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INFLUENCE OF HYDROGEOLOGICAL CONDITIONS ON FLUORINE CONCENTRATIONS IN UNDERGROUND WATER INTENDED FOR CONSUMPTION

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Abstract

This study presents the results of an analysis of factors which affect fluorine concentrations in deep water drawn for consumption. The analysis covered two water intakes in Tczew (northern Poland) consisting of 19 wells which supply water from Cretaceous (4), Tertiary (10), and Tertiary and Quaternary (5) horizons. Fluoride concentrations ranged from 0.3 to 2.8 $mg \cdot dm^{-3}$ with the Maximum Allowable Concentration of 1.5 $mg \cdot dm^{-3}$. The allowable qualitative standards were exceeded in 38% of the investigated samples. It was found that fluorine concentrations were most profoundly affected by the water-bearing horizon (the highest concentration levels were observed in water drawn from Cretaceous horizons) and well depth. As a general trend, fluorine concentrations increase with depth, but the analysis of water drawn from the same horizon indicates that bottom-layer water may be characterised by a significantly lower fluoride content. The highest fluorine concentrations were reported in water drawn from Cretaceous water-bearing horizons to a depth of 150 m. The mixing of water from various water-bearing horizons proved to be a sufficient measure to obtain water of satisfactory quality with the optimum fluoride concentration.

Key words: fluorine, underground water, hydrogeological conditions, water of satisfactory quality.

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WPŁYW WARUNKÓW HYDROLOGICZNYCH NA STĘŻENIE FLUORU W WODACH GŁĘBINOWYCH POBIERANYCH DO CELÓW KONSUMPCYJNYCH

Abstrakt

W pracy przedstawiono wyniki analizy czynników mających wpływ na stężenia fluoru w wodach głębinowych pobieranych do celów konsumpcyjnych. Badaniami objęto dwa ujęcia wody w Tczewie (płnocna Polska), na które składało się 19 otworów eksploatacyjnych ujmujących wodę z piętra kredy (4), trzeciorzędu (10) i wód trzeciorzędowo-czwartorzędowych (5). Stężenie fluorków mieściło się w granicach od 0,3 do 2,8 mg·dm^{-3} (najwyższe dopuszczalne stężenie do spożycia (NDS) to 1,5 mg·dm^{-3}). Wykazano, że 38% badanych prób przekraczało normę jakości. Stwierdzono, że istotny wpływ na stężenie fluoru ma warstwa wodonośna (najwyższe stężenie w wodach z utworów kredowych) oraz głębokość studni. Pomimo ogólnego trendu wzrostu stężeń F z głębokością, analiza wód pobieranych z tego samego pietra wykazała istotnie niższe wartości stężeń fluorków w wodach czerpanych z warstw spągowych. Najwyższe stężenia fluoru stwierdzono w wodach pobieranych z poziomów wodonośnych kredy do głębokości 150 m. Mieszanie wód pochodzących z różnych warstw wodonośnych okazało się wystarczającym zabiegiem dla uzyskania wody dobrej jakości, o optymalnym stężeniu fluorków.

Słowa kluczowe: fluor, wody głębinowe, warunki hydrologiczne, woda dobrej jakości.

INTRODUCTION

Fluorine is a relatively popular element in underground water layers, and its concentrations often significantly exceed the content of other micronutrients. The main source of fluorine enrichment in underground water are minerals which release fluorine in the weathering process: fluoroapatite $Ca_2(PO_4)_3F$, fluorite CaF_2 and cryolite Na_2AlF_6. Fluorine-bearing mineral zones usually contribute to abnormally high fluorine concentrations in underground water. The processes which are responsible for the chemical composition of underground water should also be analysed in view of fluorine's inhibited ability to migrate in a hard water environment (with a high calcium content).

Fluorine concentrations in crude water usually do not exceed 1.5 mg·dm^{-3}, but in deep underground layers in areas rich in fluoride minerals, they may reach 10 mg·dm^{-3}. Extensive fluoride anomalies are observed in Cretaceous water-bearing horizons, but solely of hydrogencarbonate and alkaline type, where the fluorine-containing minerals are dissolved at a very high rate (JACKOWSKA, BOJANOWSKA 2007).

The allowable fluorine concentration in potable water is 1.5 mg·dm^{-3} (Resolution of 2007, WHO 1998). Subject to climate, the optimum fluoride content of water ranges from 0.7 to 1.2 mg·dm^{-3} (INDULSKI 1980). Concentrations in excess of the above level carry the risk of dental fluorisis, and significantly exceeded fluoride levels pose the threat of skeletal fluorisis. WHO has classified inorganic fluorides into Group 3 carcinogens which are not classifiable as to their carcinogenicity to humans. Fluoride is added to potable water to prevent dental decay.

The threat posed by fluorides in potable water is largely determined by environmental factors (Kabata-Pendias, Pendias 1999, Koc et al. 2006). Domestic standards concerning fluoride concentrations should be set in view of climatic conditions (Pasiuk-Bronikowska 1999) as well as the quantities of water consumption and fluoride uptake from other sources (such as air and food). In areas marked by high natural fluoride levels, the recommended allowable values may be difficult to observe, mainly due to the complexity of the process of removing excess fluoride from water (Koc et al. 2005).

The aim of this study was to determine the extent to which the geological conditions that accompany the process of drawing water for consumption determine the usable properties of water and its available treatment options.

MATERIALS AND METHODS

Research area and object. The study covered underground water intakes in Tczew: „Park" and „Motława". The geological and hydrogeological background was determined based on the reports developed by the Geological Study and Research Office in Gdańsk. Water samples from two intakes were analysed between 1994 and 2004: from the „Motława" intake where 11 wells are operated, including 10 wells drawing water from the Tertiary water-bearing horizon at a depth of 93-101.5 m and one well drawing water from the Cretaceous horizon at a depth of 150 m (Fig. 1). The wells of the „Park" intake draw water from the Quaternary and Tertiary horizon (5 wells) at a depth of 92–101 m and from the Cretaceous horizon (3 wells) at a depth of 150–180 m (Fig. 2).

Hydrogeological background of the research area. The oldest deposits determined in the hydrogeological structure of the investigated area consist of Cretaceous marl and limestone to a depth of 150 m (not bored through) with a thickness of more than 50 m. The Cretaceous horizon was determined only in the roof layer where water is supplied via limestone and marl fissure deposits. Fissure water of the Cretaceous horizon is supplied solely through infiltration from the Tertiary water-bearing horizon (possibly also from Cretaceous sand layers situated below). Two water-bearing horizons were determined in the Cretaceous layer: a shallower horizon which supplies the „Motława" intake in Tczew at a depth of 150 m, and a deeper horizon which supplies the „Park" intake at 180 m. The oldest deposits determined in the „Park" intake are Cretaceous fine-grained sand deposits with

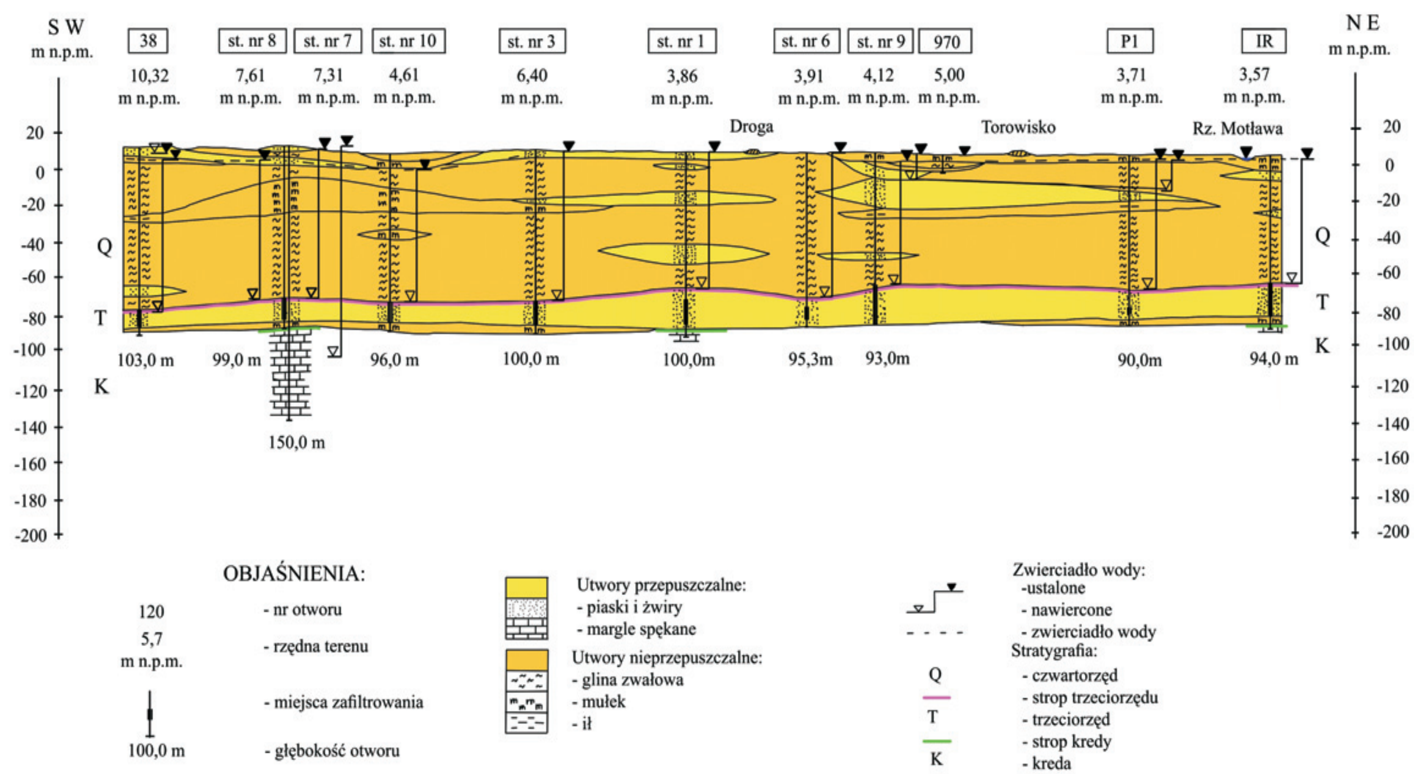

Fig. 1. Hydrogeological crossection of deep wells at the ,"Motława" in Tczew (acc. to water quality impact assessment)
Rys. 1. Przekrój hydrogeologiczny studni głębinowych w ujęciu ,"Motława" w Tczewie (wg Operatu wodnoprawnego)

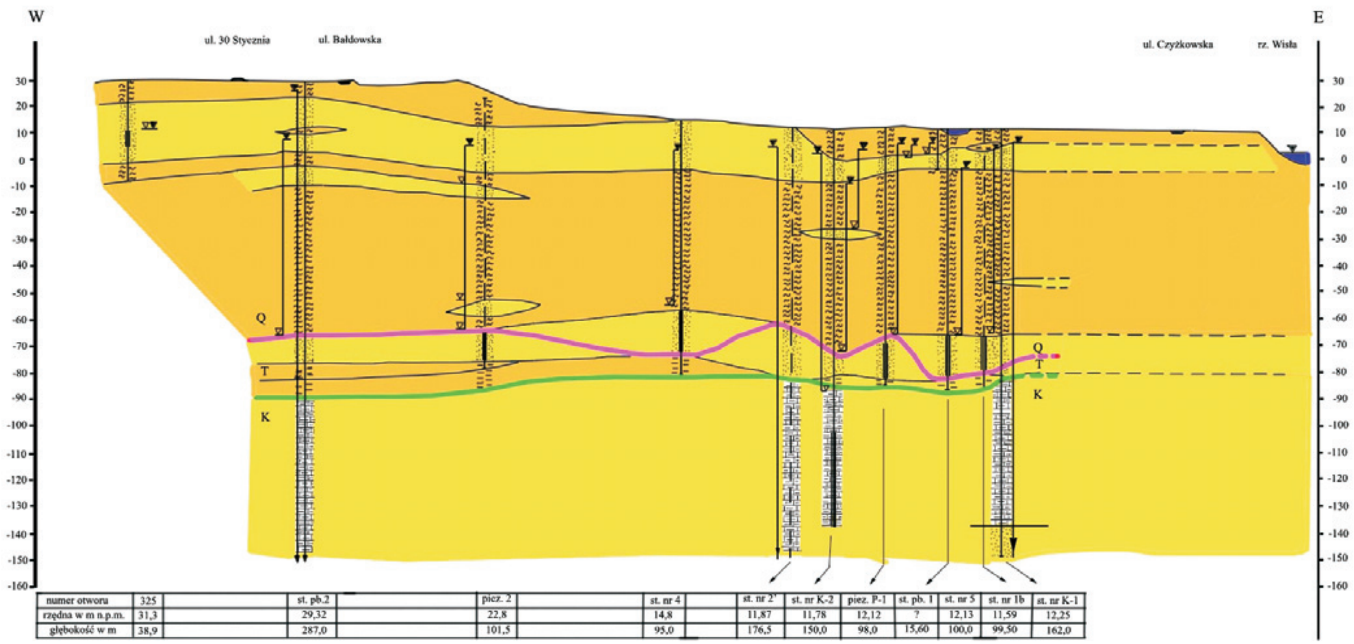

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Fig. 2. Hydrogeological crossection of deep wells at the ,"Park" in Tczew (acc. to Water uality impact assessment, 2005)

Rys. 2. Przekrój hydrogeologiczny studni głębinowych w ujęciu ,"Park" w Tczewie
(wg Operatu wodnoprawnego 2005

a roof level at around 200 m above sea level and thickness of more than 55 m (not bored through). They are covered by a marl layer, which is a frequently fissured deposit, with a thickness of 113.5 m.

The Tertiary profile begins with Oligocene clays and loams with glauconite and phosphorites with a thickness of up to several meters. They are covered by a layer of fine-grained to coarse-grained quartz sand with a thickness of 8.5 to 19.0 m. The top sand layer may date back to the Quaternary period. Sand layers are infrequently covered by carbonaceous silts. The oldest Quaternary deposits are fluvioglacial sand layers of the Middle Poland glaciation which are connected with the Tertiary sand layers situated below. The stratigraphic boundary of the Quaternary and Tertiary profile is uncertain – it is found in a sandy layer where the division of soil profiles into horizons is difficult to perform. It is covered by a boulder clay formation of the Wűrm glaciation (probably of the Middle Poland glaciation in the bottom layer), divided by at least two fluvioglacial sand and gravel layers. Holocene sands and silts are found locally in areas of land subsidence.

The Tertiary water-bearing horizon consists of fine-grained to coarse-grained sand, partially mixed with gravel. In the roof profile, sand layers are silted and contain carbonaceous substances. In the bottom profile, sand layers are silted and contain glauconite. It is estimated that the roof part of this layer may date back to the Quaternary period. The thickness of the Tertiary water-bearing horizon ranges from 8.5 to 19.0 m. The Tertiary profile is supplied by lateral input and infiltration. The natural process of water outflow from the Tertiary water-bearing horizon took place from the upland to the north, in the direction of the Motława river valley. Since then, the filtration balance has been disturbed by well operation. The initial water table, determined during local surveys before the launching of the „Motława" intake, had been found on ground surface. In consequence of well operation, the water table has been lowered and, subject to the quantity of water uptake, is presently found at a depth of 2.2 to 5.4 m.

The oldest Quaternary formations are fluvioglacial sand layers of the Middle Poland glaciation, connected with the Tertiary sand profiles found below. They are covered by a boulder clay formation of the Wűrm glaciation, divided by at least two fluvioglacial sand and gravel layers. Holocene sands and silts are found locally in areas of land subsidence. The Quaternary profile comprises up to four water-bearing horizons. They consist mostly of non-continuous lenses inside boulder clay formations, where the youngest lens fills the Motława river valley. Lenses consist of differently-grained sand layers, ranging from fine- to coarse-grained sand, with locally occurring sand and gravel layers as well as gravel layers. The detritus interbedding has a thickness of several to 26 m. Quaternary water-bearing horizons are supplied mainly by lateral input from the upland and, to a lesser degree, by infiltration from the Tertiary layer and direct infiltration of precipitation water, meltwater and surface water.

The water-bearing horizon of the shared Quaternary and Tertiary profile used by the „Park" intake in Tczew comprises from fine- to coarse-grained sand layers as well as sand mixed with gravel. In the roof profile, sand layers are silted and contain carbonaceous substances. In the bottom profile, sand layers are silted and contain glauconite. The thickness of the water-bearing horizon ranges from 12 to 19 m. The filtration coefficient is 0.13 to 0.41 m h^{-1}. The initial static water table is unknown, but according to data from post-German water wells, it was found at a level of approximately 6.0 m above sea level. The static water table is presently found at around 2.0 m above sea level (Fig. 2). The Quaternary and Tertiary horizon is supplied by lateral input and infiltration, mainly from the roof layer, but the infrequent increase in salinification may also be indicative of temporary supply from the floor layer. In an environment undisturbed by human activity, water from the Quaternary and Tertiary horizon moved from the upland to the east, in the direction of the Vistula river valley. Since then, the filtration process has been disturbed by well operation.

Analytical methods. Fluoride concentrations in underground water were determined by spectrophotometry with alizarine-zirconium reagent (PN-70/C-04.588).

The impact of environmental factors on fluorine concentrations in the analysed water samples was determined by Principal Component Analysis (PCA) with the use of the CANOCO 4.1 software package. PCA is a highly useful ordination method which supported the multivariate analysis of relations between selected environmental factors and fluoride content in the analysed underground water samples. The method also facilitated the interpretation of complex correlations and a synthetic presentation of the obtained results.

The significance of differences between groups of means was determined by analysis of variance (ANOVA, MANOVA) with the use of Duncan's test as a post-hoc procedure at $P > 0.05$ in the STATISTICAL 7.1 PL software package.

RESULTS AND DISCUSSION

Based on the results of local surveys carried out in 1994-2004 in an area with differently situated water intakes and varied well depth (from <100 m to 150 m), fluoride concentrations were determined within the range of 0.5 $mg \cdot dm^{-3}$ to 2.80 $mg \cdot dm^{-3}$ (Fig. 3 and Fig. 4). The highest fluoride content was found in the Cretaceous horizon (C) – Fig. 1 and Fig. 3, and the lowest concentrations were determined in the shared Quaternary and Tertiary profile (QT) – Fig. 2 and Fig. 4. Fluoride concentrations in water were stable during the investigated period, as indicated by the low coeffi-

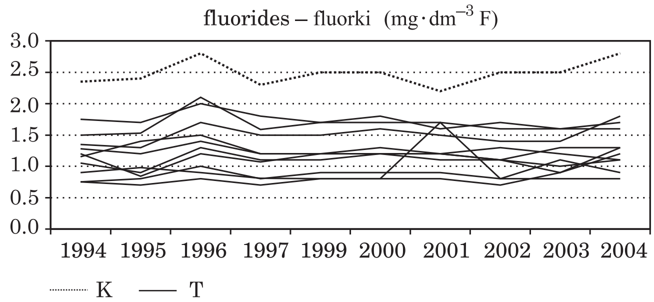

Fig.3. Quality of raw water supplied from the well no 7 from the Cretaceous (K) aquifiers as well as from the wells no 1,2,3,4,5,6,8,9,10,11 from the Tertiary aquifiers in the period of 1994-2004 at the "Motława" intake in Tczew

Rys. 3. Jakość wód surowych pobieranych w latach 1994-2004 ze studni nr 7 z warstw wodonośnych kredy (K) i ze studni nr 1,2,3,4,5,6,8,9,10,11 z warstw trzeciorzędowych (T) z ujęcia "Motława" w Tczewie

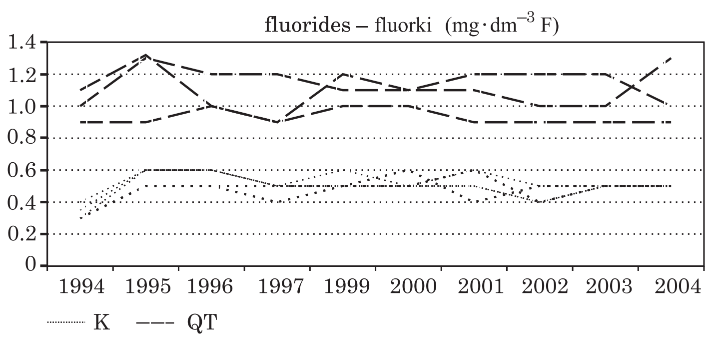

Fig.4. Quality of raw water supplied from the well no K1, K2, K3 from the Cretaceous (K) water horizon as well as from the wells no 1B, 2A, 4, 5, 6 from the common Tertiary and Quarternary aquifiers in the period of 1994–2004 at the "Park" intake in Tczew

Rys. 4. Jakość wód surowych pobieranych w latach 1994–2004 ze studni nr K1, K2, K3 z utworów kredowych (K) oraz ze studni 1B, 2A, 4, 5, 6 ze wspólnej warstwy czwartorzędu i trzeciorzędu (QT) na ujęciu "Park" w Tczewie

cient of variation ranging from 13% for C to 25% for QT, and the absence of statistically significant differences between fluoride concentrations in the successive years of the survey (ANOVA, Duncan's test, $P > 0.05$). The above is indicative of the absence of external sources of pollution and the high isolation of substratum layers, mainly limestone and marl (Fig. 1), where the highest fluoride concentrations were found in the „Motława" intake at a depth of 150 m.

The PCA ordination of factors which determine fluoride concentrations in the analysed underground water samples has revealed that the predominant role is played by the water-bearing horizon and the related depth of the deposit. The axis diagram of factors F1 and F2 (Fig. 5), i.e.

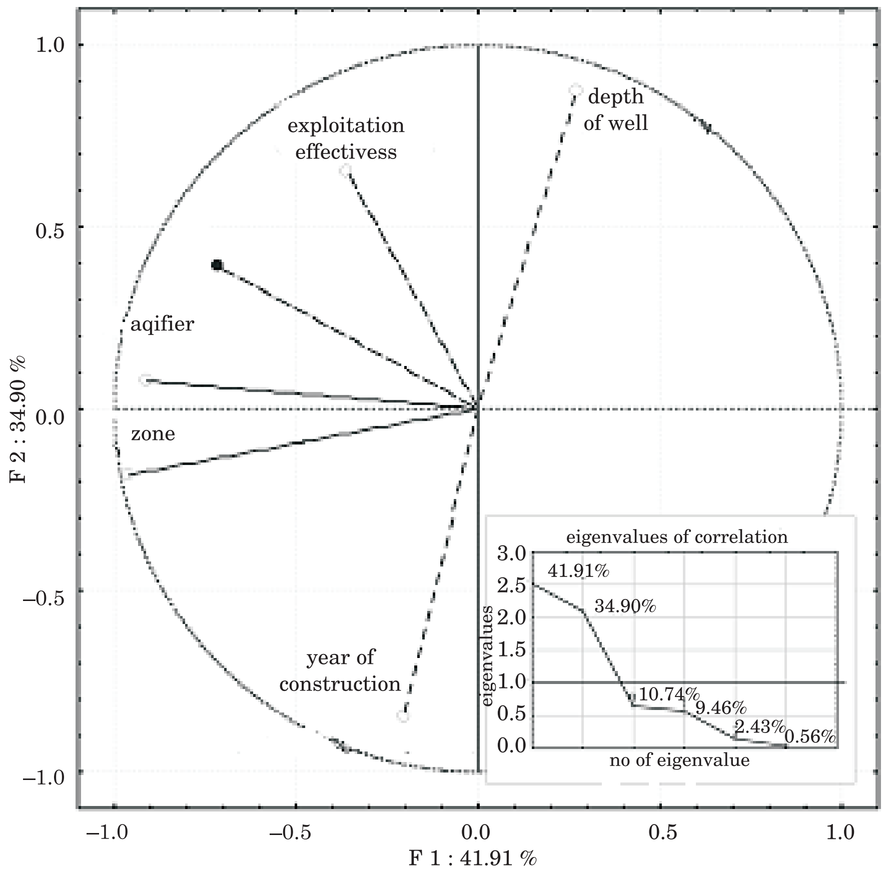

Fig. 5. Principal components analysis (PCA) of the variables influencing fluorides concentrations in undergroundwater in Tczew. Main diagram complemented with the eigenvalues graph

Rys. 5. Analiza komponentów głównych (PCA) w analizie oddziaływania na wielkość stężeń fluorków w wodach podziemnych w Tczewie. Wykres główny uzupełniono o wykres wartości własnych

the first two proper values, explains 76.81% of total variance (F1 – 41.91%, F2 – 34.90%). Negative values on the F1 axis and positive values on the F2 axis are represented by variables related to the water-bearing horizon and the volume of underground water uptake.

It was found, based on the analysis of fluoride concentrations, that water drawn from different water-bearing horizons form groups of means which are marked by statistically significant differences in Duncan's test (Fig. 6).

Cretaceous horizon water was characterised by median values of 1.1 $mg \cdot dm^{-3}$ within the overall range of 0.8 $mg \cdot dm^{-3}$ to 2.8 $mg \cdot dm^{-3}$. It should be noted,

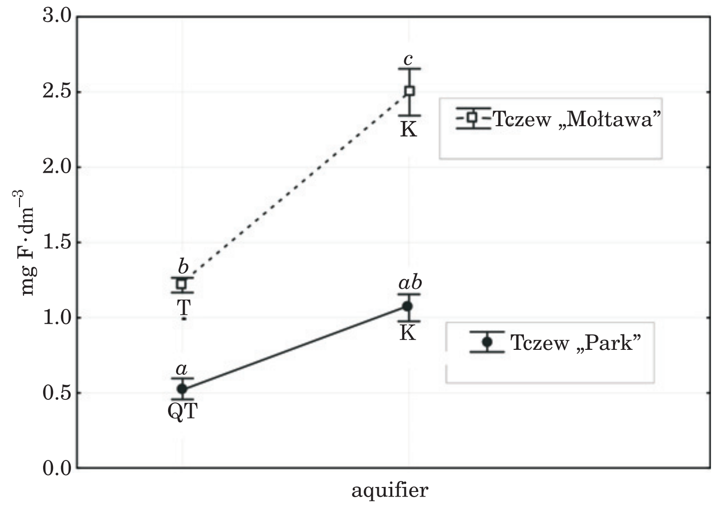

Fig. 6. Average concentation of fluorides in the undergroundwater in relation to water horizon and the depth of uptaken water. Vertical bars denote 95% range of confidence. Different letters denote groups of means that statistically differ in the Duncan test at $P > 0.05$

Rys. 6. Średnia zawartość fluoru w wodach podziemnych w zależności od piętra i głębokości ujmowanej wody. Pionowe zakresy oznaczają 95% przedział ufności. Różne symbole literowe oznaczają grupy średnich różniących się istotnie statystycznie w teście Duncana, gdy $P > 0,05$

however, that the thickness of Cretaceous water-bearing horizons (fissured marl deposits) significantly affected the fluoride content of water. Fluoride concentrations increased throughout the entire cross-section of all water-bearing horizons, as indicated by the presented regression equations and statistically significant correlation coefficients: $r = 0.89$ for the „Park” intake and $r = 0.71$ for the „Motława” intake (Fig. 7).

Nevertheless, a reversed system was determined in the same profile, in particular in two layers of the Cretaceous horizon. In the deeper layer reaching 180 m, fluoride concentrations were statistically significantly lower than in water samples drawn from the same horizon at a depth of 100-150 m.

The maximum allowable concentration of fluoride (1.5 $mg \cdot dm^{-3}$) was exceeded in some of the investigated water samples (38%), mainly from Cretaceous horizons. Water drawn from this profile is not fit for consumption without prior treatment. Fluorine concentrations cannot be lowered to the allowable level with the use of the available technological and economic treatment methods. Due to the simultaneous occurrence of water-bearing horizons with varied fluoride concentrations (Fig. 8), qualitative standards can be met through the mixing of water from various sources.

The results of the study indicate that potable water drawn from the discussed intakes is characterised by satisfactory quality. It follows that

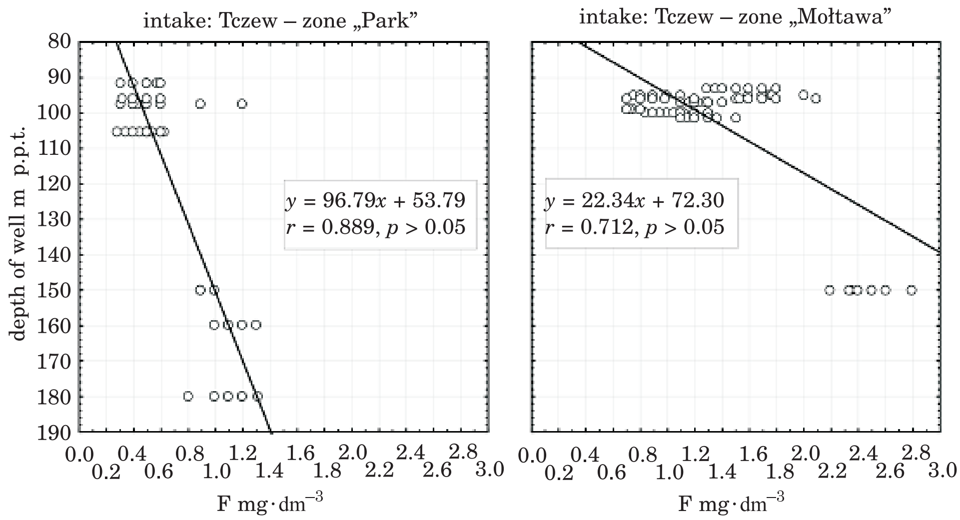

Fig. 7. Changes in fluorides concentrations in the undergroundwater at the intake "Park" and "Motlawa" in Tczew

Rys. 7. Zmiany zawartości fluorków w wodach podziemnych ujęcia Tczew w strefie „Park” i „Motława”

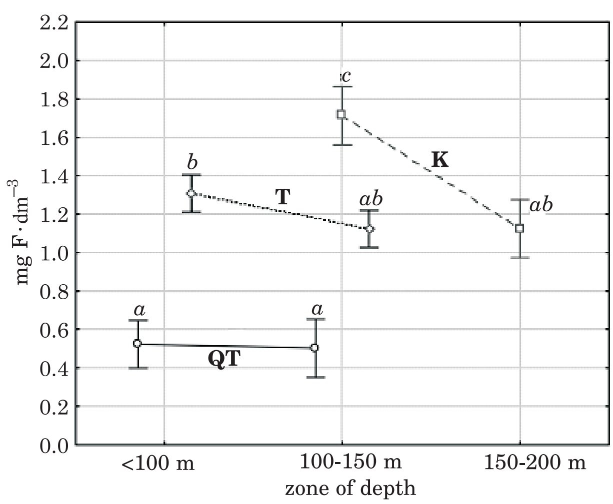

Fig. 8. Differences in fluorides concentrations in relation to water horizon and its depth. Vertical bars denote 95% range of confidence. Different letters denote groups of means that statistically differ in the Duncan test at $P > 0.05$

Rys. 8. Zmiany zawartości fluoru w zależności od warstwy wodonośnej i jej głębokości. Pionowe zakresy oznaczają 95% przedział ufności. Różne symbole literowe oznaczają grupy średnich różniących się istotnie statystycznie w teście Duncana, gdy *P > 0,05* the Cretaceous horizon in Starogard Lakeland deserves the status of a highly valuable resource which should be preserved through the protection of younger and shallower deposits operated as water intakes. In view of the growing consumption of underground water, rational use of water resources is recommended to guarantee the abundance of water supply for the future generations.

CONCLUSIONS

1. Fluoride concentrations in underground water samples from the Tczew intakes in the Starogard Lakeland varied subject to the investigated water-bearing horizon and the depth of the deposit.

2. Fluoride concentrations ranged from 0.3 to 2.8 $mg \cdot dm^{-3}$, and the maximum allowable concentration levels (1.5 $mg \cdot dm^{-3}$) for potable water were exceeded in 38% of the analysed samples.

3. The highest fluoride concentrations were determined in Cretaceous horizons which consisted of fissured marls. Significant differences were observed within the same profile at different water-bearing horizons. Water drawn from bottom layers was characterised by the lowest fluoride concentrations. The highest fluoride concentrations were reported in Cretaceous horizons at a depth of up to 150 m.

4. Mixed potable water drawn from different wells was characterised by the optimum fluoride content and did not require further treatment in this respect.

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