

## GROUNDWATER QUALITY CHANGES DUE TO IRON SULPHIDE OXIDATION IN THE Odra ICE MARGINAL VALLEY – LONG-TERM PROCESS OBSERVATIONS

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**Abstract.** In the year 1966 a well field supplying the city of Zielona Góra with water was opened in the ice-marginal valley of the Odra River, near the village of Zawada. After three years of water pumping from 22 wells tapping the shallow valley aquifer, a significant deterioration of water quality, especially involving the increase of concentrations of iron, sulphates, manganese and water hardness, as a result of the process of sulphide oxidation accumulated within the recent Holocene deposits, was observed. Despite drastic changes in quality (the increase of iron concentration to approximately 30 mg/l and sulphate concentration to above 300 mg/l), the well field was still operated as its water was used for purifying (coagulation) of the polluted surface water supplying the city of Zielona Góra.

Based on the analysis of over 30-year-long period of water pumping, it was stated that the effect of the sulphide oxidation process on the quality of water was noticeable for the period of 19 years. The period of persisting very high concentrations of iron of above 15 mg/l amounted to approximately 6 years. It was also stated that the process of reducing the concentrations following the period of their maximum increase proceeded in two stages – the stage of rapid reduction of concentrations which lasted for about 4 years and the stage of slow changes which took about 10 years. The first one was related to the exhaustion of sulphides within the formations marked by good permeability, and the period of semi-decomposition of sulphides, which lasted for about 3 years, was determined based on the changes in iron concentrations. On the other hand, the reduction of concentrations at the stage of slow changes may be linked to the oxidation of sulphides occurring in the formations marked by weak permeability (silts, clays, peats).

**Key words:** iron sulphide oxidation, ice-marginal valley, groundwater quality.

### INTRODUCTION

At the well field supplying the city of Zielona Góra located in the ice-marginal valley of the Odra River near the village of Zawada, significant and catastrophic changes in water quality were observed after three years of pumping.

The changes were related to the oxidation of iron sulphides, which resulted in particularly drastic increase of the content of iron, sulphates, manganese and water hardness as well as in pH reduction. The causes and conditions of the development of the sulphide oxidation process in the first years of the water pumping were discussed in the papers by Kubisz, Ratajczak (1972), Błaszyk, Górski (1981) and Górski (1981). This article presents a comprehensive characteristics of changes in water quality based on the observations conducted for over 30 years of water pumping. Despite

the drastic changes in water quality, the well field was still operated, and its water, marked by a high content of iron, was used for purification (coagulation) of the polluted surface water of the Obrzyca River supplying the city of Zielona Góra.

Thus, the water has been continuously pumped since the year 1966, and it seems noteworthy that for the whole period of pumping, the original structure of the well field has been preserved without any major changes and with minor influence of anthropogenic pollution. This provides a great opportunity to investigate the changes in hydrogeochemical conditions during the long pumping period, and, first and foremost, to measure the influence of the main factor generating the water change, i.e. the process of sulphide oxidation,

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and to verify the previously presented prognoses (Kleczkowski, ed., 1984; Łomotowski, 1996). The data presented in the article are mainly based on the archive material of the Water-

works Company in Zielona Góra collected and analyzed in the Master's thesis written by Agnieszka Gontaszewska (2001).

## CHARACTERISTICS OF HYDROGEOLOGICAL AND HYDROGEOCHEMICAL CONDITIONS BEFORE THE GROUNDWATER PUMPING

The Zawada well field was situated on the flood terrace of the Odra River in the distance of 1300 m from the edge of a moraine upland (Fig. 1). The well field is tapping water from the ice-marginal valley aquifer with the thickness from several to 30 metres (Fig. 2). The aquifer consists of Pleistocene fluvio-glacial sands with gravels and pebbles in the bottom part and of a several-metres-thick layer of fine and medium Holocene sands of fluvial origin in the upper part.

At the surface a layer of muds of variable thickness from 1 to 4 m exists. The water-bearing layer is underlaid by muds from the stagnant flood formation series. Before the well field was opened for pumping, the water table was situated very shallowly under the ground surface at the depth of 0.3–0.7 m, and in most wells it was confined by a layer of muds (Fig. 2). The recognition of formation lithology at the stage of documentation works was very simplified.

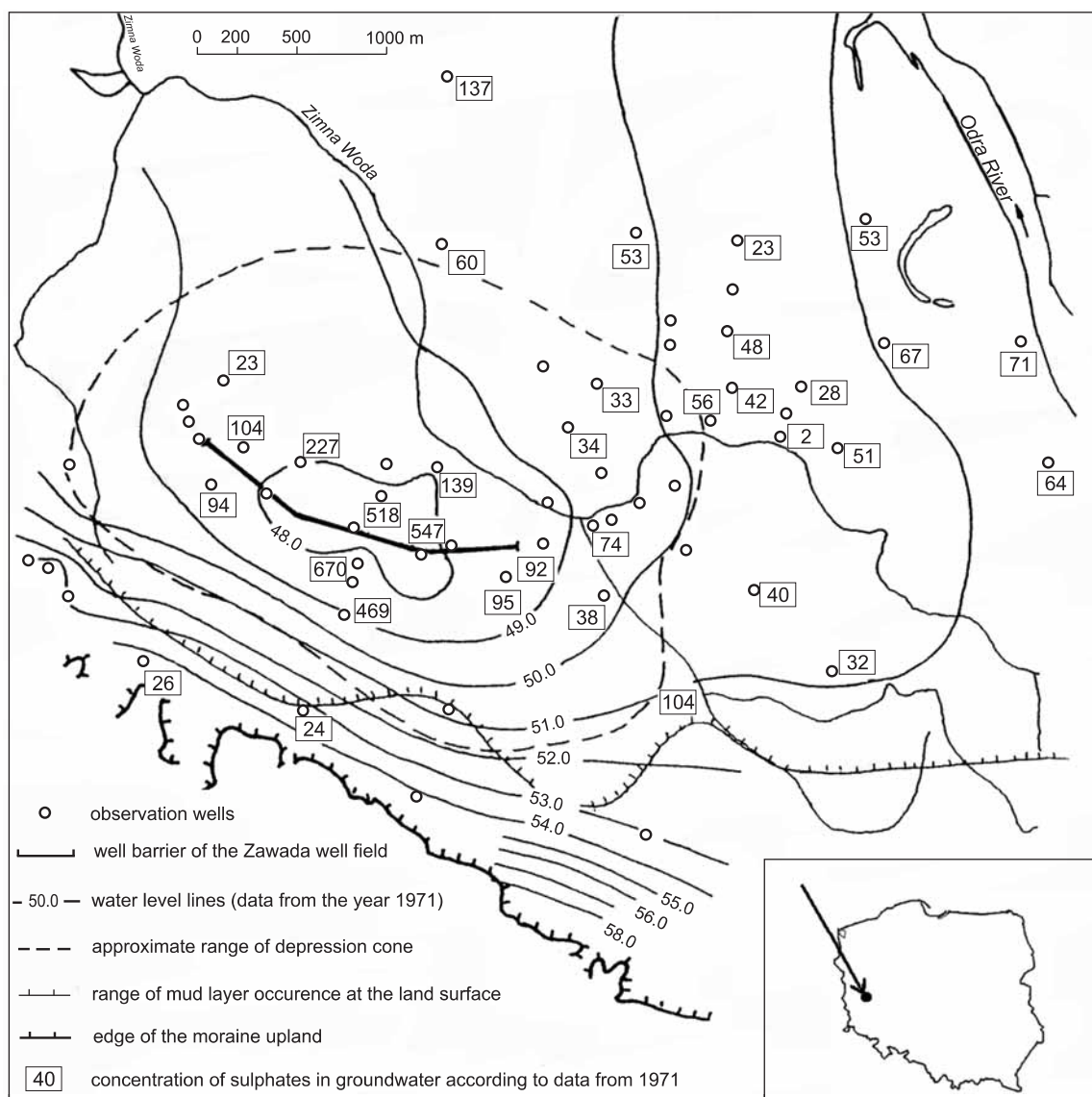
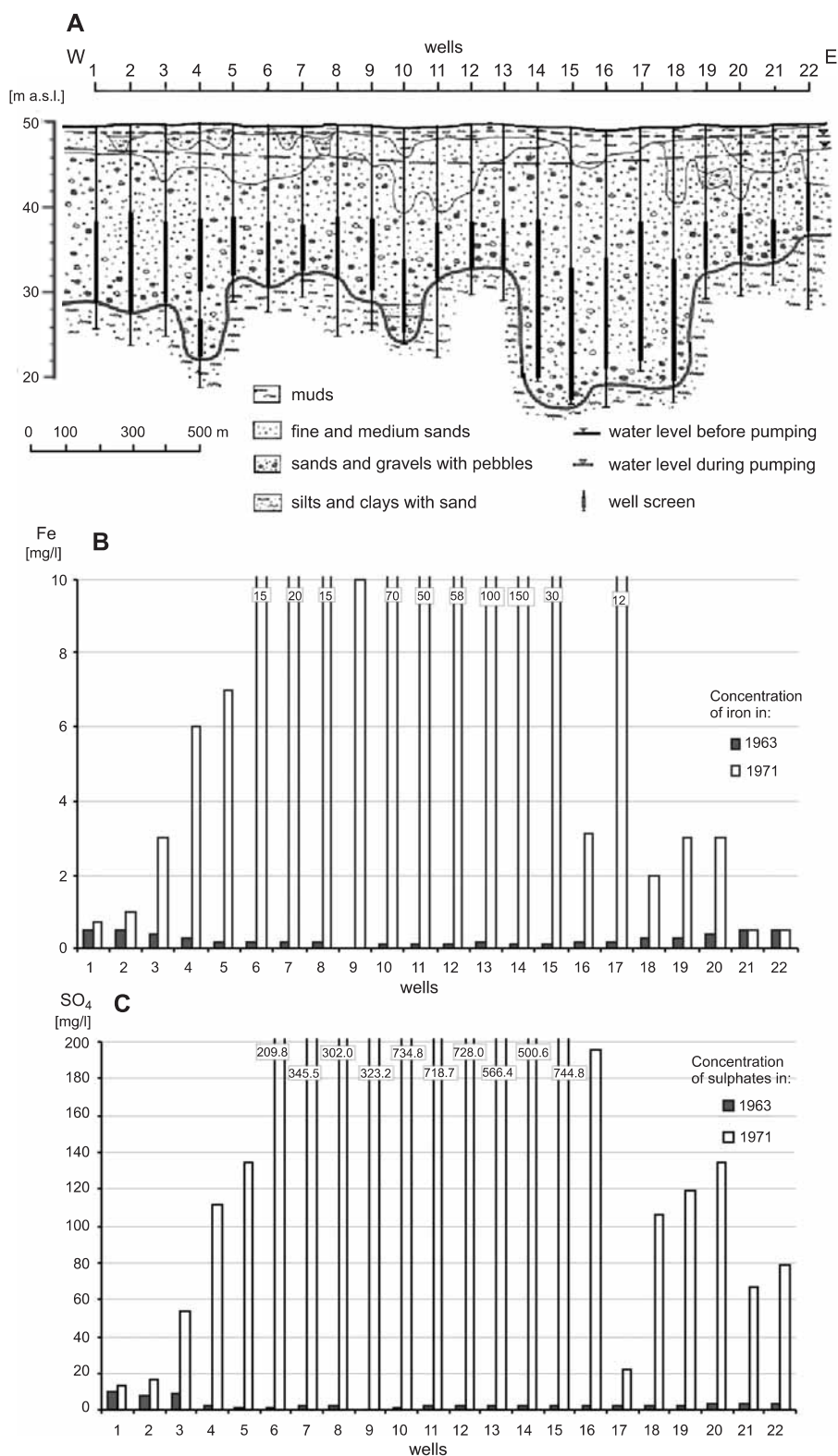


Fig. 1. Hydrogeological map of the part of proglacial stream valley near the Zawada well field



**Fig. 2. Hydrogeochemical cross-section along the Zawada well barrier**

**A** – cross-section along well barrier; **B** – concentration of iron in well water; **C** – concentration of sulphates in well water

Only when the substitute wells were constructed in the years 1971–1972, the lithology was examined more detailed. It was stated that the layer of fluvial formations under a series of muds was enriched with carbonized organic matter

and included sulphides. The occurrence of sulphides was also stated later in deeper parts of profiles within the fluvio-glacial formation series. However, the documentation lacks analytical research on sulphide concentration in deposits.

The water quality along the whole line of the well barrier was exceptionally good, which was the only reason justifying the location of well field in this part of the ice-marginal valley. The concentrations of iron did not exceed 0.5 mg/l, those of manganese – 0.19 mg/l and those of sulphates – 10 mg/l. The good quality was related to the reductive nature of the environment in which iron and manganese precipitated from water in the form of non-soluble sulphides. Anaerobic decomposition of organic matter accumulated in the Holocene formations was the source of  $S^{2-}$  ions.

## CHANGES IN WATER QUALITY IN THE PUMPING CONDITIONS

After the well field was opened in July 1966, the first minor changes in water quality were observed in December of the same year. These involved a slight increase of the iron content. A significant increase of the iron content to 3–4 mg/l was observed as soon as in January 1967. In the following period, the increase was systematic, and so at the end of 1969 the iron concentration amounted to approximately 8 mg/l. From the beginning of 1970 the rate of changes accelerated rapidly and in mid-1970 the concentration of iron in water from all over the well field exceeded 25 mg/l (Fig. 3). The increase of iron concentration was accompanied by the increased concentration of sulphates, manganese and water hardness. The pH reaction decreased significantly. Very high concentrations of iron persisted until the beginning of the year 1972, and then a systematic decrease was recorded. The stabilisation of iron concentrations at a much higher level than before the pumping was observed from the year 1985, 15 years after the maximum concentrations occurred.

Approximately at the same time, the concentrations of sulphates and manganese as well as water hardness also stabilised (Fig. 3). A significant increase of water pH reaction was observed later, after the year 1993. The water quality after the stabilisation of hydrogeochemical conditions is typical for most well fields situated on the flood terraces of ice-marginal valleys.

The analysis of changes in water quality from particular wells indicates that the largest, catastrophic changes were observed only in 5 wells of the central part of the well field

The fact that sulphides occurred also in the lower parts of the aquifer, which was stated during the construction of substitute wells in 1971, may be related to periodically occurring conditions for infiltration of flood water into deeper parts of the water-bearing layer, especially before the deposition of the mud formations series. Furthermore, it may be assumed that their distribution into the lower parts of the water-bearing layer occurred during the wells pumping in the years 1966–1971.

(wells 10 to 14 – Fig. 2). In the outermost wells, the changes were hardly noticeable. The reason for the most significant changes in the 5 above mentioned wells was mainly the fact that in this part of the well field the depth of muds was relatively large, so that the water table never lowered in natural conditions below the bottom of these formations, which only happened after the well field was opened. In the outermost parts of the well field, the depth of muds was smaller and, consequently, the aeration processes of the upper parts of the water-bearing layer could partly occur also in natural conditions, and the products of hydrogeochemical changes were taken to surface watercourses by means of shallow circulation systems. The largest changes occurring in the central part of the well field were also connected with the fact that in this part of the well field the depth of fluvial formations enriched with organic matter was the largest. Moreover, the water table was the lowest here. Relatively minor changes were also observed in wells 16 and 17. This resulted from the fact that the depth of muds was the largest here and, in consequence, some parts of the water-bearing layer were not uncovered. Moreover, no fine-grained fluvial formations enriched with organic matter occurred here.

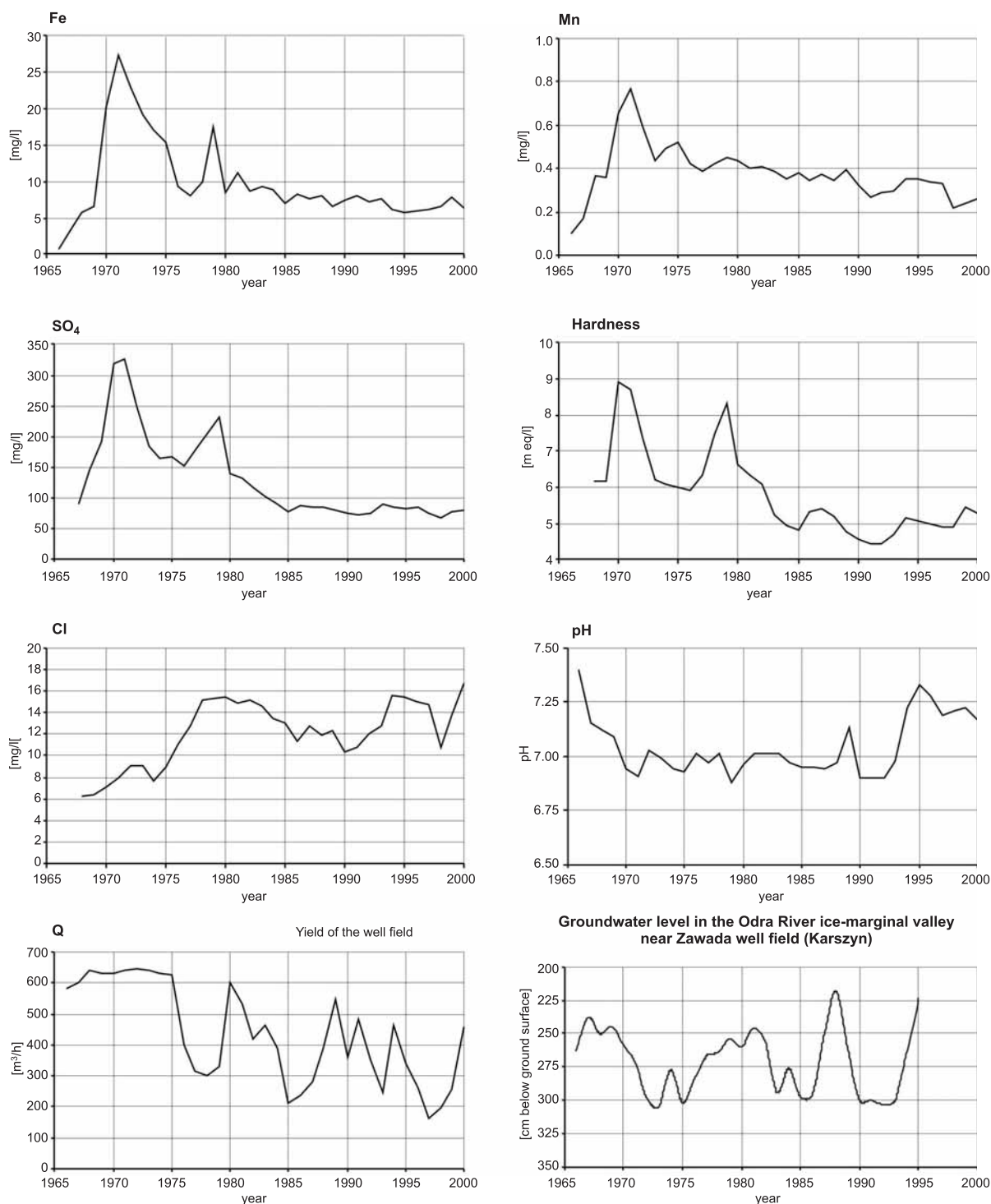
The study of variability of hydrogeochemical conditions in the vertical profile of the water-bearing layer conducted in March 1975 showed that the aerobic environment with a high redox potential occurred only in the upper part of the water-bearing layer at the depth of 2.5–3.0 m (Table 1).

Table 1

Variability of selected hydrochemical indicators at the Zawada well field in the vertical profile of water-bearing layer (measurements taken in March 1975)

No. of well	Depth of well screen [m]	Hydrochemical indicators									
		pH	Eh [mV]	O <sub>2</sub> [mg/l]	sulphides [mg H <sub>2</sub> S /l]	Fe <sup>2+</sup> [mg/l]	Fe <sup>3+</sup> [mg/l]	Mn [mg/l]	SO <sub>4</sub> [mg/l]	hardness [mg/l]	dry residue [mg/l]
11i *	2.5–3.0	2.55	+680	3.0	n.d.	23.9	10.0	1.2	1670	28.2	2900
12b *	9.0–9.5	6.65	+113	n.d.	0.08	133.5	0.35	0.15	495	9.05	853
11Z **	12.0–20.0	6.8	+180	n.d.	0.07	27.2	0.4	0.65	258	7.3	637

\* – observation well, \*\* – production well, n.d. – not detected



**Fig. 3. Changes of selected hydrochemical indicators during the Zawada well field exploitation on the background of pumping yield and unconfined, shallow groundwater level fluctuations (hydrochemical data from the collective well)**

In this zone, most of the iron was oxidized. However, trivalent iron was dissolved at very low pH (2.55). In deeper parts of the water-bearing layer, i.e. from the depth of 9 metres, anaerobic conditions still existed, which was confirmed not only by the lack of oxygen, but also by low Eh and the presence of sulphides in water. As it may be concluded from Figure 1, the spatial range of intensive hydrogeochemical

changes around the well field was smaller than the range of the depression cone and was easily noticeable in the distance of 500 m from the central part of the well field. The detailed examination conducted in 1974 in the pipeline ditch which ran perpendicularly to the well field line revealed that it was marked up to the distance of about 500–600 m towards the upland and about 1000 m towards the Odra River.



## IDENTIFICATION OF HYDROGEOCHEMICAL PROCESSES CONDITIONING THE QUALITY OF WATER IN DIFFERENT PHASES OF WELL FIELD EXPLOITATION

As a result of the analysis of the changes in water quality at the Zawada well field based on the iron concentrations graph, the following phases of the process may be distinguished (Fig. 4):

- phase I – lack of noticeable changes in water quality;
- phase II – systematic deterioration of quality with relatively small gradient of change;
- phase III – rapid deterioration of quality;
- phase IV – persisting high concentration;
- phase V – systematic decrease of concentrations with a large gradient of changes;
- phase VI – systematic decrease of changes with a small gradient of changes;
- phase VII – relative stabilisation of concentrations.

Phase I lasted for about 200 days. In this period, the depression cone was being formed and the inflow from the lower parts of aquifer influenced the water quality.

In phase II, which lasted for about 800 days, a systematic increase of iron concentration to the level of 7–8 mg/l occurred. The increase was connected with the oxidation of sulphides. There is no record concerning sulphates in the first period of pumping. However, as soon as at the beginning of 1968, the concentration of sulphates amounted to 70–90 mg/l at the iron content of about 5 mg/l. The deterioration of water quality in the second phase may also have been influenced by the water inflow from the area of the well field supply as well as from the upper parts of the aquifer, where the processes of sulphide oxidation might have developed in natural conditions.

A relatively slow course of changes in the second phase should be connected with the gradual development of *Thiobacillus thiooxidans* and *Thiobacillus thioferus* bacteria, which are necessary for catalyzing the sulphide oxidation process, and whose presence was stated during the research (Błaszyk, Górski, 1981).

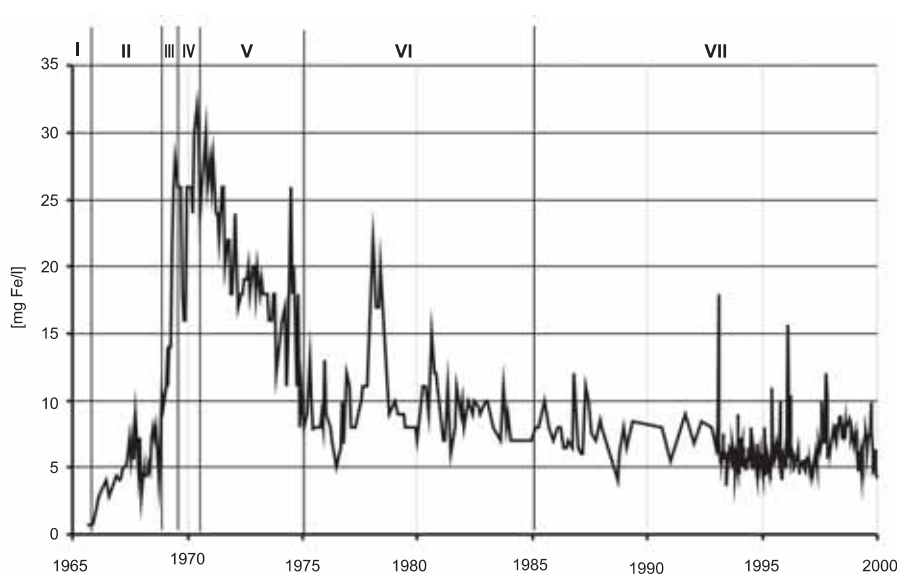
After the period of slow bacteria growth in phase II, their rapid development followed, which caused a rapid acceleration of the sulphide oxidation process (phase III duration – about 150 days). According to Łomotowski (1966), the increase of iron content in the phase of concentration growth may be described by means of the following parabolic function:

$$C^{Fe}(t) = C^{Fe}(o) + \alpha + t^2$$

where:

- $C^{Fe}(t)$  – iron concentration in time  $t$ ,
- $C^{Fe}(o)$  – iron concentration at the beginning of the analyzed growth period,
- $\alpha$  – experimental constant,
- $t$  – observation time.

The experimental constant  $\alpha$  determined based on the above formula for the period of the increase of iron concentration from the value of 3.6 to 30 mg/l, in the period from the end of the first quarter of 1968 to the end of the first quarter of 1971, amounted to  $5.7 \cdot 10^{-5}$  at the correlation coefficient between the calculated and real concentration values –  $r = 0.94$ .



**Fig. 4. Phases of iron concentration changes in groundwater from the Zawada well field**

I–VII – phases of iron concentration changes (for explanation see text)

During the next period (phase IV), a relative stabilisation of concentrations at the level of 25–32 mg/l occurred and lasted for about 300 days. Phase V, lasting for 1460 days, was the period of rapidly decreasing iron concentrations, to the level of about 10–12 mg/l. It should be assumed that this reflects the exhaustion of sulphides subjected to the process of oxidation in the permeable formations. In the next phase (VI), lasting for 9 years, the decrease of iron concentrations to the level of 7.5 mg/l was very slow. It should be assumed that this was linked to the oxidation of sulphides occurring in weakly permeable formations (silts, peats, clays).

It should be underlined that in phase VI a significant periodical increase of iron and sulphate concentrations was noticeable. The increase may be correlated with the increased consumption of water from the well field, as well as with the groundwater table increase after a long period of its lowering (see Fig. 3). According to Frost (1979) (after Witczak, in Kleczkowski, ed., 1984), the decrease of concentration cau-

sed by the exhaustion of leached sulphides, may be described by an exponential correlation

$$C = C_m \cdot \exp(-k \cdot t)$$

where:

- $C_m$  – concentration of the discussed component at the beginning of the concentration decrease phase ( $t = 0$ ),
- $C$  – concentration after time  $t$ ,
- $k$  – constant characterising the leaching conditions.

In the investigated case, assuming for phase V that  $C_m = 28$  mg/l,  $C = 12$  mg/l,  $C_0 = 0,3$  mg/l and  $t = 1460$  days, it may be calculated that the period of semi-decomposition ( $C = 0.5 C_m$ ) for iron amounts to 1174 days (3.2 years), which is in accordance with the calculations by Witczak (in Kleczkowski, ed., 1984) and with the data provided by Frost for the English coal mines, at dehydration, whose time of semi-leaching of sulphides amounted to about 1 to 5 years.

## SUMMARY

At the Zawada groundwater well field in the ice-marginal valley of the Odra River, a particularly good quality of water occurred. Such a state was connected with the persistence of extremely reductive hydrogeochemical conditions which were the effect of the enrichment of deposits with organic matter and sulphides, as well as of the isolation of the water-bearing layer from the influence of atmospheric factors. After the beginning of the pumping and the permanent lowering of water table, the process of sulphide oxidation in the aeration zone and in the upper part of the water-bearing layer occurred, which lead to drastic changes in water quality, and especially to the increase of concentrations of iron, sulphates, manganese and water hardness.

The process of sulphide oxidation developed gradually within the period of 3 years, and its rapid acceleration at the end of that period was connected with a massive growth of sulphate bacteria, catalytically affecting the course of the process. The influence of the sulphide oxidation process on the water quality was observed in the period of about 19 years of the well field pumping.

High concentrations of iron of above 15 mg/l occurred in the period of 6 years. The decrease of the concentrations of iron, sulphates, manganese and hardness, after the period of their maximum growth, initially proceeded at a large change gradient, and then significantly slowed down. The stage of the quick decrease of concentrations lasted for about 4 years and may be linked with the exhaustion of sulphides in the formations marked by good permeability.

The time of sulphide semi-decomposition defined for this phase, based on the changes in iron concentrations, amounted to 3.2 years. The phase of gradual decrease of concentrations may be related to oxidation of sulphides occurring in the formations marked by weak permeability (silts, peats, muds). It should be underlined that water quality after the stabilisation of hydrogeochemical conditions is much worse than before the pumping began. This results from the changes in conditions of water circulation and initiating the influence of atmospheric factors on the formation of water quality, especially in relation to iron and manganese, in the pumping conditions ( $\text{CO}_2$ ,  $\text{O}_2$ ).

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