DETERMINATION OF ORGANOCHLORINE PESTICIDES IN DRINKING WATERS SAMPLED FROM CLUJ AND HUNEDOARA COUNTIES

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Abstract. – Determination of organochlorine pesticides in drinking waters sampled from Cluj and Hunedoara counties. Pesticides are found scattered in different environmental factors (water, air, soil) wherefrom they are drawn off by vegetal and animal organisms. Water pollution by pesticides results from the plant protection products industry and also from massive application of these resources in agriculture and other branches of economy. Pesticides can reach surface water along with dripping waters and by infiltration may reach the groundwater layers, organochlorine pesticides are most often found in the water sources (dieldrin, endrin, DDT, aldrin, lindane, heptachlor, etc.) due to their increased persistence in the external environment. This study followed up the determination of organochlorine pesticides in 14 drinking water samples collected from the output of water treatment plants in Cluj and Hunedoara counties that process surface water and deep-water sources. For identification of organochlorine pesticides, the gas chromatographic method after liquid-liquid extraction was used, by a gas cromatograph Shimadzu GC 2010 with detector ECD (Electron Capture Detection). There were not detected higher values than the method detection limit (0.01 µg/l) in the drinking water samples collected and analyzed for both total organochlorine pesticides and components, which were well below the maximum concentration admitted by Law 452/2002 regarding drinking water quality. Results are correlated with the sanitary protection areas for water sources and with the use of agricultural lands in the area. The solution to reduce risk of pesticides use is ecological agriculture , which gains increasingly more ground in Romania too.

Keywords: organochlorine pesticides, dinking water, gas cromatograph

1. INTRODUCTION

Pesticide is defined as a substance or mixture of substances, natural or synthetic, aimed to control and remove any pest that competes with man for food, destroys property and carries diseases. [13] Most POPs (persistent organic pollutants) are ***organochlorine pesticides***, namely, aldrin, endrin, clordane, DDT, heptachlor, mirex, toxaphene and hexachlorobenzene. They have been banned for agricultural or domestic uses in Europe, North America and many countries of South America in accordance with the **Stockholm Convention** (ratified in 2004). However, some organochlorine pesticides are still used – e.g. DDT is used to

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control malaria in some developing countries. Monitoring pesticides in surface waters, drinking water and deep-water is very important in the current period. [8] Dispersed in the environment, pesticides are found in various factors (air, water, soil - propagation vectors), wherefrom they are drawn off by vegetal and animal organisms. Through ingestion of food, water, breathing and other processes, pollutants (pesticides) reach the human body, where can cause severe disorders. [3] Exposure to pesticides as a result of their extensive use in agriculture is the most important route of exposure for the rural population. Among the most serious diseases caused by pesticide poisoning, the following distinguish: neurological disorders, internal organs disorders, skin disorders and cancer. [1,2,10] The ecological effect of any pesticide is intended to protect the population against certain pests, by reducing their abundance. Pesticides are included in a wide range of organic micropollutants having ecological impact. Although the terrestrial impact of pesticides exists, water contaminated by pesticide runoff is the main route which determines the ecological impact. [4] The chemicals used by farmers for pest removal are drawn off by precipitation and thus the infested water flows into the streams and rivers. Some of these chemicals are biodegradable and decompose quickly in harmless or less harmful substances, but the non-degradable are the most common ones that persist for a long period of time. The rate of pesticides removal from the water during processing processes for drinking purpose varies within extremely wide limits, depending on the type of pesticide and treatment methods. Coagulation with aluminum sulfate and rapid filtration lead to a decrease of 96-98% of a 10-25 ppb DDT content, while dieldrin is reduced by 55%, eldrin by 33%, parathion by 20% and lindane by less than 10%. Water treatment with ozone is more active than chlorination for a number of pesticides such as lindane, dieldrin, DDT and parathion. By oxidation, however, some pesticides such as parathion generate more toxic compounds. [9]

The purpose of this paper is the drinking water quality assessment, in terms of contamination with organochlorine pesticides in Cluj and Hunedoara counties at water treatment plants using different water sources.

2. MATERIALS AND METHODS

2.1. Sampling

The drinking water treatment plants monitored in Cluj county are managed by Compania de apa Somes (Somes Water Company) and in Hunedoara county by the company SC APA PROD SA Deva. The water treatment plant is designed to supply *drinking water* to residents, economic agencies and public institutions in neighbouring localities. Water treatment for surface water sources consists in coagulation/settling $\rightarrow$ filtration $\rightarrow$ disinfection with chlorine, while in case of deep-water sources only chlorine disinfection is used for the water treatment.

Table 1 shows the water treatment plants in study and the type of water source that is processed. Out of the 14 water treatment plants, 4 use surface water and one uses a mixed source. In their case, the treatment system is the conventional one (coagulation, settling, rapid filtration and disinfection with chlorine) while the deep-water sources are treated only by chlorination.

Table 1. ***Water sources used in the 14 drinking water treatment plants***

No.	Sampling location (water treatment plants)		Water source		
			deep-water	surface	mixed
1.	**Cluj** county	Aghireşu	✓		
2.		Bologa	✓		
3.		Dej		✓	
4.		Muntele Băişorii	✓		
5.	**Hunedoara** county	Bocşa	✓		
6.		Certej		✓	
7.		Cinciş-Cerna	✓		
8.		Crişcior		✓	
9.		Densuş	✓		
10.		Folorât-Geoagiu	✓		
11.		Hondol	✓		
12.		Roşcani	✓		
13.		Sânpetru-Hunedoara			✓
14.		Săntămărie Orlea		✓	

Drinking water samples from the water treatment plants in Cluj county were collected in 2009 and in Hunedoara county in 2010. Figures 1 and 2 show the sampling locations.

Fig. 1. ***Sampling locations of drinking waters in Cluj county***

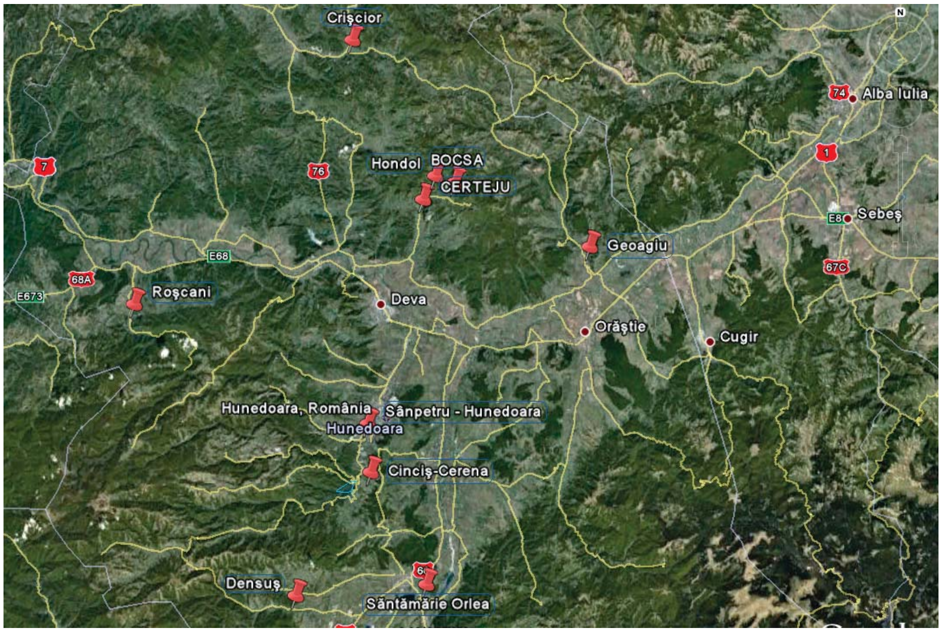

Fig. 2. ***Sampling locations of drinking waters in Hunedoara county***

Water sampling is a very important step in the process of pesticides determination, because collected samples must be representative and must not cause changes in the water composition and quality due to defective techniques or improper conditions of material preparation.

Before sampling, the polyethylene recipients are prepared to be clean, rinsed with distilled water, dried, rinsed with dichloromethane, then dried again. Drinking water samples were collected from the output pipe of the water treatment plants, according to SR ISO 5667-5 from June 1998 and transported in insulated packages at 6ºC-10ºC to protect them against changes of their chemical properties and deterioration. [11]

2.2. Analysis of collected samples

The analysis method derives from SR EN ISO 6468/2000 - Water Quality. Determination of organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatography method after liquid-liquid extraction [12] and Method 8081B - Determination of organochlorine pesticides by gas chromatography.

Organochlorine pesticides in drinking water are extracted with dichloromethane in a separating funnel and concentrated to a volume of 5 ml. During concentration the solvent is changed with hexane. The extract is measured by the gas chromatograph with electron capture detector Shimadzu GC 2010 – with detector ECD (Electron Capture Detection). Preparation and bringing to working conditions of the gas chromatograph and column are performed according to the instructions manual for the device.

For drawing the calibration curve, two sets of standard solution with the solvent used for extraction are prepared with the following concentrations: 20 μg/l, 40 μg/l, 60 μg/l, 80 μg/l, 100 μg/l in a series of five measuring bottles of 5 ml. The chromatogram for each standard solution is recorded. The calibration curves are drawn by the device's software inserting concentrations on abscissa, in organochlorine pesticides micrograms per liter solvent, and on ordinate the corresponding areas. Linear curves are thus obtained. Calibration curve should be verified at least each 12 months and always when new reagents are used.

For reading the pesticides concentrations in the sample, 1 liter of sample is transferred quantitatively in a separating funnel. It is extracted in two series of 15 ml each by stirring for 10 minutes. The organic phase is concentrated to 5 ml, the solvent is changed with hexane and analyzed by gas chromatography. The amount of organochlorine pesticides corresponding to the respective area is read on the calibration curve. Results are reported in μg/l sample, with two decimals.

3. RESULTS

Before sampling, the source site and surroundings were inspected. It was observed that all water sources framed within sanitary protection areas with strict regime in compliance with the legislation. All sources are located in relatively isolated areas, surrounded by pasture-type lands, except orchard-type farms.

Sanitary protection area with strict regime secure each water treatment plant, but not all have also constituted the sanitary protection perimeter with restriction regime. In neither perimeter of the water treatment plants, organochlorine pesticides or other biocides have not been used for over 10 years.

Table 2 includes results for the analysis of organochlorine pesticides in the treated water from water treatment plants in study. Results show that drinking water at the output of the water treatment plants in the two counties (Cluj and Hunedoara) have an appropriate quality for the indicator of total organochlorine pesticides, well below the maximum admitted concentration according to Law 458/2002 regarding drinking water quality. [6] Law no.458/2002, which regulates drinking water quality in Romania transposes Directive 98/83/EC on *drinking water*. The following organochlorine pesticides were analyzed in the water samples: HCH, DDE, TDE, DDT, Methoxychlor, Dieldrin, Heptachlor, Heptachlor-epoxide, Endosulfan.

Table 2. ***Results of drinking water analysis at the output of the water treatment plants***

Analyzed parameters (Measuring unit)	Sampling location		Analysis results	Maximum admitted concentration according to Law 458/2002 - regarding drinking water quality
Organochlorine pesticides (HCH, DDE, TDE, DDT, Methoxychlor, Dieldrin, Heptachlor, Heptachlor-epoxide, Endosulfan**)** **(µg/l)**	**Cluj** county	Aghireşu	<0,01	**0,10 µg/l**
		Bologa	<0,01	
		Dej	<0,01	
		Muntele Băişorii	<0,01	
	Hunedoara county	Bocşa	<0,01	
		Certej	<0,01	
		Cinciş-Cernă	<0,01	
		Crişcior	<0,01	
		Densuş	<0,01	
		Folorât-Geoagiu	<0,01	
		Hondol	<0,01	
		Roşcani	<0,01	
		Sânpetru-Hunedoara	<0,01	
		Săntămărie Orlea	<0,01	

Figure 3 shows a chromatogram model in which the only peak is that of the solvent, unlike the chromatogram of a pesticide mixture of concentration 60µg/l/compound shown in Figure 4, where clearly differentiated peaks corresponding to each pesticide are observed.

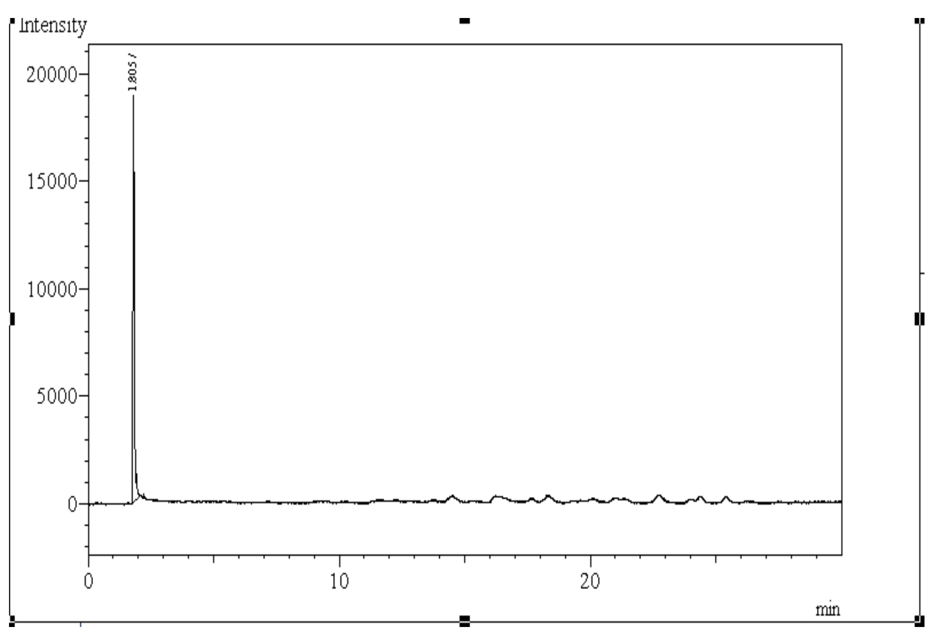

Fig. 3. ***Chromatogram of drinking water samples with no organochlorine pesticides***

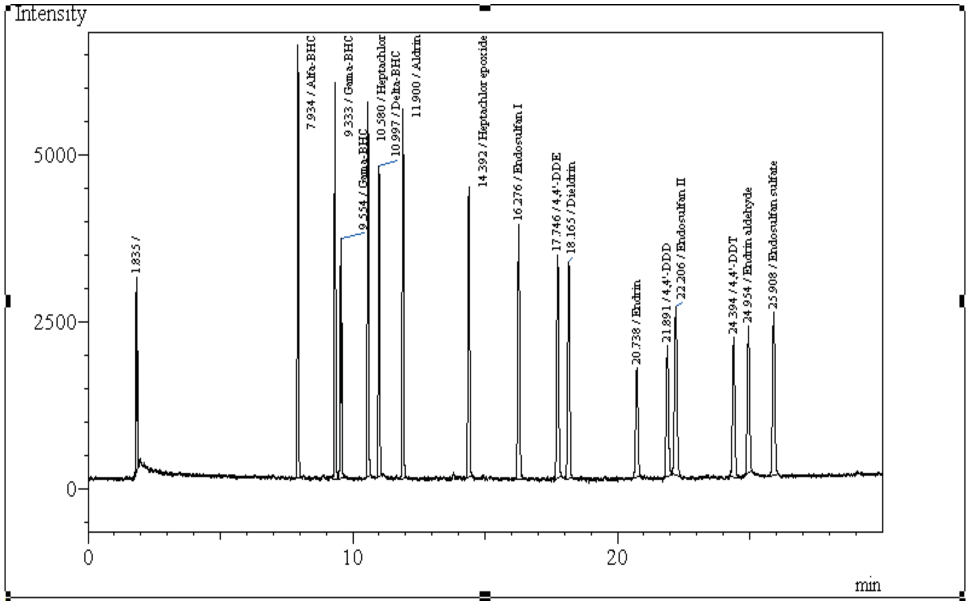

Fig. 4: ***Chromatogram Standard 60 µg***

Studies conducted in Mures county detected pesticides in 16 water samples. Diazinon (20 ng/l), dichlorvos (20 ng/l) and α-HCH (an average of 5.8 ng/l) were measured in Mures, Niraj, Lechinta, Tarnava Mare and Tarnava Mica rivers. Drinking water samples from fountains and tap-water also contained α-HCH (6 ng/L) and γ-HCH (4 ng/L). The half-life of HCH isomers is relatively high, while 2,4-D and atrazine (with concentration of 110 ng/L) have shorter half-life period, higher water solubility and low adherence to soil particles. In one water sample, the concentration of 2,4-D was 100% above for the standard criteria for EU (70 ng/L). [5]

Some pesticides are characterized by being very persistent in the environment. They may represent long-term dangers as they biomagnify up the food-chain. Humans, and particularly breastfed babies, are at the top of the food-chain. There is concern about potential endocrine and developmental effects of the pesticides, especially in children. [14]

4. CONCLUSIONS

Rural population may be exposed to pesticides in several ways: by spraying into the air and ingestion of pesticide residues via food and drinking water. Grazing lands can be dangerous if the animals are washed and disinfested externally (such as sheep) in the area. It is therefore important to determine precisely not only the restricted sanitary protection areas but also the activities permitted within.

Monitoring the drinking water quality at water treatment plants shows compliance with Law 458/2002, for the parameter organochlorine pesticide, but they must continue to be monitored as required by legislation. According to the results obtained in this study, the drinking water quality at the outputs of the water treatment plants in Cluj and Hunedoara counties does not represent a risk factor for the population health in terms of exposure to organochlorine pesticides.

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