4

CONCLUSIONS

Using an SPE-GC-MS method, auxin herbicides were determined and quantified from surface water and soil samples. The detected concentrations of dicamba and fluroxypyr were found at residual level of µg/kg for soils, and the highest level for water samples in terms of median (153.2 ng/L dicamba, 228.6 fluroxypyr). Also, the maximum amount of detected herbicide in surface water was 526 ng/L fluroxypyr. Assessed with underground and drinking water, all herbicides exceeds the established concentration limits for 12.5-100% samples. The statistical analysis highlighted the normal distribution of herbicide concentration in the analyzed samples, but not a high correlation between the data for different rivers and the sampled locations.

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