

## STUDY OF AN ISSUE OF PROVIDING THE PEOPLE OF TOPORIV VILLAGE WITH DRINKING WATER

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**Abstract.** Monitoring findings regarding fluorine concentration in drinking water of Toporiv Village in Busk District of Lviv Region are analyzed. Reasons for biogeochemical endemic of hypoplasia and fluorosis in the local population are found. The quality of drinking water has been investigated by means of biotesting using flax and lupine seeds.

**Key words:** drinking water, fluorine, defluorination, biotesting, teeth affection.

### Introduction

Consumption of drinking water containing high concentrations of harmful compounds, in particular fluorine, results in deterioration of people's health. There are four concentration levels for each element: deficit, optimal, increased (acceptable) and very high (lethal) [1]. Microelements in certain doses are necessary for functioning of the human body, but their excess in the environment may cause various diseases or affections of the entire body. It is known that both lack and excess of fluorine in food and drinking water affect the human body, resulting in different diseases. Fluorine in the body is in a bound state, usually in a form of poorly soluble salts of calcium, magnesium, and iron. Fluorine compounds are present in all tissues of the human body. Around 99% of total fluorine is in bones and the tooth enamel. Fluorine content in water in the amount of 0.7 to 1 mg/dm<sup>3</sup> contributes to normal development and mineralization of bones and teeth. Lack of fluorine in drinking water (below 0.6 mg/dm<sup>3</sup>) causes tooth cavity. Excessive fluorine (above 1.5 mg/dm<sup>3</sup>) leads to fluorosis of teeth and bones, muscle-skeleton

disorders, hepatitis, neurocirculatory asthenia, myocardosis, gastritis, rhinitis, ECG alterations, pulmonary tissue calcification, and slowdown in growth and sexual development [2]. Therefore, ensuring ecological safety of water resources is an urgent issue.

The fluorine circulation in nature involves lithosphere, hydrosphere, atmosphere and biota. Widely spread soluble fluorine-containing compounds in rocks and soils make fluorine present in natural water used for public water supply. Fluorine concentration in natural water varies within a wide range (from 0.01 to 27 mg/dm<sup>3</sup>) and depends on solubility of its compounds. Ground waters get saturated due to their contact with fluorine-rich rocks like fluorspar, aluminosilicates, apatites, phosphorites, etc. Fluorine contained in mineral thermal water is related to magmatic processes in volcanic formations. Surface water gets contaminated by emissions and discharges from certain productions – during processing apatites into superphosphate fertilisers, coal washing, glass melting as well as application of fluorine-containing mineral fertilisers and silicon-fluoride salts as insecticides by agribusiness.

Migration capability of fluorine in natural water depends on the content of calcium ions in it, forming low-solubility compounds together with fluorine ions. The increased pH causes higher fluorine mobility. Fluorine content in river water varies within 0.05 to 1.9 mg/dm<sup>3</sup>, in atmospheric precipitations within 0.05 to 0.54 mg/dm<sup>3</sup>, and in ground water within 0.3 to 4.6 mg/dm<sup>3</sup>. Concentration of fluorine in thermal water in certain cases reaches up to 10 mg/dm<sup>3</sup>, and fluorine content in the oceans is around 1.3 mg/dm<sup>3</sup> [3].

Ground (artesian and well) water is richer in fluoride ions as compared to surface water, and sources of concentration of fluoride ions exceeding the maximum allowable concentration are more common for it.

Today, there are norms for drinking water applied in Ukraine and around the world as to fluorine intake by the human body, which are presented in Table 1.

People may also consume daily mineral water for drinking. Table 2 presents fluorine norms for mineral water. It should be mentioned that EU Directives require additional marking if mineral water contains more than 1 mg/dm<sup>3</sup> (“contains fluoride”) as well as more than 1.5 mg/dm<sup>3</sup> (“product not intended for babies and children under seven”).

Table 1

Fluorine Norms for Drinking Water [4]

| WHO | USA  |                 | European Union<br>(Directive 98/83/EC) | Ukraine<br>(DSanPiN 2.2.4.-005-98)<br>(by climatic zones): |
|-----|--|-----------------|--|--|
|     | (FDA, 2002, 21CFR Part 165.110)  | IBWA Model Code |  |  |
| 1.5 | 1.4–2.4<br>(based on local air temperature at place of water distribution) | 3.0             | 1.5                                    | IV – up to 0.7<br>III – up to 1.2<br>II – up to 1.5        |

Table 2

Fluorine Norms for Mineral Drinking Water [4]

| USA                             |                 | European Union (Directives 2009/54/EC, 2003/40/EC<br>CODEXSTAN 108-1981,<br>Rev. 2-2008) | Ukraine<br>(DSTU 878-93,<br>DSTU 42.10.02-96) |                       |
|---------------------------------|-----------------|--|---|-----------------------|
| (FDA, 2002, 21CFR Part 165.110) | IBWA Model Code |  | table water                                   | medicinal table water |
| 1.4-2.4                         | 3.0             | 5.0  | 1.5   | 10.0                  |

In order to bring fluorine content to normal limits, mineral drinking water is allowed to be fluorinated and defluorinated. At that, with defluorination of mineral water, preservation of its basic chemical composition is mandatory.

Nowadays, methods of removal of fluorine ions from water are a matter of study of many scientists.

In practice, there are different methods used for water defluorination. Most of them can be divided in two groups:

1. Precipitation methods:

A) contact-sorption methods of precipitation with ammonium salts, magnesium oxy-hydrate, and tricalcium phosphate, based on sorption of fluorine by different solutions;

B) defluorination by electrocoagulation and electroflotation, based on anodic dissolution of electrodes;

2. Methods based on volumetric ion-exchange sorption:

A) fluorine is removed by filtration through fluorine-selective materials (activated alumina, phosphate (bone coal, tricalcium phosphate, hydroxyapatite, superphosphate, etc.) or magnesium sorbents, activated carbon, ionites, and clinoptilolite;

B) Hyperfiltration method.

## Experimental Part

The experiments were aimed at finding implication of the increased fluorine content for the incidence of teeth affection in the people of Toporiv Village in Busk District of Lviv Region as well as defining the quality of drinking water by biotesting.

First cases of hypoplasia of the enamel among the population of Toporiv were revealed in 1996. In order to find the reasons for this pathology, at the beginning of 1997, Busk District Sanitary-Epidemiological Station

initiated detailed study of the composition of the local ground water.

Wells are one of the most common sources of water intake for household and drinking needs in this region, as they are present almost in each household. By chemical composition, the well water is sulphate-fluoride-chloride- hydrocarbonate-sodium water with  $0.63 \text{ g/dm}^3$  mineralisation. The water meets standards of DSanPiN 2.2.4-171-10 "Hygienic Requirements for Drinking Water Intended for Consumption by People".

Artesian Well No. 1 is located in Lviv Region, Busk District, Toporiv Village. The intended purpose of the artesian well (according to the water use needs and the classifier of minerals) is the water use for household and drinking. The artesian well is 58.0 m deep with the aquifer in upper cretaceous deposits formed by grey fractured marl. By chemical composition, the water is sulphate-fluoride-chloride-hydrocarbonate-sodium water with  $0.88 \text{ g/dm}^3$  mineralisation. The water meets standards of DSanPiN 2.2.4-171-10 "Hygienic Requirements for Drinking Water Intended for Consumption by People".

All the existing sources of water supply in the Toporiv area were found to have excessive fluorine content. According to medical examination data as of 29 October 1997, hypoplasia of the enamel of different

severity was diagnosed in over 80 students in the Toporiv area. Based on studies conducted by the Busk District Sanitary-Epidemiological Station and an analysis of their statistical materials, we can make a conclusion that the excessive fluorine concentration in drinking water in the specified period is related to the beginning of uncontrollable tapping by the local people in the water main and the use of service water for drinking needs due to drying out of a number of wells in Toporiv.

Many researches also show that calcium and fluorine are antagonists. Therefore, low calcium content in drinking water combined with high fluorine concentration may provoke biogeochemical endemic hypoplasia and fluorosis. At the same time, the lowest calcium content in water of the cretaceous aquifer is noticed just within Chervonohrad water intake [3].

During 2011–2017, authorized entities (the Sanitary-Epidemiological Station and Lviv Regional Laboratory Centre) sampled the water directly in Well No. 1 as well as at different points of the water-supply main at the following addresses: 8, Shkilna Str. (a school), 37, Krakova Str. (a residential building) and 2, Shpytalna Str. (an outpatient clinic) and submitted for an analyses to Lviv Regional Laboratory Centre (see Fig. 1).



**Fig. 1.** Diagram of the water-supply main in Toporiv Village. Points of sampling of main (1) and well (2) water

The results of drinking water sampling for fluorine content are given in Table 3. Observed fluorine exceeds the MAC 1.2-2.6 times. Fluorine concentration dynamics in water is a variable value, so a number of people who have had fluorosis symptoms and general deterioration of health, caused by excessive fluorine, varies.

During 2010–2017, there were 32 % of the people diagnosed with fluorosis (with the population of 1043 people): 23 % of the children and 9 % of the adults. The tendency to decline in morbidity is due to the fact that after making the population acquainted with the

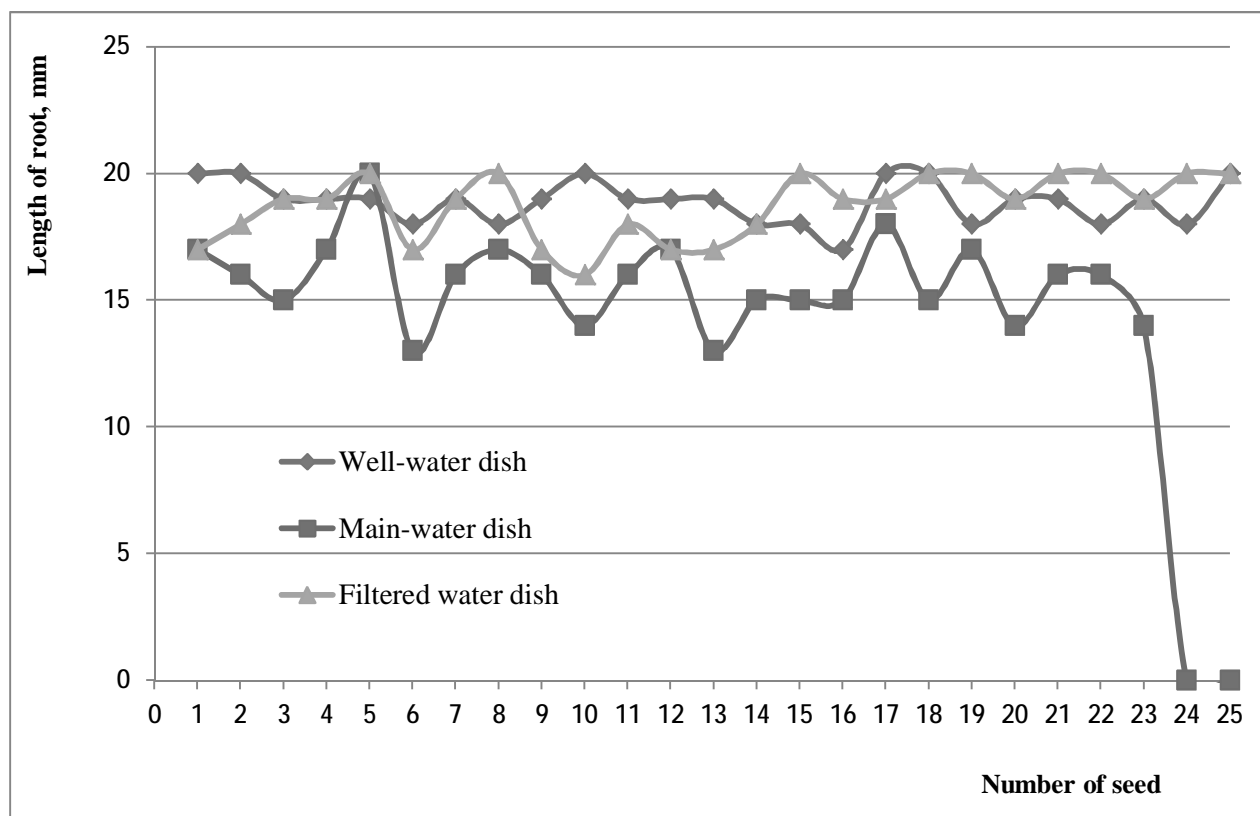
contamination issue, the utilization of the main water supply has been reduced in favour of mine and home wells up to 35 metres deep, where fluorine concentration is within normal limits.

In 2017 water samples were also used in a test to determine the impact of fluorine on biosensitive plants (bioindicators). It involved sprouting of plant test-systems: flax and lupine seeds. There were 25 seeds of each of the test samples. 25 seeds were put in each of the 3 double-dishes and topped with tested (well, main and filtered) water during 7 days. The test results are presented in Fig. 2–6.

*Table 3*

**Monitoring Data on Fluorine Concentration in Drinking Water (2011-2017)**

| Sampling site     | Concentration of fluorides in water, mg/dm <sup>3</sup> |      |      |      |      |
|-------------------|---|------|------|------|------|
|                   | 2011  | 2014 | 2015 | 2016 | 2017 |
| Water-supply main | 3.89  | 3.59 | 1.12 | 1.33 | 2.70 |
| Well No. 1        | 4.01  | 3.62 | 1.24 | 1.81 | 3.27 |



**Fig. 2.** Flax seed sprouting dynamics

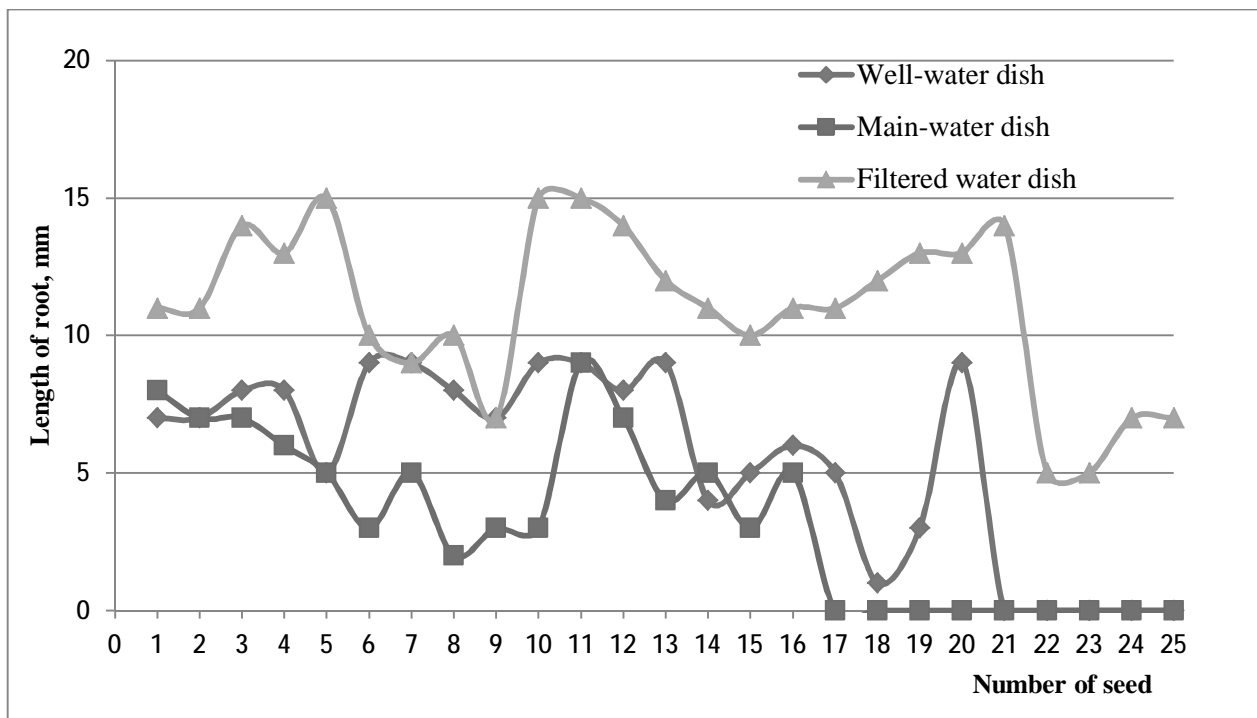


Fig. 3. Lupine seed sprouting dynamics

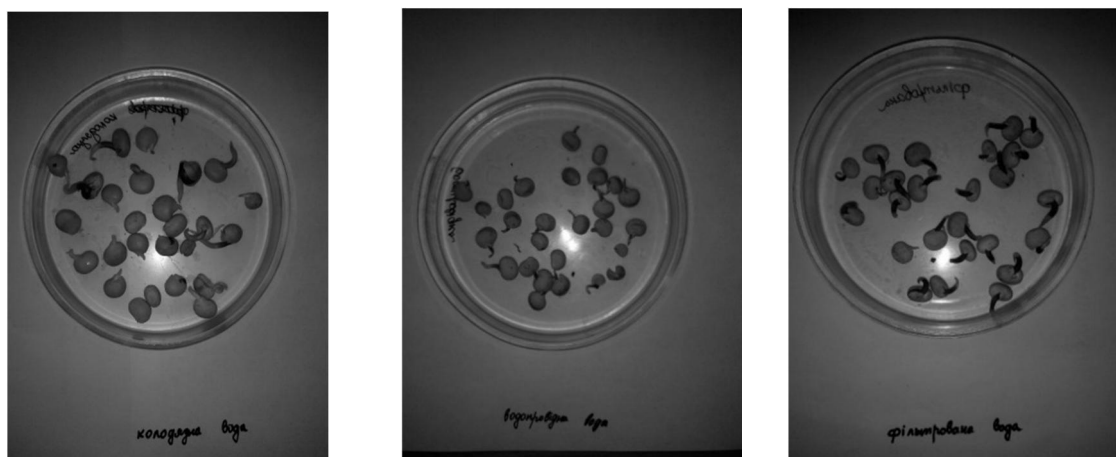


Fig. 4-6. Double-dishes with sprouted lupine seeds in well, main and filtered water

### Test Results

The biotesting method is simple and inexpensive. It does not require special equipment, and allows visual evaluating of toxic impact of a pollutant on life processes of the bioindicator. It is suitable for evaluating water with low contaminant concentration and covers the synergism effect. The results received in the test during 7 days and presented in Fig. 2-3 demonstrated the average length of roots of the sprouted flax of 17-20 mm and destruction of 2 plants in the main water. Lupine turned out to be more sensitive, and the action of the main water on the lupine seeds was more intensive. The average length of roots of the sprouted lupine in the filtered water varied from

11 to 15 mm. In the well-water dish, we observed destruction of 5 lupine seeds (20 %). In the main-water dish, 36 % of the seeds died and the remaining ones almost did not sprout. Thus, we observed the reduction of flax and lupine radicles in size in the main water as compared to the reference sample.

### Conclusions

Based on our analysis of the monitoring data and experimental studies, we found that the situation with drinking water in Toporiv Village is unsatisfactory and unstable as to fluorine content during the last seven years. We observed destruction of plants in the well and main fluorine-contaminated water, while in the filtered

water they developed normally. The biotesting results should be accompanied by chemical analytical studies. In order to eliminate the high incidence of fluorosis, it is necessary to prohibit the use of the service water-supply main in Toporiv for drinking needs and urgently develop defluorization technology. This would allow decreasing the incidence of fluorosis in the local population. The District State Administration must keep activities on elimination of consequences related to the toxic impact of the increased fluorine concentration in the water-supply main under control.

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