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## THE OCCURRENCE OF ACID HERBICIDES CONCENTRATIONS IN SOME ENVIRONMENTAL SAMPLES FROM ROMANIA

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### **Introduction**

Herbicides are used worldwide in order to treat the agricultural crops, garden soil or aquatic cultures. Due to known environmental effects as aquatic organism toxicity (mortality, growth inhibition, population abundance) or fast soil percolation to groundwater, accompanied by low degradation in water treatment stations, this compounds are usually monitored in developing countries. Based on accessible reported data, it is little known about the amount of herbicides uses in Romania, and not at all about, the target compounds concentrations in different environmental sectors. The few studies that analyzed the organic contamination of Danube River and its major tributaries identify hundreds of ng/L of persistent pollutants as pesticides, pharmaceuticals or musk fragrances.

This paper investigates the occurrence of four acidic herbicides (triclopyr, fluroxypyr, dicamba and clopyralid) in Romania's Tarnava River bank and in some surface waters upstream and downstream the Wastewater Treatment Plants (WWTPs).

### **Materials and methods**

The soil samples were taken above and below of the main cities located on the edge of the Tarnava River, between Mihalt and Tiur area. The samples were air dried and ground. Water samples were obtained from Jiu, Someș and Dambovita rivers, upstream and downstream the 4 WWTPs of the cities: Targu Jiu, Craiova, Cluj Napoca and Bucharest. The spot sampling was done in one campaign in October. A volume of 100 mL each liquid sample was filtered and acidified to pH 2. The selected compounds were determined by gas chromatography with mass spectrometry method (GC-MS/MS Thermo TSQ 8000Evo) after solid-liquid extraction with methanol, solid phase extraction (SPE Dionex AutoTrace 280) and derivatisation with MTBSTFA. In addition to water samples, soils were first extracted with methanol then centrifuged. The supernatant was diluted with acidified water. It was used ethyl acetate solvent for all steps: extraction, derivatization and GC analysis; the SPE cartridge was Strata-C18-E. All used analytes were analytical standards acquired from Sigma Aldrich.

### **Results and conclusions**

The Tarnava River collects the storm water runoff from a known wine-growing area. The selected herbicides are usually applied in viticulture from May to July. The residues identified in October indicate a low contamination in time. As shown in the table below, only small concentrations of fluroxypyr and dicamba were detected,

maybe due to moderate persistence, and none of clopyralid and triclopyr. Unfortunately, these analytes have a great potential in leaching into groundwater. Otherwise, all four synthetic auxins were found in analyzed surface waters, where the highest concentration was for fluroxypyr (526 ng/L). There is not a significant difference between the data for upstream and downstream water near Bucharest and Craiova, while for Targu Jiu and Cluj Napoca the residues diminished after the effluent discharge. This suggests that the effluents of the treatment stations are free of selected herbicides, while the volume of discharged water dilutes substantially the analytes concentration. Based on obtained data, it was also revealed that Jiu River is more contaminated near Targu Jiu than near Craiova, and the compounds determined concentrations are 18-30% higher than for Somes and Dambovita. All rivers cross-agricultural lands, which means that the above-mentioned contamination is isolated. There is no suitable Romanian legislation to assess the surface water quality, but the maximum concentrations exceed the 100 ng/L limit for pesticides from potable water established by law 458/2002. Even the current European directives do not limit the maximum concentration of these herbicides in surface water or soil.

**Table 1.** Determined values of herbicides in surface water and sediments

	Surface water				River bank soil			
	frequency %	min ng/L	max ng/L	mean ng/L	frequency %	min µg/kg	max µg/kg	mean µg/kg
Clopyralid	62.5	<LO Q	137	78.1	0	<LO Q	<LO Q	-
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	<LO Q	305	105	0	<LO Q	<LO Q	-

*LOQ – limit of quantification (0.25 µg/kg soil, 10 ng/L water)*

The performed study describes punctually the level of contamination with acid herbicides of some scattered soil and water samples and reveals the necessity of further complex analysis of contaminant occurrences in environmental samples from Romania.

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