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## **Fluorine Pollution of Underground Waters in the Area of the Repository of the Former Aluminium Metallurgy Plant in Skawina\*\***

### **1. Introduction**

Fluorine is one of the most common microelements in underground waters. Its concentration in most underground waters in the world does not exceed  $1.5 \text{ mg F/dm}^3$ , which is the maximum acceptable concentration for drinking waters, recommended in Poland. However, there are regions, where the concentration of fluorine reaches several  $\text{mg F/dm}^3$ , causing health problems for people using such waters [2, 5–7]. Increased fluorine contents in underground waters can be caused by natural (geogenic) factors, climatic factors, as well as human interference in natural environment [6, 10]. In Poland, due to geological structure and climatic conditions, exceeded geogenic fluorine concentrations in underground waters are basically absent, while local anthropogenic threats for waters are connected with industrial activities [1, 4]. One of the technologies producing harmful for the environment wastes containing fluorine compounds is aluminium metallurgy [12]. In Poland there were two aluminium metallurgy plants: in Skawina, opened in 1954, based on Soviet technology and in Konin – established in 1966, much more modern, still functioning. The surroundings of the Aluminium Metallurgy Plant in Skawina were characterised by significant pollution of all the environmental components with fluorine compounds. In 1981, due to the popular pressure and scientific reports on the environmental situation of the region, the electrolysis section, where aluminium was produced was closed [1]. This resulted in significant improvement of the atmosphere quality, but the wastes deposited in the repository containing fluorine compounds that can be easily washed out, still make threat for underground waters. Despite the reclamation works in 2002, the degradation of environment and in particular underground waters with fluorine still makes problems, which was confirmed by the results of the monitoring [8].

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## 2. Study Area

The waste repository of the Aluminium Metallurgical Plant in Skawina of the area of 11 ha (nowadays the Nowoczesne Produkty Aluminiowe [Modern Aluminium Products] "Skawina" Sp. z o.o.) is located in the pit formed after the exploitation of sands, situated north of the buildings of the plant. The average depth of the pit was 10 m, and the exploitation of sands was basically carried out to the water horizon, thus on the bottom of the pit there were initially several water bodies of various depth (Figs 1 and 2). Waste deposition started in 1974 and finished in 1998, that is several years after closing the electrolysis division. During the reclamation works, the southern part of the pit was covered with concrete blocks, so only in the northern part there are some water bodies of the maximal depth of 1 m, locally disappearing during droughts [11].

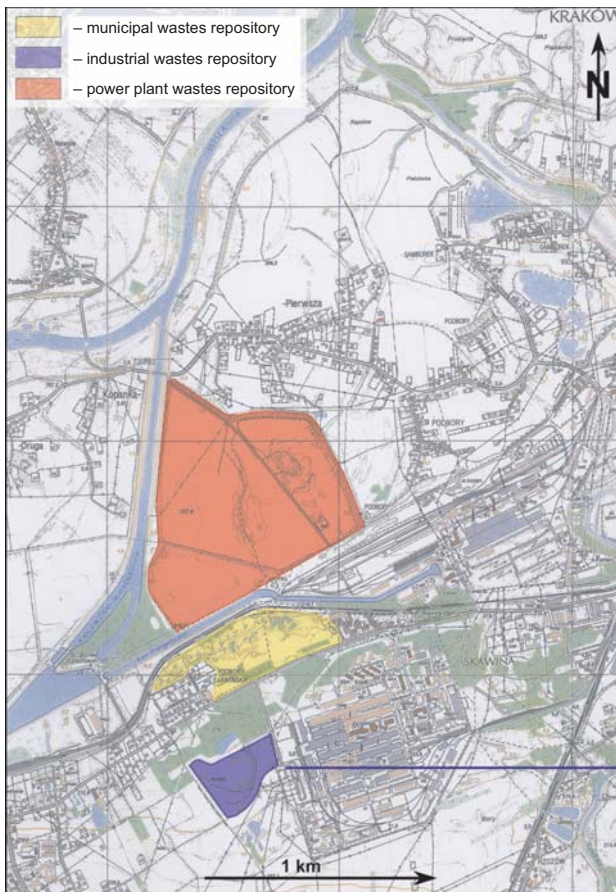


Fig. 1. The map of the study area – localization of the pollution sources

### 3. The Scope and Methods of the Studies

To define the chemical composition of underground waters samples were taken in the profiles of subsequent boreholes and the samples of water were taken every 1 m after reaching the horizon of the underground water. From one borehole the samples were obtained from the Quaternary water horizon, usually from 5 m of depth. The total depth of boreholes depended on the presence of impermeable Miocene loam deposits and ranged from 5.0 to 15.0 m. In the area of the landfill 11 boreholes were made, which allowed accurate recognition of the lithological profiles [8]. The localization of the study boreholes was presented in figure 2.

In 2004 and in the area of the repository the water-bearing horizon was sampled twice by making shallow boreholes of maximum depth 1 m, to get the water horizon. Also the samples of water from water bodies were taken up to 2009. The basis for the assessment of the quality of underground waters and waters from the water bodies were the result of physical and chemical analyses of 100 water samples taken in 1981–2009. Due to the type of danger, the basic indicator during the studies was fluorine, analysed in all the water samples with a potentiometric method with the application of the ionometer of Elmetron CP-316 and ion-selective electrode with double coating (Polish production). In most water samples also basic cations and anions were determined as well as physical indicators that, due to their range, had a character of index analysis used in the network of local monitoring around the pollution sources.

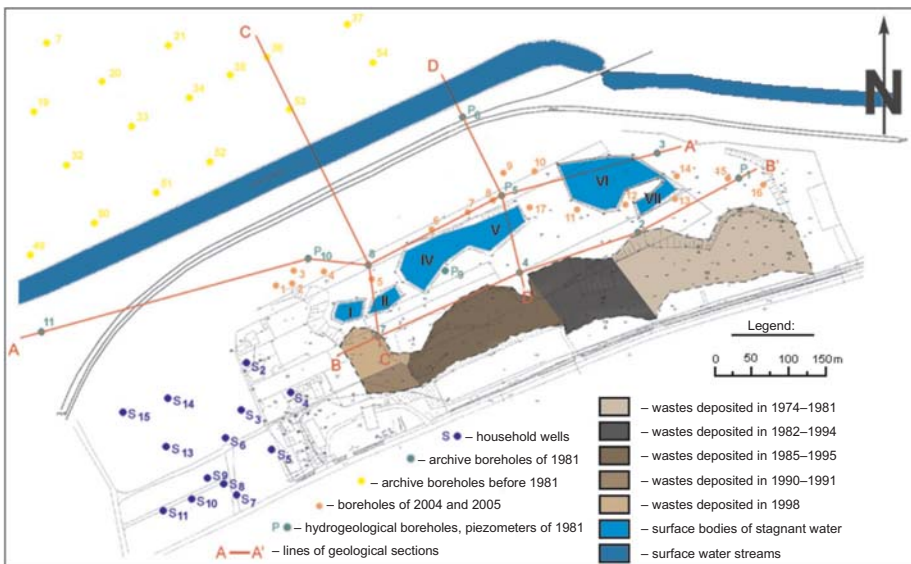


Fig. 2. The map of the study area – localization of the boreholes

The description of chemical composition of waters was based on the classification by M.J. Altowski and W.M. Szwiec, while at comparing the results of the analyses to compare the participation of individual elements in chemical composition of waters a computer program Aqua-Chem by Waterloo Hydrogeologic was used. Filtration coefficients were determined based on the grain-size distribution curve with formula  $k = 0.36 \cdot d_{20}^{2.3}$  [cm/s].

#### 4. Results

The carried out hydrogeological observations showed that in the area of metallurgical waste repository in Skawina there are two water-bearing horizons: the Quaternary and Tertiary ones. In the Quaternary formations one water bearing horizon was found. It was connected with sand and gravel deposits of the Pleistocene (Fig. 3).

These deposits, within the borders of the repository, occur almost on the surface, under a thin stratum of sandy soil, because the Holocene clay-sand cover was removed during the exploitation of sands. The thickness of the water bearing horizon in the pit is usually 5 m on average. Sands, sands with gravels and gravels building the water bearing horizon, in the vertical and horizontal profile are characterized by a great variability of grain size, which makes significant variability of filtration formations.

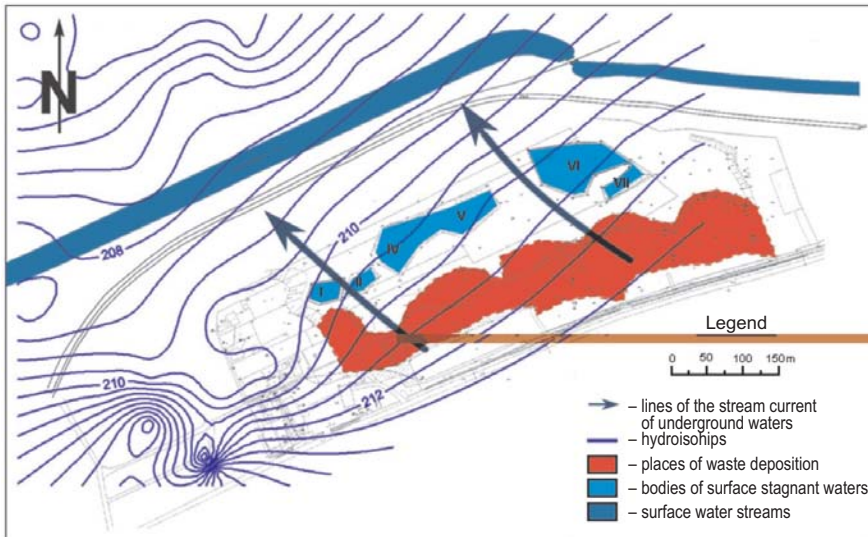


Fig. 3. The map of the hydroisohips of the Quaternary water-bearing horizon – state of 1981

The filtration coefficients for moderate size grain sands are 19.5 m/d; for large size grain sands are up to 31.8 m/d, and for gravel and aggregates (sand gravel) the maximal size is 37.1 m/d. The bottom of the water bearing horizon is covered with impermeable Miocene deposits, the roof of which is inclined in the north-western direction, which makes underground waters flow towards the Vistula river, about 1.5 km from the northern border of the repository (Fig. 1). The roof stratum of the Tertiary formations is made of the loam deposits in some places with the layers of water-logged dusty sands. Locally, where the Tertiary dusty sands lie directly under the Quaternary water bearing horizon, there is a contact between these levels. There are 98 thousand tons of wastes deposited in the repository, and almost a half of them contains easy soluble fluorine compounds in the concentrations above 0.5% [11, 12]. The possibilities of leakage were tested and the analysis of filtrates showed that the dominant ions were sodium and fluorine and the percentage of the remaining ions was very small [8]. Filtrates of very high contents of fluorine were characterized by high pH and very low hardness, which was probably caused by the ability of binding fluorine by calcium in a poorly soluble  $\text{CaF}_2$ . The maximal content of fluorine was obtained in the water extract of electrolyte and was about 3800 mg F/100 g of a sample. The variability of chemical composition of underground waters in the studied area, depending on the degree of the fluorine was presented in a triangular Piper's diagram and on the Langelier-Ludwig's graph (Fig. 4). The main meaning for the carried out interpretation was detail recognition of hydrochemical types of waters with higher contents of fluorine. In case of waters of high fluorine concentrations, above  $5 \text{ mg/dm}^3$  the sodium  $\text{Na}^+$  cation dominated. In the waters of the reaction close to neutral hydro-carbonate ion  $\text{HCO}_3^-$  dominated and carbonate ion  $\text{CO}_3^{2-}$  dominated in waters of high pH of 8.5–10.

The waters of lower fluorine contents generally contained more calcium  $\text{Ca}^{2+}$  and magnesium  $\text{Mg}^{2+}$  cations, with very variable participation of all the anions, mainly chlorines  $\text{Cl}^-$  and sulphates  $\text{SO}_4^{2-}$ . Mutual relationships between all the main ions for the studied samples was presented in the Piper's diagram (Fig. 4). Fluorine occurring in the studied water sample of the concentrations above  $5 \text{ mg/dm}^3$  shows distinct, practically linear correlation with the concentration of  $\text{Na}^+$  ion, which was presented in figure 4A. For waters of lower fluorine concentration this relationship does not have a clear characteristic, and the points make a cluster of an irregular shape. A similar scheme was found between the concentrations of fluorine and the value of Na/Ca index, which confirms dominating influence of the contents of sodium on the level of the concentration of fluoride ions (Fig. 4C). In the studied set of samples, no correlation between fluorine concentrations and chloride  $\text{Cl}^-$  concentration occurred, which is clearly seen in figure 4B.

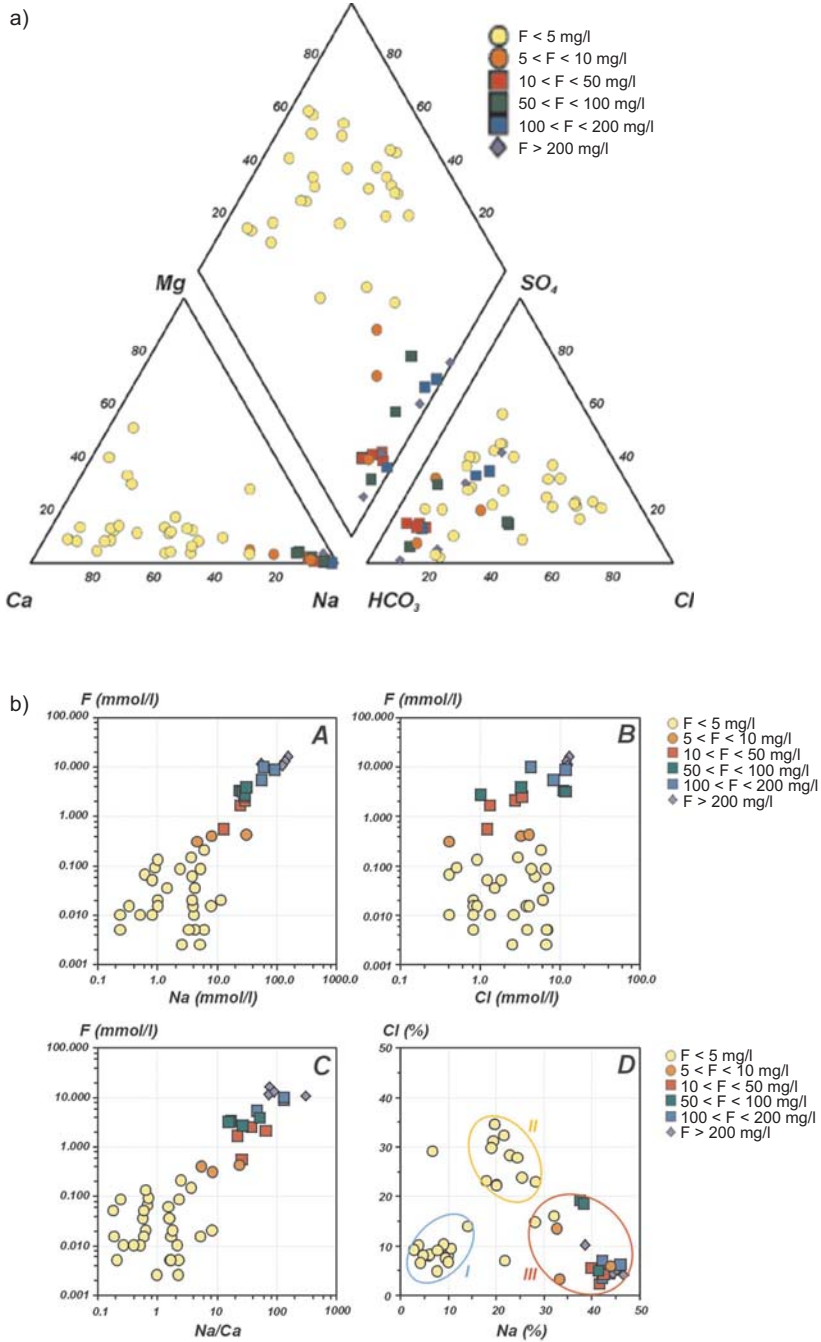


Fig. 4. The chemical composition of underground waters from the region of the repository of metallurgical wastes in Skawina – the Piper (a) and Langerier–Ludwig’s (b) graphs

Waters of high concentration of chlorides  $\text{Cl}^-$ , about  $10 \text{ mval/dm}^3$ , were characterized by both high (about  $20 \text{ mval/dm}^3$ ) and low fluorine concentration (of about  $0.0025 \text{ mval/dm}^3$ ).

The problem of the relationship between fluorine concentration, and the contents of subsequent main ions from one side and the hydrochemical type is difficult for the interpretation, because their chemical composition is formed by several potential pollution sources (Fig. 1). In the Langelier–Ludwig’s graph (Fig. 4D) the percentage of chlorides  $\text{Cl}^-$  and sodium  $\text{Na}^+$  is presented in the relation to the sum of cations and anions, which allowed making three characteristic groups of water quality:

- group I – waters of both low content of chlorides ( $\text{Cl}^-$ ) and sodium ( $\text{Na}^+$ ) below 15% of the sum of cations and anions;
- group II – waters of the high content of chlorides ( $\text{Cl}^-$ ) ranging within 20–35% of the sum of cations and anions and elevated content of sodium ( $\text{Na}^+$ ) of about 15–25% of the sum of cations and anions;
- group III – waters of the high content of sodium ( $\text{Na}^+$ ) – above 25% and low content of chlorides ( $\text{Cl}^-$ ), like group I; in this group the highest percentage of sodium was found for water samples of the highest concentrations of fluorine.

The highest fluorine concentrations were found in the waters flowing through gravel formations of high filtration coefficient, which was presented for the selected borehole (Fig. 5). It also clearly shows the blocking influence of loam formations and the differentiation of the content of fluorine connected with variable filtration abilities of the water bearing horizon. The binding of fluorine by loam minerals can occur as a result of diadoch substitution of  $\text{F}^-$  ions instead  $\text{OH}^-$ , because their radius sizes are similar [3]. Probably the border between polluted and clean waters goes alongside the surface of the roof of the Miocene deposits, characterized by low permeability and significant content of loam material. As a result of carried out in 2002 reclamation works the ponds in the closest vicinity of the deposited material were filled with ground and secured with concrete plates. Several small ponds remained. These were ponds I, II, IV, V, VI in the northern part of the pit. Namely, the Enterprise of Water Supply and Sewerage (Zakłady Wodociągów i Kanalizacji) in Skawina carried out the observations of fluorine concentrations since 1982 until 2006. Water from the water bodies is in a direct contact with underground waters and the state of their pollution is also characteristic for underground waters, for which the underground water horizon occurs on small depths and in a small distance. Despite the time that passed, the concentration of fluorine in the waters of ponds is still several  $\text{mg F/dm}^3$ , which was confirmed in May 2009.

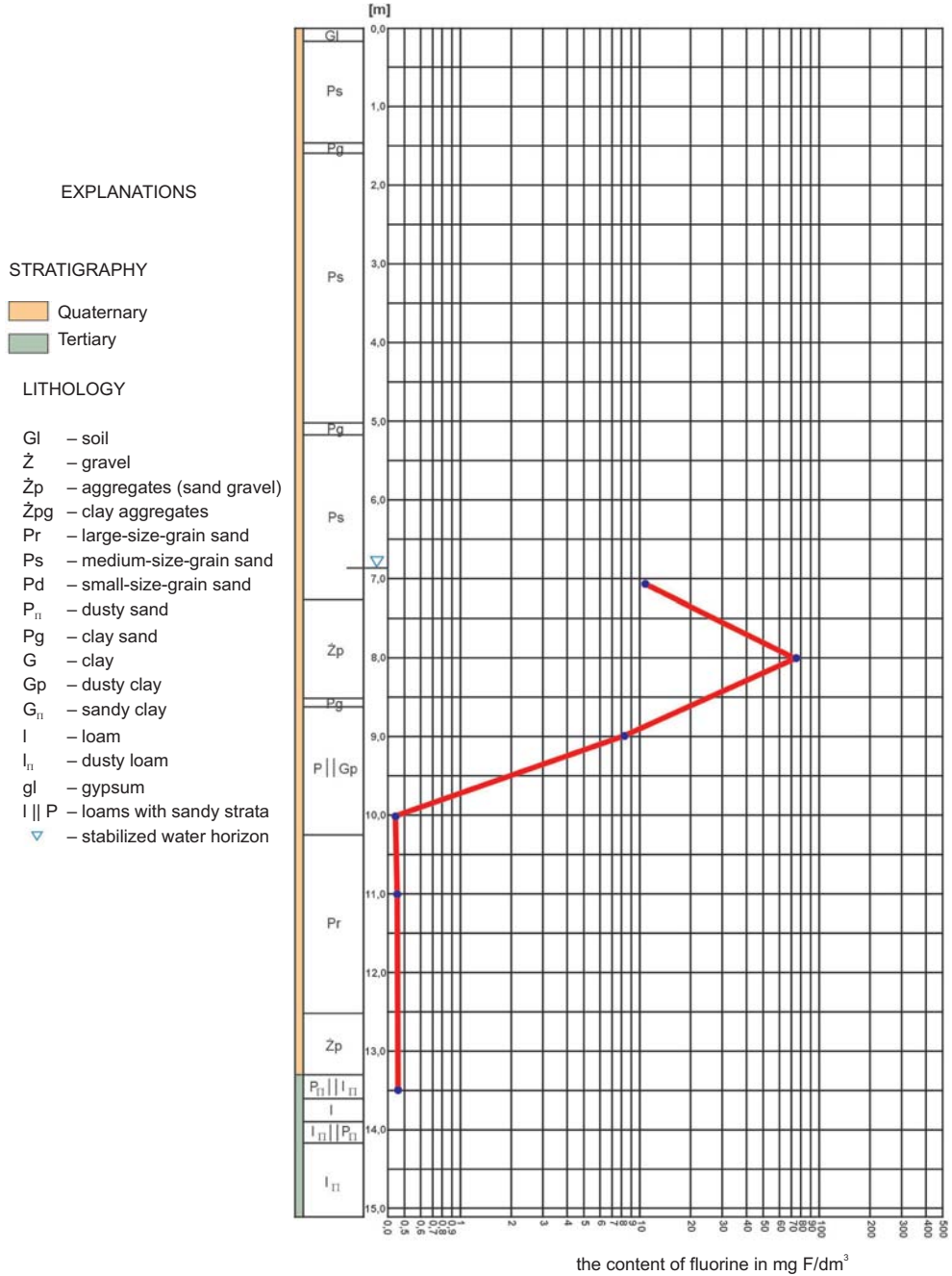


Fig. 5. The variability of fluorine contents in underground waters in the profile of borehole no. 6



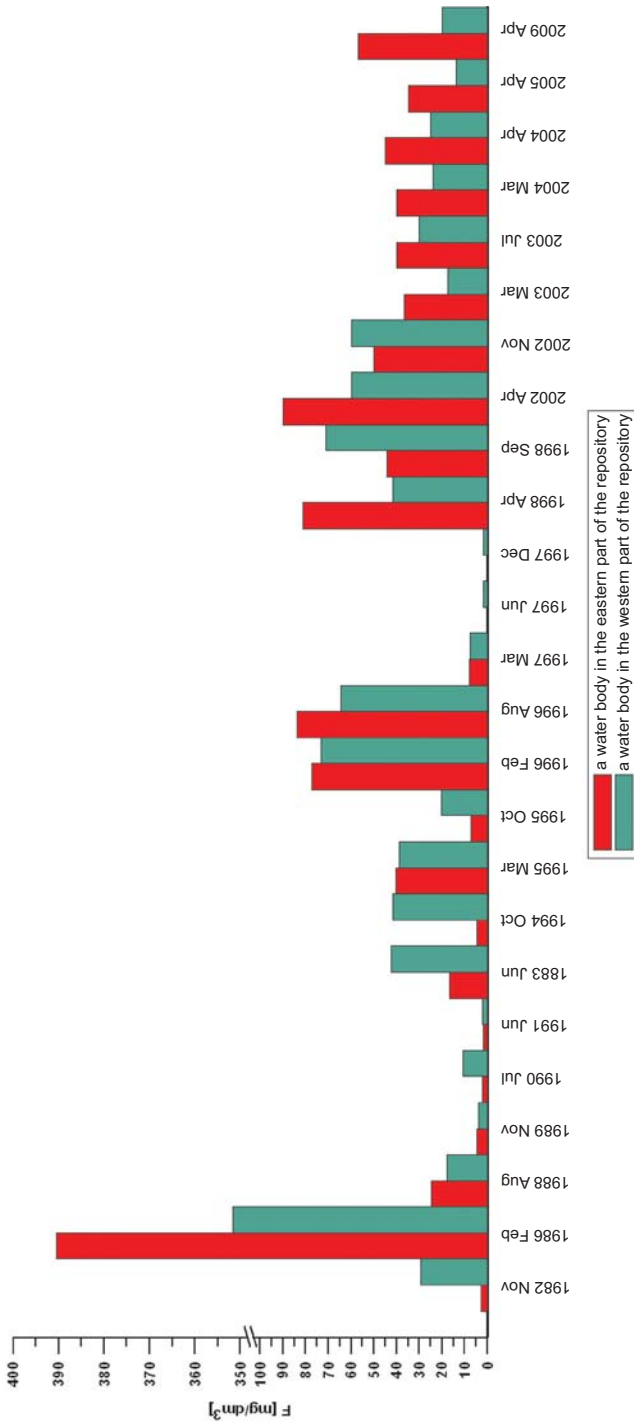


Fig. 6. The variability of fluorine concentration in water bodies: 1982–2009

Distinctly higher fluorine concentrations, of above 300 mg F/dm<sup>3</sup> occurred only in 1981 in the ponds situated directly at the foothill of the repository scarp (nowadays pond III, covered with ground during the reclamation works), where a direct contact between wastes and waters was possible.

Higher contents of fluorine occurred in waters taken from the eastern part of the repository, which was probably connected with the fact that the cathode wastes, thus wastes of a large degree of washing out of the fluorine compounds was deposited mainly in this part. In the final phase of the filling the repository, which was finally in 1998, wastes containing fluorine compounds were deposited alongside the whole southern scarp both from the eastern and western side (Fig. 2, 6).

## 5. Final Remarks and Conclusions

The threat for the environment in the region of the former Aluminium Metallurgy Plant in Skawina is connected with the repository of metallurgical wastes, put in the pit remaining after the exploitation of sands. The localization of the wastes repository was not proper due to geological and hydrogeological conditions. The wastes were only about 1.5 m above the horizon of underground water, and leakage and the propagation of washable substances becomes easier due to lithological conditions of water bearing horizon, characterized with a high filtration coefficient. High permeability makes large quantities of infiltration waters leaking through the aeration zone in the region of the wastes repository, and easily soluble substances get washed out. Polluted waters are moving with the main stream of the underground waters, according to the flow direction from south to north towards the Vistula river the bed of which is 1.5 km from the northern border of the repository.

The analyses of existing documenting materials and the carried out field work allow the following conclusions:

- The deposited wastes distinctly influenced the pollution of underground and surface waters. The chemical composition of waters has been changed compared to the hydrochemical background of the area and is typical for anthropogenically transformed environment. In underground waters the fluorine content exceeded the concentration in the unchanged areas even up to 200 times. The chemical type of clean waters changed from multi-ion with the content of calcium and magnesium ions into waters polluted with fluorine compounds of sodium-hydrocarbonate chemical type, with a high content of alkalis, high specific conductivity and alkaline reaction. The transformed waters contain small amounts of calcium and magnesium

ions, and in the chemical type often fluoride ion dominates. Generally it can be stated that in waters where high concentrations of  $F^-$  ion occur, there is a considerable content of  $Na^+$  and  $HCO_3^-$  ions, with low  $Ca^{2+}$  and  $Mg^{2+}$  content.

- The carried out reclamation work on the repository improved the aesthetic values of this area, but did not decrease threat for was. The fluorine concentration defined in 2004–2009 still range within several  $mg\ F/dm^3$ , like in 1970s. Harmful effects of waste deposition will still be visible for many years.
- In case of such a high and long lasting degree of the pollution of water environment one should attempt to minimize these effects and propose methods of remediation, aimed at the immobilization of the main factor causing these changes, i.e. fluorine compounds in the water bearing horizon.
- The supplementation of the project of the protection and purification of underground waters in the region of the repository should be the project of the water monitoring system, according to the directives of the European Union.

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