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Migration of organic and inorganic pollutants in groundwater, based on example industrial waste site "Zielona" in "Zachem" Chemical Plant (Bydgoszcz City, north Poland)

ABSTRACT OF DOCTORAL THESIS

Analysis of pollutant migration in industrial areas, strongly transformed by anthropogenic activity, is a relatively difficult task. What is particularly distinctive of these areas is the formation of numerous pollution hotspots within their boundaries, often very diverse in terms of the types of substances harmful to the soil and water environment and/or migrating within. In addition to the identified typical pollution hotspots, such as landfills, the industrial areas are characterized by high density of technological infrastructure (including pipelines, sewerage systems, technological ponds and reservoirs). In emergency situations, which cannot be avoided even in a perfectly functioning plant all these elements may have negative impact on the natural environment.

Chemical plants are among the objects with potentially very high risk for soil and water environment. They produce chemicals, both inorganic and organic ones, with a high toxicity potential, which often creates many possibilities for the penetration of pollutants into the soil and water. Often these substances do not appear in natural conditions and their occurrence is related to the specificity of the industrial production.

Based on the analyses of groundwater and soils, their significant contamination by both inorganic and organic substance was detected in the area of the former "Zachem" Chemical Plant in Bydgoszcz, which until recently was one of the largest producers of organic chemistry in Poland.

This PhD thesis presents a methodological solution to the problem of pollutant migration in the aquatic environment. This issue however is not restricted to the computer simulations for the numerical hydrogeological model of the study area. It consists of labor-intensive and thorough field

studies, understanding and accurate mapping of the geological structure of the study area and hydrogeological conditions and, above all, hydrogeochemical processes occurring in the aquifer. Only after considering all of the research stages it is possible to create a final model of pollutant migration. This is because only based on reliable migration models that are verified by detailed studies we can develop and design optimum scenarios for the remediation of soil and water environment for individual hotspots and contaminant plumes.

The first step in modeling the migration of chemical substances consists in a detailed analysis of the production profile of the factory in order to recognize the expected pollutants.

"Zachem" Chemical Plant was established at the site of the former German factory of explosives Dynamit-Aktien Gesellschaft (DAG) Fabric Bromberg, built during the Second World War. The basic products intended for military tasks of the Third Reich included nitrocellulose ($C_6H_7N_3O_{11}$), smokeless powder and nitroglycerin ($C_3H_5N_3O_9$), TNT ($C_7H_5N_3O_6$), dinitrobenzene ($C_6H_4N_2O_4$), V1 missiles, as well as aerial bombs, artillery shells and powder charges. Under the Polish government, after the year 1948, the plant initially produced blasting materials for the mining industry and then TNT ($C_7H_5N_3O_6$), pentaerythritol tetranitrate ($C_5H_8N_4O_{12}$) and tetryl ($C_7H_5N_5O_8$) for the military and civil needs. It also produced dyes, dyeing intermediates, pigments and phenol (C_6H_6O), as well as dinitrotoluene (DNT $C_7H_6N_2O_4$), nitrobenzene ($C_6H_5NO_2$), aniline (C_6H_7N) and products from the recycled PVC.

At the beginning of the 60s of the last century experimental installations for the production of isocyanates, dienes and polycarbonates were tested in this Chemical Plant and studies were carried out on the development of the polyurethane complex. In the next decade the investment was made in the production of flexible polyurethane foams, installations for the electrolysis of brine, phosgene (CCl_2O), dinitrotoluene (DNT $C_7H_6N_2O_4$), toluene diamine (TDA $C_7H_{10}N_2$), toluene diisocyanate (TDI $C_7H_6N_2O_2$) and epichlorohydrin (EPI C_3H_5ClO) as well as rigid polyurethane foams and fittings from PUR foams for the automotive industry. The production profile of the Chemical Plant evolved over the decades addressing the needs of the market and political and economic situation of the country. Basic and most important products manufactured in the Plant include among others toluene diisocyanate (TDI), allyl chloride (C_3H_5Cl), epichlorohydrin (EPI), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium hypochlorite (NaClO).

Until 2013 "Zachem" Chemical Plant in Bydgoszcz was one of the largest producers of organic chemistry in the Polish market. The use and production of various substances both organic and inorganic ones was not without the effect on the condition of soil and water environment. The pollutants were detected in the past and are now being detected within all of the components of natural environment – particularly in soils and groundwater.

A key stage in understanding the migration of contaminants in groundwater is to develop a conceptual model. Therefore the geological structure of the ground and hydrogeological conditions of the quaternary aquifer were analyzed in details.

The complex geological structure of the region of the "Zachem" Chemical plant in Bydgoszcz is one of the crucial factors determining the conditions of pollutant migration in soil and water environment. Accurate recognition and understanding of the structure, with emphasis on the morphology of the aquifer floor and the presence of impermeable inserts, in the form of glacial tills as well as fossil valleys and hydrogeological windows forming the contact zones between aquifers, is the key in solving the problem raised in this doctoral dissertation. Mesozoic (Jurassic, Cretaceous) and Cenozoic (Paleogene, Neogene, Quaternary) formations were identified in the studied area.

Complex geological structure of the substrate of the "Zachem" Chemical Plant in Bydgoszcz results from the high lithological (and tectonic) variability of the Quaternary formations. Quaternary formations in the area of the Chemical Plant are represented by Pleistocene deposits (undivided Quaternary) and Holocene. The study area is covered by a complex of Quaternary formations with thickness from 0 to 170 m. The distribution and thickness of the sand and gravel complex and glacial tills with silt and loam are diverse. The valleys of the rivers Vistula and Brda are dominated by sands of different grain size with thickness from a few to several meters, while in the Vistula valley they are covered with alluvions and peats with thickness up to 5 m. The valley of Brda lacks Quaternary deposits in some places.

The north-eastern part of the proglacial terrace is characterized by a sand and gravel complex, residual on Pliocene clays with thickness of 15 ÷ 25 m. The complex is covered with discontinuous layer of glacial till, frequently cut by inserts of sand and loam, with thickness up to 8 m.. The overlying layer is represented by sands of different grain size and thickness up to 5 m, and aeolian fine sands.

The presence of two Quaternary fossil valleys, where the Neogene sediments are strongly reduced or absent, was identified within the boundaries of the Chemical Plant. The valley with the WSW-ENE course is the deepest one in the studied area and cuts into the Cretaceous formations to a depth of approximately 80 m (elevation of c.a. -120 m. a.s.l.). It is filled with glacial tills. The second fossil valley with the NW-SE course is filled with unsorted sands and gravels and cuts into the formations to the elevation of -30 m. a.s.l. The course of the remaining valleys is unknown, as so far they have been identified by one or two drillings.

From the viewpoint of tectonics, the glacitectonic processes within the Chemical Plant did not play any major role. In older glacial periods the Neogene sediments were disturbed, which is reflected in the forms of the outcropping occurrence of the Pliocene sediments in Quaternary substrate. Subsequent stages of erosion, during which the proglacial terraces were formed, destroyed the glacitectonic forms, which makes it difficult to identify their size and age.

The complex geology of the region of the "Zachem" Chemical plant in Bydgoszcz implies complex conditions of groundwater circulation. This situation is particularly evident in the Quaternaty aquifer. The general direction of water flow is towards the regional drainage bases, towards the north-

east to the river Vistula and to the north to the left tributary of the Brda. This is because the local watershed of groundwater passes through the Chemical Plant.

The Quaternary aquifer occurs throughout the study area and is commonly exploited in the Chemical Plant. The formations building the aquifer are genetically related to the Mazowiecki interglacial and fluvioglacial deposits. These are deposits with strongly variable granulation – from silty sands to gravels. The layer is supplied with water by infiltration of groundwater from the overlying, subsurface layer and infiltration of precipitation. The main area of supply is located to the south-west from the border of the Chemical Plant in the area of the proglacial terrace, covered with dunes. The groundwater table is unconfined, locally slightly confined. The stream of water is divided and flows to the north towards Brda, along the axis of the fossil valley filled with sands and gravels, and to the east and north-east towards the Vistula valley. The groundwater flow directions in the aquifer are disturbed by the zones of increased conductivity, water intake "S", that forms a localized depression cone, as well as the zones in which the discussed layer is absent.

Precise recognition of the location of any element affecting the direction of flow is the key to reliable mapping of the geological structure and hydrogeological conditions of the model. From this point of view, computer mapping is the verification or confirmation of understanding the analyzed aquifer system by the model's author. Errors made at this stage are fundamental to the credibility of pollutant migration model. The common use of models carries the risk related to the usage of the calculation tool with a lack of hydrogeological knowledge.

The creation of a numerical hydrogeological model, and then the model of chemical substances migration is the third key step in modeling the pollutant migration in industrial areas. The main aim of developing the pollutant migration forecasting model is to replicate the direction of spreading pollutants from the hotspot located in the "Zachem" Chemical Plant in Bydgoszcz. Due to very complex hydrogeological conditions of the discussed area and co-occurrence of organic and inorganic substances, the studied case is relatively very difficult. The processes accompanying the migration of the analyzed substance, i.e. advection, dispersion, sorption and decay, should be taken into consideration. A very important aspect is to obtain parameters characterizing the aquifer, in which the migration takes place, that are required by the software used in the modeling process. These values were measured directly in the field and/or acquired during the successive iterations of the model. This is because the migration process parameters cannot be reproduced in laboratory studies (i.e. batch tests, column analyses) due to the problem of the scale.

The projected ranges of contaminated groundwater plumes and the ranges of the pollutant concentrations were treated as preliminary and requiring further investigation. The developed numerical and conceptual models required verification, therefore it was necessary to perform detailed studies. Understanding of the study area, recognition of the geological structure and hydrogeological conditions allowed to clarify the range of the contaminant plume. From this viewpoint it was the most important to understand the hydrogeochemical processes that determine the chemical composition of

groundwater and spreading of the contamination. In heavily polluted areas the conditions are favorable for a number of complex chemical reactions, including oxidation (decomposition) of organic matter in groundwater leading to the consumption of dissolved oxygen and changing towards the reduction conditions. The organic compounds migrating in aquatic environment originate from the industrial waste site "Zielona" (primary substance) but at the same time they are subjected to transformation due to the reactions with other compounds (organic and inorganic), occurring within the contaminant plume. New organic compounds (secondary substances) may therefore emerge in the stream of contaminated groundwater. Due to the diverse chemical composition of individual contaminant streams and varying pH – Eh conditions, the chemical reactions of both degradation and the formation of new compounds may proceed in different directions, leading to a wide range of products. Clarification of the results showed that the general contaminant plume from the industrial waste site "Zielona" is a complex heterogenic object, consisting of plumes of different contaminants, composed of both organic compounds and inorganic substances (Fig. 1).

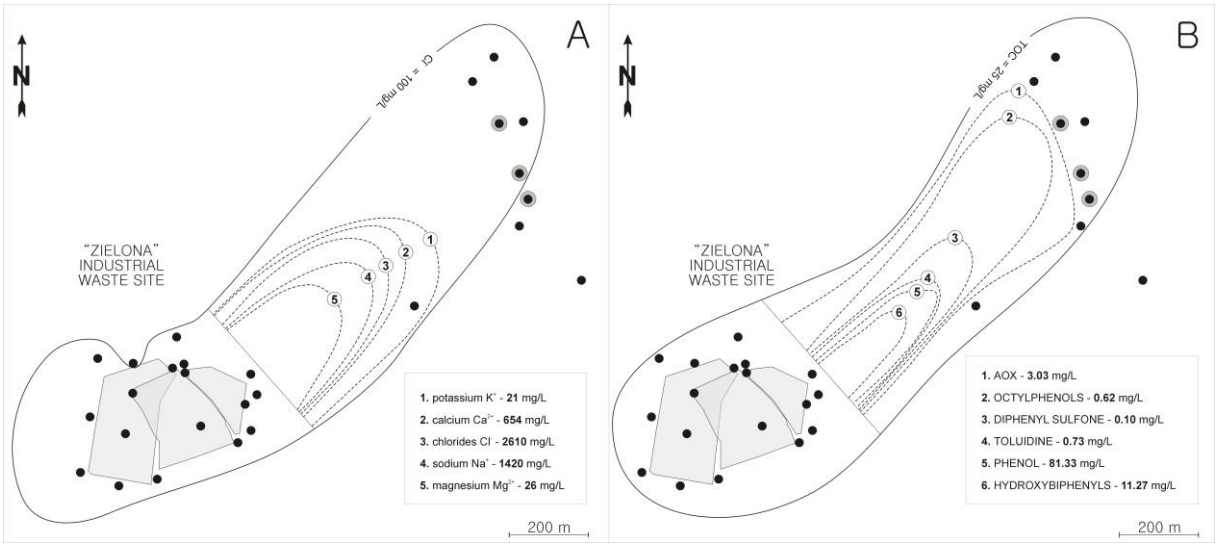

Fig. 1. The ranges of average concentrations of selected both inorganic (A) and organic substances (B) in the area of "Zielona" industrial waste site

Complex hydrogeochemical processes, including those between organic and inorganic compounds are the most important factors influencing the migration of pollutants in groundwater in the area of the "Zachem" Chemical Plant in Bydgoszcz. Based on the hydrogeological study the following processes were identified: (a) decomposition of organic matter in the availability of oxygen, (b) decomposition of organic matter in the absence of oxygen, (c) diversification of speciation forms of elements, (d) dehalogenation, (e) denitrification and desulfatization and (f) degradation of characteristic organic compounds.

The concentrations of organic compounds in the area of the industrial waste site "Zielona" were expressed as TOC. It is a parameter that includes the sum of all organic substances present in the solution. A hydrogeochemical process of organic matter decomposition under the conditions of oxygen availability is described by the scheme TOC $\rightarrow$ CO_2 $\rightarrow$ HCO_3^- $\rightarrow$ CO_3^{2-}. The conducted study showed a clear and statistically significant (R^2 = 0.88) relationship HCO_3^- = f(TOC). The process is very complicated and generally spatially varied. The pH of groundwater (5,72 ÷ 9,93) diversifies at the same time. Hydrogen ions H^+ excreted during the degradation of organic substance may react with: (a) silica SiO_2 (concentrations 0 ÷ 24 mg/L), (b) carbonate minerals (e.g. calcite spread in Quaternary formations) and (c) be adsorbed on the quartz grains. The reaction that accompanies the organic matter decomposition is the oxidation of reduced inorganic forms of Fe^{2+} and Mn^{2+}. Oxides (MnO_2) and hydroxides ($Fe(OH)_3$) of metals precipitate from the solution and occur in the solid phase.

The lack of oxygen, which has been entirely consumed for the standard oxidation of organic substances (decomposition under the conditions of oxygen availability), is not a barrier for further decomposition of organic matter in the soil and water environment. This process is associated with the acquisition of electrons needed for the oxidation of organic substances from source other than oxygen atoms. Metal atoms in high oxidation states, which are primarily bound in the form of oxides and hydroxides, act as the electron donors. Then the metals pass again into the solution in the form of cations in lower oxidation states.

The reactions of organic matter decomposition, both under the conditions of oxygen availability and its lack, are the processes that occur simultaneously in the Quaternary aquifer of the area of the "Zielona" industrial waste site. The simultaneous breakdown of organic matter with the oxidation and re-reduction of inorganic substances (Fe, Mn) increases the effectiveness of its complete decay.

The occurrence of particular elements in the water environment in the form of different speciations was described based on detailed spatial analysis of the pH of the environment and redox conditions. The pH within the contaminant plume ranges from 5.72 to 9.93, which results from the presence of CO_2 in groundwater and the decomposition of organic matter under the conditions of oxygen availability. The differentiation of Eh from -129 to +179 mV results from the decomposition of organic matter in the lack of oxygen. The variability of the redox potential depends on, among others, the solubility of metals, as it may affect the electron structure of atoms of a given element.

Organic matter decomposition affects the differentiation in pH and Eh of the water environment, which is in turn reflected in the changes in the speciation forms of elements occurring in groundwater of the industrial waste site "Zielona". It is one of the most important processes, in which the occurrence and reactions of organic substances have direct effect on inorganic substances.

Chlorinated hydrocarbons, i.e. AOX and identified components of volatile haloorganic compounds, VOX (the group of chlorinated ethene and methane), are important groundwater pollutants. Starting from classical course of degradation of chlorinated etens by dehalogenated

reduction and retaining the double bond between the carbon atoms, TCE breaks down to DCE and Cl^-. The next stage is the decomposition of unstable substances - DCE and VC - due to the oxidation under the conditions of both availability and lack of oxygen (in the presence of Fe and Mn) and immediate, complete mineralization of H^+ and Cl^- ions to CO_2. In the case of breaking the bond between the carbon atoms, TCE breaks down into two functional groups CHCl- and CCl_2-. The reaction in the solution with high concentrations of Cl- and H+ ions may result in the formation of chlorinated methane, and precisely TCM and DCM. Moreover, TCM is subjected to classical breakdown under aerobic conditions by dehalogenation into DCM and Cl^- ion. Complete mineralization of the substance is the final result of the process.

The hydrochemical transformations of chlorinated etens and methanes with the presence of inorganic substance come down to the following scheme:

$$PCE \rightarrow TCE \rightarrow DCE \rightarrow CO_2 + 2H^+ + 2Cl^-$$

and $PCE \rightarrow TCE \rightarrow (TCM) \rightarrow DCM \rightarrow CO_2 + 2H^+ + 2Cl^-$.

Another process that occurs in the soil and water environment in the area of the "Zielona" waste site includes denitrification - the reduction of nitrogen speciation. The process of dissimilative denitrification is mediated by anaerobic bacteria, in which gaseous nitrogen $N_{2(g)}$, released to the atmosphere is the final product. In the presence of organic matter in the environment the reaction results in the reduction of nitrogen compounds with the simultaneous organic matter oxidation. The process of assimilative denitrification comprises the reduction of nitrates into amines with ammonification being the final process of the reduction in nitrogen speciation. This process occurs in the vicinity of the "Zielona" waste site with respect to high concentrations of chloroaniline (ClC_6H_4-NH_2 – 370 μg/L), aniline (C_6H_5-NH_2 – ok. 2 mg/L) and toluidine ($CH_3C_6H_4$-NH_2 – ok. 8 mg/L) in groundwater. These substances are used in the production of dyes.

The reduction in sulfur speciation has direct impact on the chemical composition of groundwater with variable redox conditions. The process of dissimilative desulfatization is mediated by strictly anaerobic bacteria which use sulfates in the respiration process as terminal electron acceptors. Hydrogen sulfide, H_2S, released into the atmosphere is the final product. Speciation forms of sulfur as oxidized sulfates (maximum concentration of SO_4^{2-} above 7800 mg/L), are replaced by hydrogen sulfide as a result of reduction processes (Eh= -129 mV on drainage barrier). The presence of hydrogen sulfide is an important aspect of the analysis of the soil and water environment condition, mainly due to the direct threat to health and even life of the local inhabitants of the villages situated on the outflow of groundwater towards the Vistula. The assimilative desulfatization process represents the reduction of inorganic sulfates to thiols which are organic substances.

Decomposition of phenol in the rock mass is the characteristic hydrogeochemical process occurring in the area of the industrial waste site "Zielona". As a result of the production of phenol in the "Zachem" Chemical Plant in Bydgoszcz, this compound occurs in very high concentrations, up to 613 mg/L. In the classic undisturbed process, the breakdown of phenol leads to the formation of

glyoxylic, formic and acetic acids. Finally, CO_2 is produced which ultimately decreases the pH of groundwater.

Thorough understanding of the problem of chemical substance migration in the area of the "Zachem" Chemical Plant in Bydgoszcz is the most important element which allowed to design an effective scenario for the remediation of the studied area. Treatment of the soil and water environment is in this case particularly important due to the real threat to the health and life of the local inhabitants of Bydgoszcz and nearby villages: Otorowo, Plątnowo, Łęgnowo. Specific conditions in the study area, i.e. the occurrence of a broad spectrum of different chemicals determines the use of specialized remediation methods adapted to the type of contaminants, i.e. to particular chemicals. Designing optimum scenario for the remediation of soils and groundwater must be based on accurate identification of the reactions and chemical processes occurring within the contaminant plume and on reliable and credible migration model.

The most important element of the procedure of effective remediation is to determine the environmental aim of the undertaken operations. In most general terms, it is associated with the level of environmental treatment, for instance either to the original or acceptable condition.

Initially, the proposed operations consist of the analysis of contaminant plume migration including the possibility of limiting the spread of contaminants. Starting the process of removing contaminants from the aquifer results in a reduction of the contaminated area and additionally leads to improving the condition of the environment. The proposed remediation scenario of the study area includes 3 stages of remedial actions, beginning with the pump-and-treat method which consists in pumping out contaminated groundwater with its simultaneous purification and the use of reactive barriers and systems of insulating shutters for controlling the direction of contaminant migration (funnel-and-gate) and then, if needed, the use of the best available complementary techniques. The final stage involves the MNA method (i.e. monitored natural attenuation) with the possibility of intensification by means of bioremediation.

Regardless of the designed and completed elements of active remediation, the ISO part of the industrial waste site "Zielona" should be removed. The estimated total cost of restoring the soil and water environment in the area of the industrial waste site "Zielona" to an acceptable condition was estimated at around 800 million PLN, which has to be incurred in the period of 11 years. The valuation was based on the assumption of pumping out and treatment of 1 volume of heavily contaminated water, which is 6 million m^3, and then the use of remediation techniques aiming to intensify the decomposition of organic substances (oxidation) or decreasing their concentrations in the solution (sorption and chemical reactions).

The cost of remediation of the industrial waste site area "Zielona" is very high and it is hard to expect that it will be fully secured until the end of the project. Due to the high potential hazard of the contaminant plume, it needs to begin as soon as possible and it is very important to secure the expenditures at least for the initial steps, aimed at effectively limiting the further spread of the plume.

Currently, however, due to the disabled drainage barrier, the contaminant plume from the area of the "Zielona" industrial waste site has the possibility of free migration to the area of Plątnowo, Otorowo and Łęgnowo, which is used both for agricultural and residential purposes.