

FLUORIDE CONTENT IN DRINKING WATER FROM SHALLOW DUG WELLS IN THE AGRICULTURAL AREA OF SUBCARPATHIAN PROVINCE (POLAND)

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ABSTRACT: The results of many studies indicate that private water intakes may pose a threat to the health of consumers due to poor water quality. The aim of this study was to assess the possible health risks associated with the fluoride (F) levels in drinking water from shallow dug wells using, as a sample study area, the shallow dug wells in the agricultural area of Subcarpathian Province (Poland). Analyses of the F content and the basic physicochemical parameters of water quality, such as pH and electrical conductivity, were performed with the use of an ion-selective F electrode, a digital pH-meter, and a conductometer, respectively. All the examined parameters were within the recommended limits although they differed significantly from those of water from the main public water supply ($p < 0.05$). The water from the private intakes had a higher level of F, a higher conductivity, and a lower pH, as compared to the public water supply. The results we obtained did not confirm that the F content in dug wells from an agricultural area was a cause of concern. However, dentists who plan to use systemic F for the prevention of dental caries should take into consideration the source of water used by a patient.

Keywords: Agricultural area; Drinking water; Fluoride; Subcarpathian Province; Well water.

INTRODUCTION

Monitoring the fluoride (F) content in water is important because excessive F intake can cause a number of adverse effects.^{1,2} The presence of a high natural F concentration in groundwater is a complicated issue for drinking water providers in many regions of the world. Deep groundwater from drilled wells is bacteriologically safe, but it is often not suitable for consumption because of the presence of excessive amounts of chemicals such as F.^{2,3} Traditional shallow dug wells are considered to be able to provide water containing low concentrations of F.^{4,5} However, the opposite trend has also been reported with shallow aquifers which may have higher concentrations of F than those of bore wells from deep aquifers.^{2,6,7} This suggests contamination of groundwater may occur from seepage, especially in areas of intensive agricultural and industrial pollution.^{1,7,8}

Poland belongs to countries with generally low levels of F in the drinking water and from 2014 to 2015, the Polish State Sanitary Inspection granted only three derogations for F content (> 1.5 mg/l).⁹⁻¹¹ However, in 2015 more than 2 million people in Poland still used private water wells and in 2013 only 76.6% of the Subcarpathian Province population had access to a public water network.^{11,12} The results of a recent series of studies carried out in Poland revealed that water from private wells can contain increased levels of nitrites and heavy metals.¹²⁻¹⁷ These studies, however, did not include examination of the F content.

The concentration of F in the public water supplies is continuously monitored and the results are available from local sanitary inspectorates. Decisions about the

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introduction of safe dental caries prevention regimens using F are routinely based on these results, despite the fact that some people use alternative sources of water.

The aim of the present study was to assess if there are any health risks associated with the F concentrations in water from shallow dug wells in the agricultural area of Subcarpathian Province. In order to screen for water quality problems, analyses of the F content were performed in conjunction with the measurement of the basic physicochemical parameters of pH and electrical conductivity.

MATERIALS AND METHODS

The study areas included villages and cities located in two different parts of Subcarpathian Province, one of 16 provinces of Poland (Figure).

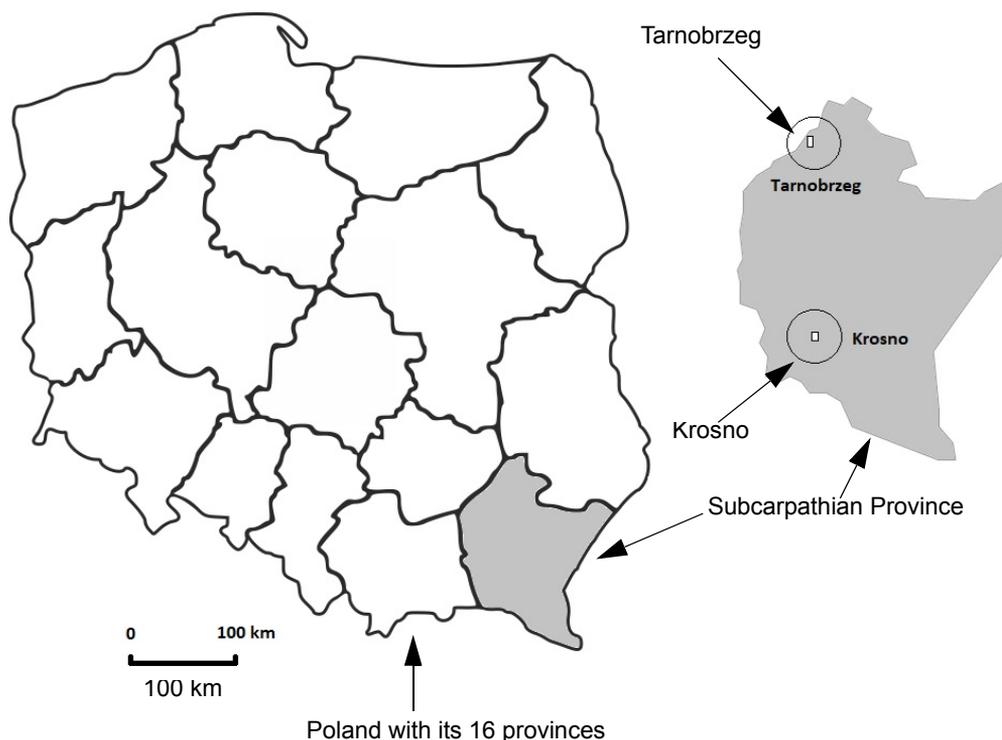


Figure. Map of Poland with the Subcarpathian Province highlighted in grey and the location of the two study regions from which samples were taken: the vicinity of Krosno and the vicinity of Tarnobrzeg (black circles).

Samples of drinking water were collected in April 2016 from private dug wells (depth: 7–12 m) located in the vicinity of Tarnobrzeg and Krosno, (11 and 14 samples, respectively) after obtaining verbal permission from the owners. Additionally, 7 samples of public tap water were collected at buildings located in the approximate center of each of the two study areas. Transparent 70 mL polypropylene containers (Sarstedt) were filled with 50 mL of water and marked accordingly.

All samples were taken to the laboratory for analysis within 48 hours of collection. Analyses of F content, pH, and electrical conductivity were performed with the use of an ion-selective F electrode (09-37 type) and a RAE 111 chloride-silver reference electrode (MARAT), a digital pH-meter of N517 type (MERA-ELWRO), and a CC-411 conductometer (ELMETRON), respectively.

After checking the source of the public water in the village/city from which the sample of water was collected, the data on the F content in the public water supply were obtained from local sanitary inspectorates and compared with the results of our own analyses.

Data analysis was performed with Statistica (version 12) for Windows 10, assuming $p < 0.05$ as the level of statistical significance.

RESULTS

According to data obtained from the sanitary inspection, the F levels in the public water supply ranged from < 0.10 mg/L in the vicinity of Krosno and most of the localities near Tarnobrzeg, through to 0.1–0.2 mg/L in Siedleszczany, Trześćń and Furmany, and up to 0.33 mg/L in Bogoria Skotnicka. The results of the assessments of 7 samples from the water mains were generally in agreement with the data provided by the sanitary inspection (Tables 1, 2, and 3).

Table 1. F concentrations (mg/L), conductivity ($\mu\text{S}/\text{cm}$), and pH of water from the dug wells in the vicinity of Krosno

Sample	Village or city	F content in the sample (mg/L)	Conductivity ($\mu\text{S}/\text{cm}$)	pH
Wells in the vicinity of Krosno				
1	Miejsce Piastowe	0.26	351	7.6
2	Łężany	0.46	1225	7.8
3	Krościenko Wyżne	0.27	387	8.1
4	Korczyna	0.53	743	8.4
5	Odrzykoń	0.48	1075	7.9
6	Ustrobrna	0.59	835	7.6
7	Potok	0.31	697	7.9
8	Jedlicze	0.23	288	8.4
9	Dobieszyn	0.26	793	7.7
10	Żamowiec	0.46	866	7.6
11	Zręcin	0.42	758	8.1
12	Głowienka	0.27	964	7.7
13	Wrocanka	0.24	750	7.9
14	Niżna Łąka	0.25	306	8.1
Mean \pm SD for wells in the vicinity of Krosno		0.36 \pm 0.12 [§]	717 \pm 289	7.9 \pm 0.3 ^{**}

p values: Mann-Whitney U test: * $p=0.017$, † $p=0.048$, ‡ $p=0.013$ as compared to public water supply, § $p=0.722$ (NS), || $p=0.027$, ** $p=0.021$ as compared to water from wells in the vicinity of Tarnobrzeg.

†† significant positive correlation with F content in water ($p < 0.05$), Spearman's rank correlation coefficient = 0.47 for all sources of water and 0.42 for well water.

‡‡ significant negative correlation with pH of water ($p < 0.05$), Spearman's rank correlation coefficient = - 0.49 for all sources of water.

Table 2. F concentrations (mg/L), conductivity ($\mu\text{S}/\text{cm}$), and pH of water from the dug wells in the vicinity of Tarnobrzeg, and all wells in both Krosno and Tarnobrzeg,

Sample	Village or city	F content in the sample (mg/L)	Conductivity ($\mu\text{S}/\text{cm}$)	pH
Wells in the vicinity of Tarnobrzeg				
15	Siedleszczany	0.58	2005	7.7
16	Łukowiec	0.58	913	7.9
17	Ciszyca	0.53	1073	7.6
18	Kamieniec	0.32	1194	7.6
19	Bogoria Skotnicka	0.48	1079	7.8
20	Trześć	0.42	819	7.7
21	Sokolniki	0.23	879	7.6
22	Furmany	0.23	452	7.5
23	Żupawa	0.21	1456	7.5
24	Siedlisko	0.42	726	7.6
25	Cygany	0.32	992	7.9
Mean \pm SD for wells in the vicinity of Tarnobrzeg		0.39 \pm 0.14	1053 \pm 408	7.7 \pm 0.1
Wells in both Krosno and Tarnobrzeg				
Mean \pm SD for all wells in both Krosno and Tarnobrzeg		0.37 \pm 0.13 [*]	865 \pm 379 ^{†,††}	7.8 \pm 0.3 [‡]

p values: Mann-Whitney U test: *p=0.017, †p=0.048, ‡p=0.013 as compared to public water supply, §p=0.722 (NS), ¶p=0.027, **p=0.021 as compared to water from wells in the vicinity of Tarnobrzeg.

†† significant positive correlation with F content in water ($p < 0.05$), Spearman's rank correlation coefficient = 0.47 for all sources of water and 0.42 for well water.

‡‡ significant negative correlation with pH of water ($p < 0.05$), Spearman's rank correlation coefficient = -0.49 for all sources of water.

Table 3. F concentrations (mg/L), conductivity ($\mu\text{S}/\text{cm}$), and pH of water from the public water supply and for all sources of water (the wells in Krosno and Tarnobrzeg, and the public water supplies)

Sample	Village or city	F content in the sample (mg/L)	Conductivity ($\mu\text{S}/\text{cm}$)	pH
Public water supply				
26	Krosno	0.11	314	7.9
27	Targowiska	0.11	460	8.1
28	Tarnobrzeg	0.11	770	8.0
29	Ostrołęka	0.31	590	8.0
30	Zawisielcze	0.33	681	8.0
31	Chodków Stary	0.33	564	8.1
32	Stale	0.11	824	8.0
Mean \pm SD for public water supply		0.20 \pm 0.11	600 \pm 177	8.0 \pm 0.1
All sources of water (the wells in Krosno and Tarnobrzeg, and the public water supplies)				
Mean \pm SD for all sources of water		0.34 \pm 0.14	807 \pm 360 ^{††,‡‡}	7.9 \pm 0.2

p values: Mann-Whitney U test: * $p=0.017$, [†] $p=0.048$, [‡] $p=0.013$ as compared to public water supply, [§] $p=0.722$ (NS), ^{||} $p=0.027$, ^{**} $p=0.021$ as compared to water from wells in the vicinity of Tarnobrzeg.

^{††} significant positive correlation with F content in water ($p<0.05$), Spearman's rank correlation coefficient = 0.47 for all sources of water and 0.42 for well water.

^{‡‡} significant negative correlation with pH of water ($p<0.05$), Spearman's rank correlation coefficient = -0.49 for all sources of water.

As seen in Tables 1, 2, and 3, the concentrations of F in the samples of well water ranged from 0.21 to 0.59 mg/L and they were significantly higher than those detected in samples of water from the mains of the public water supply ($p=0.017$). The F content in the water from the wells located in the two regions did not differ significantly ($p=0.722$). The electrical conductivity and the pH of the well water ranged from 288 to 2005 $\mu\text{S}/\text{cm}$ and from 7.5 to 8.4, respectively. There were significant differences between both the conductivity and the pH of the water coming from the vicinity of Krosno vs. Tarnobrzeg ($p=0.027$ and $p=0.021$, respectively), and from the wells of Krosno and Tarnobrzeg vs. the public supply ($p=0.048$ and $p=0.013$, respectively). A significant positive correlation between the electrical conductivity and the F content of the water was detected ($p<0.05$, Spearman's rank correlation coefficient = 0.47 for all the sources of water and 0.42 for the well water, respectively). A significant negative correlation between the pH and the conductivity

was revealed when the data from all the sources of water were analyzed together ($p < 0.05$, Spearman's rank correlation coefficient = -0.49).

DISCUSSION

The major sources of contaminants from anthropogenic activities to surface and groundwater include: industrial effluents, agricultural run off, urban run off, and atmospheric deposition.¹⁸ Since almost half of the Subcarpathian region territory is covered with forests, the level of environment pollution is one of the lowest in Poland. The exceptions are areas with a well-developed level of industrialization including the glass and petrol industries in Krosno, an oil-refinery in Jedlicze, the power plant in Połaniec, aircraft factories in Mielec and Rzeszów, a military plant in Nowa Dęba, mineral and sulfur-based fertilizer production in Tarnobrzeg, an area of revitalization after opencast mining carried out by the Machow Sulfur Mine, and the neighboring dolomite mine in Sandomierz.¹⁹⁻²² Moreover, in the regions with intensive agricultural practice, the fertilizers and pesticides used for cultivation ultimately leach to the aquifers.¹⁸

In a study carried out in Pakistan, natural sources were the major contributing factors in elevating the F content in shallow groundwater, while agricultural and industrial activities such as the use of fertilizers and the presence of glass manufacturing, sugar and food processing, and smelting industries turned out to be less important.²³ Similarly, the results of the current study do not indicate that either intensive agriculture or the presence of industrial sources of F contribute to excessive F in the dug wells. All the water samples collected in the vicinity of Tarnobrzeg and Krosno presented with F levels below the upper limit of 1.5 mg/L established by the Polish and European legislation^{24,25} and below the upper limit of 1.0 mg/L, the so-called optimal concentration of F recommended by WHO.²⁶ Thus, there is no health risk associated with the F content in well water, although dental practitioners should be aware of the fact that the F exposure of individuals drinking water from private intakes might be higher than expected on the basis of the public water monitoring. Especially before introduction of systemic F caries prevention, they must take into consideration the source of water used by a patient. According to the current recommendations of the European Academy of Paediatric Dentistry, systemic F supplementation may be used only in children consuming water with a low F content (< 0.3 mg/L).²⁷

With regard to the additional physicochemical parameters, both the electrical conductivity and the pH of the water were within the permissible limits (6.5–9.5 and $\leq 2,500$ $\mu\text{S}/\text{cm}$, respectively).^{24,25} However, it is widely accepted that the conductivity of natural unpolluted water should not exceed 1,000 $\mu\text{S}/\text{cm}$ and that values higher than 1,200 $\mu\text{S}/\text{cm}$ result in a “mineral taste” of drinking water due to the elevated ion content.^{28,29} Conductivity gives a good approximation of water hardness and is usually positively correlated with alkalinity. The magnesium and calcium ions dissolved from limestone rock in an aquifer contribute to the hardness, while the carbonate ion is responsible for the alkalinity and consequently for the pH of the water.²⁸ On the other hand, F concentrations are supposed to decrease with increasing water hardness due to the ion-exchange processes occurring in water systems.^{28,30} Nevertheless, in our study, we detected a positive correlation between the conductivity and the F content of the water, and a negative association between

the pH and the conductivity of the water. One could argue that both hydrogen cations and F anions are also carriers of electric current, and that more acidic water with higher F content may present with a higher conductivity. The different physicochemical parameters of water from the private intakes, as compared to the public water, might be attributed to their susceptibility to contamination (e.g., by F-containing fertilizers, and nitrogen and sulphur compounds).^{13,17} Similarly, the lower pH and the higher conductivity of the shallow groundwater in the vicinity of Tarnobrzeg might result from the pollution of the ground by sulphur in a post-mining area and from the production of mineral fertilizers.¹⁹⁻²²

The lack of a significant correlation between the F content and the pH of the water is at variance with the results of previous studies which suggest that a higher pH favours the dissolution of F from rocks and alkaline waters are usually richer in F.^{7,23} However, it must be remembered that the shallow wells in our study are recharged mainly by the infiltration of rainfall and that they contain water which does not have a long contact with F-bearing minerals.

CONCLUSION

The assessment of the concentrations of chemicals in water and the evaluation of their possible health effects provides the important information required to make decisions regarding regulatory initiatives, monitoring, and remediation. The results we obtained did not confirm that the F content in shallow dug wells in an agricultural area should be a cause of concern. Nevertheless, the measurement of selected parameters does not guarantee the safety of water from private sources, which are not subject to obligatory water quality testing and health protection requirements.

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