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title: Groundwater quality changes due to iron sulphide oxidation in Odra ice marginal valley – long term of the process observations

author(s): Józef Górski

Adam Mickiewicz University, Department of Hydrogeology and Water Protection, Poland, gorski@amu.edu.pl

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INTRODUCTION

At the well field supplying city of Zielona Góra located in the ice marginal valley of the Oder 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, water has been continuously pumped since the year 1966, and it seems noteworthy that for the whole period of pumping, original structure of the well field has been preserved without any major changes and the influence of antropogenic pollution is minor. This provides a great opportunity to investigate the changes in hydrogeochemical conditions during the long pumping period.

CHARACTERISTICS OF HYDROGEOLOGICAL AND HYDROGEOCHEMICAL CONDITIONS BEFORE THE GROUNDWATER PUMPING

The Zawada well field was situated on the flood terrace of the Oder River in the distance of 1300 m from the edge of a moraine upland (Figure 1).



Figure 1. Hydrogeological map of the part of proglacial stream valley near the Zawada well field. Explanations: 1 — observation wells, 2 — well barrier of the Zawada well field, 3 — water level lines (data from the year 1971), 4 — approximate range of depression cone, 5 — range of mud layer occurrence at the land surface, 6 — edge of the moraine upland, 7 — concentration of sulphates in ground water according to data from 1971.

The well field tapping water from the ice marginal valley aquifer with the thickness from several to 30 meters (Figure 2). The aquifer consists of Pleistocene fluvioglacial sands with gravels and pebbles in the bottom part and of a several-meters-thick layer of fine and medium Holocene sands of fluvial origin in the upper part.



Figure 2. Hydrogeochemical cross section along the Zawada well barrier. Explanations: 1 — muds, 2 — fine and medium sands, 3 — sands and gravels with pebbles, 4 — silts and clays with sand, 5 — water level before pumping, 6 — water level during pumping, 7 — well screen.

At the surface a layer of muds of variable thickness from 1m 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 (Figure 2). The recognition of formation lithology at the stage of documentation works was very simplified. Only when the substitute wells were constructed in the years 1971–1972, the lithology was examined in more detail. 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 fluvioglacial formation series. 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.

CHANGES IN WATER QUALITY IN THE CONDITIONS OF EXPLOITATION

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 (Figure 3). The increase of iron concentration was accompanied by the increased 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 occured.

Approximately at the same time, the concentrations of sulphates and manganese, as well as water hardness also stabilised (Figure 3). 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 (wells 10 to 14 — Figure 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 surface 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.



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

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.

IDENTIFICATION OF HYDROGEOCHEMICAL PROCESSES CONDITIONING THE QUALITY OF WATER AT DIFFERENT STAGES 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 stages of the process may be distinguished (Figure 4): stage I — lack of noticeable changes in water quality, stage II — systematic deterioration of quality with relatively small gradient of changes, stage III — rapid deterioration of quality, stage IV — persisting high concentrations, stage V — systematic decrease of concentrations with a large gradient of changes, stage VI — systematic decrease of changes with a small gradient of changes, stage VII — relative stabilisation of concentrations. Stage 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.





At stage 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 at the second stage 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 at the second stage should be connected with the gradual development of *Thiobacillus thiooxidans* and *Thiobacillus thiopharus* 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 at stage II, their rapid development followed, which caused a rapid acceleration of the sulphide oxidation process (stage III duration — about 150 days).

During the next period (stage IV), a relative stabilisation of concentrations at the level of 25– 32 mg/l occurred and lasted for about 300 days. Stage 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. At the next stage (VI), lasting for 9 years, the decre ase 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 at stage 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 increased after a long period of its lowering (see Figure 3). According to Frost (1979) (after Witczak, 1984), the decrease of concentration caused by the exhaustion of leached sulphides, may be described by an exponential correlation $C = C_m \cdot \exp(-kt)$ where: C_m — concentration of the discussed component at the beginning of the concentration decrease stage (t=0), C — concentration after time t, k — constant characterising the leaching conditions.

In the investigated case, assuming for stage V that $C_m = 28 \text{ mg/L}$, C = 12 mg/L, $C_o = 0.3 \text{ mg/L}$ 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 (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 year to 5 years.

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