

**Pesticides content in mineral waters of the Transcarpathean Region**

*V.M. Shestopalov N.P. Osokina I.P. Onishchenko (Institute of Geological Sciences NAS of Ukraine)*

**SUMMARY**

The Transcarpathian region is the richest province of Ukraine, its main recreation resources being mineral waters, climate and landscape. About 50 fields with medical waters of different types are known, among those the most widespread and valuable are carbonic waters. In 1989 and 1997 the Institute of Geological Sciences, NAS of Ukraine, carried out examinations of mineral waters fields for the content of strong organochloric pesticides: DDT and its metabolites, HCCH and its isomers, aldrin, heptachlor; organophosphoric pesticides: methaphos, carbophos, phosphamide, phozallon; fluorine- containing pesticides: trephlane a. o. In 1989 16 fields were examined, and 3 fields in 1997. Analytical experiments were performed using gas chromatographs. It was established that simultaneously in the same sample there could be present up to 8 substances and their metabolites, derivatives of chemical compounds of different groups in the concentrations lower than MPC for potable water, however the total effect of their influence on human body is not studied yet.



**XIV International Scientific Conference “Monitoring of Geological Processes and Ecological Condition of the Environment”**

10–13 November 2020, Kyiv, Ukraine

## Introduction

The Transcarpathian region is the richest natural province of Ukraine, its main recreation resources being mineral waters, climate and landscape. It's here that on the relatively small territory fields of different types mineral waters are concentrated. All over the territory of NIS variability of mineral waters, in this region could be compared only with Caucasian mineral waters. About 50 fields with medical water are known, among those the most widespread and valuable are carbonic waters. In the region 15 sanatoria and pensions with medication function, as well as several rest homes, 13 tourist' centres and complexes, departmental health-improving organizations. Six enterprises for mineral water spillage function here.

The Transcarpathian region comprises a complex system of hydrogeological districts that differ in the conditions of ground waters formation. Here there occur groundwaters of modern formation emerged as a result of dissolution and leaching of salts in near-surface and deep zones of the Earth crust, thermal stratal waters and waters of tectonic fractures.

The Transcarpathian region is one of the most successful from an ecological point of view among regions of Ukraine. This is favoured by mountain relief, extensive forests, absence of big industrial enterprises. However, technogenous pressure on the territory, such as environment pollution by oil products, heavy metals, agricultural chemicals, social vastes could hardly escape hydromineral resources of the region.

One of the most widespread and dangerous types of mineral waters pollution is their pollution with pesticides that are widely used in agriculture and forestry of Transcarpathian.

Factors that make the danger of mineral waters pollution with pesticides even worse are good permeability of the gravel deposits in the valleys of rivers Latoritza, Uzh, Tisa, Piniya a. o., where there are concentrated both the main mineral water fields and settlements with adjoining agricultural lands. Moreover, in the geological section of these districts there present a lot of fractured zones, which are characterized by increased permeability.

There were performed two cycles of sampling of the transcarpathian mineral waters of different types in the years of 1989 and 1997.

## Gas chromatography method.

There were investigated strong organochloric pesticides (DDT and its metabolites: n,n'-DDT; n,n'-DDE, o,n'-DDD, HCCH and its isomers:  $\alpha$ -HCCH,  $\beta$ -HCCH,  $\gamma$ -HCCH, aldrin, heptachlor); organophosphoric pesticides (methaphos, carbophos, phosphamide, phozallon); fluorine-containing pesticides (trephlane). Along with mineral waters, there was also investigated pesticides content in surface stream-flows and soils.

In 1989 there were examined 16 fields that exploit mineral waters of different types: Polyanske, Ploskovske, Novo-Polenske, Svalyavske, Golubinskoye, Nelipenskoye, Medvezhye, Shayanskoye (Borzhomi type); Soimenske, Kelechenske, Uzhgorodske, Dragivske, Gorno-Tisenske (Synjogirske type), Pasikske (Krintitza type), (Tabl. 1) ( Molozhanova et. al.,1990).

Dr. E.Molozhanova took part in expedition 1989 and the authors express their thanks for her contribution to this work.

In 1997 there were performed determinations in three fields of mineral waters: Luzhanske, Poljanske, Uzhgorodske (Tabl. 2).

Examined fields are intensively exploited by different resorts and sanatoria (Sonjachne Zakarpattya», «Kwitka Poloniny», «Shajan», «Karpaty», «Verchovyna»), as well as by factories for spillage of mineral waters «Luzhanskaya», «Dragivskaya», «Polyana Kwasova» a. o.



**Table 1** Pesticides content in hydromineral resources of Transcarpathian region (July, 1989)

Sampling sites	Object	Pesticides, mg/dm <sup>3</sup> , mg/kg					ED
		DDT Dt	ΣHCCH	Dilor	Metaphos	Carbophos	
Svalvava district, village Golubinnoye, depression Lug, right bank of the river Piniya, well 4RE	Mineral water	2.5·10 <sup>-4</sup>	4.7·10 <sup>-7</sup>	2.9·10 <sup>-5</sup>	3.1·10 <sup>-6</sup>	1.0·10 <sup>-6</sup>	2.8·10 <sup>-4</sup>
River Piniya	Fresh water	1.3·10 <sup>-4</sup>	5.2·10 <sup>-7</sup>	1.3·10 <sup>-5</sup>	5.2·10 <sup>-6</sup>	Not detected	1.5·10 <sup>-4</sup>
Depression Lug, 300 m to the west from well 4 RE	Rock loam	3.1·10 <sup>-1</sup>	1.8·10 <sup>-3</sup>	2.8·10 <sup>-1</sup>	Not detected	1.0·10 <sup>-6</sup>	-
Depression Lug, 300 m to the west from well 4RE	Rock sandy loam	8.9·10 <sup>-2</sup>	7.0·10 <sup>-3</sup>	2.5·10 <sup>-1</sup>	2.4·10 <sup>-2</sup>	5.0·10 <sup>-5</sup>	-
Depression Lug, 300 m to the west from well 4 RE	Fresh water	7.3·10 <sup>-5</sup>	2.3·10 <sup>-7</sup>	2.4·10 <sup>-5</sup>	5.2·10 <sup>-6</sup>	Not detected	1.0·10 <sup>-4</sup>
Village Polyana, well 3R	Mineral water	1.1·10 <sup>-5</sup>	3.0·10 <sup>-7</sup>	3.0·10 <sup>-5</sup>	4.1·10 <sup>-7</sup>	1.0·10 <sup>-7</sup>	4.1·10 <sup>-5</sup>
Sanatorium «Sonyachne Zakarpatty», depression Nova Polyana, well 10-K	« «	1.5·10 <sup>-5</sup>	3.1·10 <sup>-7</sup>	2.5·10 <sup>-5</sup>	3.1·10 <sup>-6</sup>	1.0·10 <sup>-7</sup>	4.4·10 <sup>-5</sup>
Village Polyana, water intake Lug, spring 7 km from Polyana	Fresh water	6.0·10 <sup>-6</sup>	7.8·10 <sup>-8</sup>	5.1·10 <sup>-6</sup>	Not detected	1.0·10 <sup>-7</sup>	1.1·10 <sup>-5</sup>
Sanatorium «Karpaty», stream Labij Potok	« «	4.8·10 <sup>-5</sup>	1.9·10 <sup>-7</sup>	8.0·10 <sup>-6</sup>	2.0·10 <sup>-7</sup>	Not detected	5.6·10 <sup>-5</sup>
Mukachevo district, sanatorium «Karpaty» 4 km along the road Chinadieva-Svalyava, well 5	Mineral water	1.2·10 <sup>-4</sup>	1.8·10 <sup>-7</sup>	1.4·10 <sup>-6</sup>	3.2·10 <sup>-7</sup>	1.0·10 <sup>-7</sup>	1.3·10 <sup>-4</sup>
Chust district, village Shayan, sanatorium «Shayan», well 242	« «	2.2·10 <sup>-4</sup>	2.0·10 <sup>-7</sup>	3.5·10 <sup>-6</sup>	1.0·10 <sup>-7</sup>	Not detected	2.2·10 <sup>-4</sup>
Chust district, village Vyshkove, well 713	Fresh water	1.4·10 <sup>-6</sup>	1.7·10 <sup>-7</sup>	3.5·10 <sup>-6</sup>	1.2·10 <sup>-6</sup>	1.0·10 <sup>-7</sup>	6.3·10 <sup>-6</sup>
Chust district, village Shayan, sanatorium «Shayan», well 9T	Mineral water	2.2·10 <sup>-6</sup>	5.8·10 <sup>-7</sup>	1.8·10 <sup>-5</sup>	2.4·10 <sup>-6</sup>	Not detected	2.3·10 <sup>-5</sup>
Mezhgirskej district, village Soimy, sanatorium «Verchovyna», well 4R	« «	5.0·10 <sup>-7</sup>	5.6·10 <sup>-5</sup>	1.2·10 <sup>-6</sup>	1.2·10 <sup>-6</sup>	1.0·10 <sup>-7</sup>	5.9·10 <sup>-5</sup>
Mezhgirskej district, village Soimy, stream Kwasovets (the place of falling into r. Rika)	Fresh water	4.6·10 <sup>-6</sup>	7.1·10 <sup>-8</sup>	4.3·10 <sup>-6</sup>	2.4·10 <sup>-7</sup>	1.4·10 <sup>-7</sup>	9.4·10 <sup>-6</sup>
Mezhgirskej district, village Soimy	Soil	2.2·10 <sup>-2</sup>	1.8·10 <sup>-2</sup>	9.3·10 <sup>-1</sup>	2.4·10 <sup>-2</sup>	Not detected	
Mezhgirskej district, village Kelechin, well 359	Mineral water	1.5·10 <sup>-4</sup>	6.5·10 <sup>-7</sup>	8.6·10 <sup>-6</sup>	4.8·10 <sup>-7</sup>	1.0·10 <sup>-7</sup>	1.6·10 <sup>-4</sup>
Factory «Polyana Kwasova», village Polyana Kwasova, well 7R3	« «	2.0·10 <sup>-4</sup>	5.1·10 <sup>-7</sup>	5.2·10 <sup>-6</sup>	1.2·10 <sup>-6</sup>	1.0·10 <sup>-7</sup>	2.1·10 <sup>-4</sup>
Village Polyana, Medvezhe, well 4P	« «	8.0·10 <sup>-5</sup>	2.6·10 <sup>-7</sup>	6.3·10 <sup>-5</sup>	2.1·10 <sup>-6</sup>	Not detected	1.5·10 <sup>-4</sup>
Factory «Lugy» (near Golubinnoe), well 3R3	« «	5.0·10 <sup>-7</sup>	4.0·10 <sup>-7</sup>	5.0·10 <sup>-6</sup>	2.1·10 <sup>-6</sup>	1.0·10 <sup>-7</sup>	8.1·10 <sup>-6</sup>
The city of Svalyava, factory «Svalyava», well 26K	« «	3.0·10 <sup>-7</sup>	7.0·10 <sup>-7</sup>	1.3·10 <sup>-5</sup>	Not detected	2.0·10 <sup>-7</sup>	1.4·10 <sup>-5</sup>



**Table 2** Organochloric pesticides content in mineral waters of Transcarpathian region (October, 1997)

Sampling sites	n,n - DDT	n,n' - DDE	o,n' - DDD	∑ DDT	α-HCCH	β- HCCH	γ-HCCH	∑ HCCH	Aldrin	Heptachlor	Trephlane	∑ D
Kwitka Poloniny (Luzhanskaya type)	$8.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$	$8.7 \cdot 10^{-5}$	$1.2 \cdot 10^{-6}$	Not detected	$6.0 \cdot 10^{-7}$	$1.8 \cdot 10^{-6}$	Not detected	$6.0 \cdot 10^{-8}$	$3.0 \cdot 10^{-8}$	$8.9 \cdot 10^{-5}$
Polyana Kwasova (carbonic carbonate- chloride sodium )	$2.8 \cdot 10^{-5}$	$3.0 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$3.5 \cdot 10^{-5}$	$8.0 \cdot 10^{-7}$	« »	Not etected	$8.0 \cdot 10^{-7}$	$4.0 \cdot 10^{-7}$	Not detected	$4.0 \cdot 10^{-8}$	$3.6 \cdot 10^{-5}$
The city Uzhgorod Bozoz.hdoksiki park (Darasun type)	$5.4 \cdot 10^{-5}$	$4.6 \cdot 10^{-6}$	Not detected	$5.9 \cdot 10^{-5}$	$3.2 \cdot 10^{-6}$	« »	$8.0 \cdot 10^{-7}$	$4.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-7}$	« »	Not detected	$6.3 \cdot 10^{-5}$

Note: ∑ D - total concentration of the pesticides, mg/dm<sup>3</sup>, mg/kg

## Results

Analysis of mineral waters for pesticides content was carried out in the Laboratory for pesticides determination in ground waters and soil of the Department of hydrogeological problems, Institute of Geological Sciences, NAS of Ukraine, with the gas chromatographs. Total concentrations of the examined pesticides in the mineral waters vary in the range of  $n \cdot 10^{-4}$  –  $n \cdot 10^{-6}$  mg/L; the same range of concentrations was typical for surface waters. In the soils and water-bearing rocks pesticides concentrations are considerably higher and reach decimal fractions of mg/kg. In the mineral waters ∑ DDT was detected in 100% of samples in the concentration range  $n \cdot 10^{-4}$  –  $n \cdot 10^{-7}$  mg/L. ∑HCCH is present in 100% of samples in the concentration range  $n \cdot 10^{-6}$  -  $n \cdot 10^{-7}$  mg/L. Dilor was detected in 100% of samples in the concentration range  $n \cdot 10^{-5}$  –  $n \cdot 10^{-6}$  mg/L. Metaphos is present in 82% of samples in the concentration range  $n \cdot 10^{-6}$  –  $n \cdot 10^{-7}$  mg/L. Carbophos is present in 71% of samples in the concentration range  $n \cdot 10^{-6}$  -  $n \cdot 10^{-7}$  mg/L. An together, in the waters there were detected 9 pesticides and their derivatives. Simultaneously, there were detected up to 8 substances in some samples. There were revealed no clear correlations between pesticides content in the mineral waters and their type, chemical composition and location. Both maximal and minimal total concentrations of the pesticides are detected in the hydrocarbon sodium waters of Polyana-Svalyava group (maximum equals  $2.8 \cdot 10^{-4}$  mg/L in the well 4RE, v. Golubine; minimum -  $4.6 \cdot 10^{-6}$  mg/L, in the well 21 on the territory of food products factory, v. Nelipine). However, pesticides products belong to the list of substances which are the most dangerous environmental pollutants, according to classification of WHO and some other international organizations. It seems to be particularly dangerous a simultaneous presence of several substances and their metabolites in the same probe, due to the fact that their combined effect on the human body is not studied yet.

## Conclusions

Analysis of the situation at the mineral water fields in the Transcarpathian region revealed primary stages of mineral waters quality changes due to a man impact. In case the situation is not controlled, this could cause irreversible negative consequences in the near future. Despite the variability of hydrogeological conditions in Transcarpathian, there were revealed no regional correlations between pesticides concentrations in the mineral waters and geological structure of the territory, type and chemical content of the waters. Pesticide content in the mineral waters is characterized by mosaic character of distribution which relates to the



quantity and assortment of pesticides that are utilized at agricultural lands and forests, protection of underground waters, microinclines, permeability of aeration zone and filtration properties of water-saturated zone, technical state of wells and regime of their exploitation, permeability of the near-well surface, confined and unconfined character of the aquifer. During the last ten years (1987-1997) DDT content in the waters significantly (for one order) decreased, while HCCH concentrations remained practically at the same level.

This indicates that HCCH was periodically used at the agricultural lands and forests of Transcarpathian. As soon as DDT is concerned, there were no new income to natural ecosystems, and retrospective pollution gradually decreases. It's necessary to conduct systematic observations over pesticides content in hydromineral resources, to perform ecological expertize of the territories in order to eliminate or diminish negative influence of pesticides due to change of assortment of the products used, decrease of standards, in some cases prohibition of their utilization. Fundamental investigations are needed to reveal the main regularities of these substances migration in the underground ecosystem, to elaborate the criteria for estimation of danger of simultaneous presence of pesticides belonging to different groups in mineral waters and other natural objects.

## References

Molozhanova, E.G., Osokina, N.P., Shestopalov, V.M. [1990]. Soderzhanie pestitsidov v gidromineral'nykh resursakh razlichnykh regionov Ukrainskoj SSR. *Soderzhanie ostatochnykh kolichestv pestitsidov v ob'ektakh prirodnoj sredy Sovetskogo soyuza*. Ezhegodnik – Obninsk, Ch.5, R.2, 242 – 256. [in Russian]

