MODELLING OF CHEMICAL MIGRATION UNDER THE OVERLAPPING IMPACT OF MULTIPLE AND DIVERSE POLLUTION SOURCES IN THE AREA OF THE „ZACHEM" CHEMICAL PLANT (BYDGOSZCZ, NORTHERN POLAND)

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Abstract: Modeling studies of chemical migration in the area of the “Zachem” Chemical Plant in Bydgoszcz started from the analyses of the production profile. Those studies were conducted to investigate the potential contamination. Organic compounds still represent a substantial concentration in soil and water environment, including total organic carbon (TOC) reaching values above 1600 mg/L, aniline, nitrobenzene and phenol (up to 500-800 mg/L), organochloride and organometallic compounds, as well as hydrocarbons, such as benzene, toluene and PAHs. Groundwater contains most of the major ions (chlorides, sulphates and bicarbonates, sodium and calcium) and trace elements (Al, Co, Cr and Ni).

A reliable conceptual model of the geological structure was constructed for 3 continuous layers with variable bottom morphology. This model represents the complex structure containing permeable and impermeable Quaternary and Neogene deposits. A hydrogeological numerical model was created for the area of the “Zachem” Chemical Plant using the Visual MODFLOW program. Low values of two key statistical measures confirm a good model fit to the measured data: root mean square (RMS) amounts to only about 1.5 m and normalized RMS reaches only about 4.4%. The differences between measured and calculated values are normally distributed. A Modpath module was used to analyze the potential extent of contaminant plume. Accurate hydrogeological 3D sampling was conducted using a “low flow” technique.

The results of full and reliable modeling of the chemical migration under the overlapping impact of multiple and diverse pollution sources in the area of the “Zachem” Chemical Plant are essential for further planning of remedial strategies.

Key words: groundwater pollution, “Zachem” Chemical Plant, organic and inorganic contamination, pollution migration, numerical model

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INTRODUCTION

Chemical plants are objects of potentially high risk to the soil and water environment. Production of chemical substances with a high potential for toxicity, both organic and inorganic ones, poses high risk of pollutant infiltration into the soil and groundwater. These substances do not occur in natural conditions and are strongly related to the specificity of the manufacturing industry.

Modeling of chemical migration in industrial areas, heavily modified by human activity, is a relatively difficult task. One of the particularly characteristic features of such industrial areas is having a number of pollution sources, often extremely varied in terms of the type of chemical substances hazardous to soil and water environment and/or migrating within. In addition to typical pollution sources (industrial waste dumps), industrial areas are characterized by technological infrastructure of high density, including pipelines, technological ponds, pools and sewage systems. In case of accident, all these elements can negatively affect the environment, which cannot be avoided even in a perfectly functioning plant (Witkowski et al. 2008; Weingran, Meiners 2015).

Until recently (year 2013) the "Zachem" Chemical Plant in Bydgoszcz was the largest producer of organic chemicals for the Polish market. Hydrogeological studies revealed a significant environmental contamination by both organic and inorganic substances within the area of the plant.

This paper presents methodological solution to the problem of migration modeling, emphasizing the importance of the field work and sampling stages, described in this paper. Credible hydrogeological model is not restricted only to computing. The entire study consists of: laborious and detailed fieldwork, understanding and accurate mapping of the geological structure of the area as well as hydrogeochemical processes occurring in the aquifer. Only consideration of all stages of research allows to create a correct and reliable model.

PRECEDING STUDIES

The modeling of chemical migration should always begin with a detailed analysis of the plant's production profile in order to identify the expected pollutants (Figure 1). Initially, the "Zachem" Chemical Plant in Bydgoszcz produced explosive materials for the mining industry. Then the production was adapted to both military and civilian needs, producing trinitrotoluene $C_7H_5N_3O_6$, PENT $C_5H_8N_4O_{12}$ or tetryl $C_7H_5N_5O_8$. It also produced dinitrotoluene $C_7H_6N_2O_4$, nitrobenzene $C_6H_5NO_2$, aniline $C_6H_5NH_2$, products from recycled PVC (mer structure -CH_2CHCl-), dyeing intermediates, dyes, pigments and phenol C_6H_6O. Experimental isocyanate systems (isocyanate group -N=C=O-), diene (chemical bonds -CH=C=CH- or -CH=CH-CH=CH-) and polycarbonates were tested in the plant in the early 60's of the last century. Studies on the construction of polyurethane complex were also conducted. Allyl chloride C_3H_5Cl, dinitrotoluene $C_7H_5N_2O_4$, epichlorohydrin C_3H_5ClO, phosgene CCl_2O, hydrochloric acid HCl, sodium hypochlorite NaClO, toluenediamine $C_7H_{10}N_2$, toluene diisocyanate $C_9H_6N_2O_2$ and sodium hydroxide NaOH were also produced from the 70's until 2013. Polyurethane, rigid foams and polyurethane foam fittings for the automotive industry were also among the products manufactured in the "Zachem" Chemical Plant (Pietrucin 2013).

The use and production of various substances, both organic and inorganic, in the "Zachem" Chemical Plant had an impact on the conditions of adjacent soil and water environment. Contaminants have been reported in the past and currently detected within all components of the natural environment, particularly in soil and groundwater. Identification of all substances used in production processes of the plant is the most important task to recognize the type of soil and water pollution.

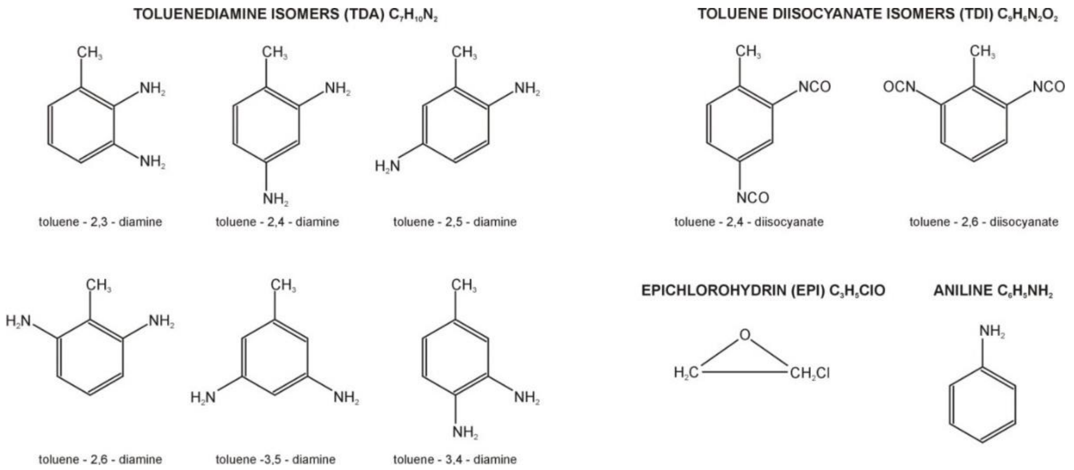

Fig. 1. 'Zachem' Chemical Plant production profile - selected chemical compounds

Very high concentration of organic compounds is one of characteristic features of groundwater polluted by chemical plants. It is manifested by an extremely high concentration of total organic carbon (TOC), reaching values above 1600 mg/L. The identified organic substances in groundwater included aniline, nitrobenzene and phenol (with determined concentrations up to 500-800 mg/L). Groundwater contains also organochloride and organometallic compounds as well as hydrocarbons, including benzene, toluene and PAHs.

Among inorganic components found in groundwater in the vicinity of the chemical plants there were very high concentrations of most of the major ions (chlorides, sulphates, bicarbonates, sodium and calcium) and trace elements, including those of high toxicity to living organisms and humans (Al, Co, Cr and Ni).

CONCEPTUAL MODEL

The development of a conceptual model is the second key step in understanding the migration of pollutants in groundwater. It is the basis and foundation for any further action. This includes understanding of the system layout and structure together with the development of its objectives. Errors made at this stage are of fundamental importance for the adequacy of hydrogeological model. Computer modeling from this point of view, is a verification or confirmation of the author's understanding of the analyzed aquifer system (Woessner 1995).

Organic and inorganic substances originating from different sources of pollution after infiltrating into the soil, migrate with the direction of groundwater flow (Pietrucin 2013). In general, in the area of the former "Zachem" Chemical Plant groundwater flows to the north and north-east to the rivers Vistula and Brda. The most important factors affecting the direction of groundwater flow include simultaneous occurrence of permeable sands and gravels together with impermeable boulder clays, buried valleys and hydrogeological windows constituting contact zone between aquifers. Groundwater flowing from the High Plane towards the Vistula Valley emerges at the surface in the form of leaks and wetlands. Precise recognition and understanding of the geological structure is the key element of credible mapping of the geological structure and hydrogeological conditions of the model, leading to the solution of the problem of chemical migration in groundwater. Emphasis should be put on the precise recognition of the location of any elements disturbing groundwater flow directions (boulder lenses and buried valleys) and bottom morphology of the aquifer. All these aspects allow to conclude that the geological structure of the area of the former "Zachem" Chemical Plant is highly complex (Czop 2010).

A numerical model was prepared based on lithological profiles of approximately 90 boreholes (wells and piezometers). The conceptual model of geological structure is composed of 3 layers which reflect lithological separations. This is the key of the description of hydrogeological conditions within the "Zachem" Chemical Plant area. Model layers were created taking into consideration their morphology and variable thickness (Figures 2, 3). The numerical model includes:

- 1st layer – Quaternary deposits predominantly present in the form of sand and locally boulder clay,
- 2nd layer – Pliocene clays and silts in the area of the moraine upland and Quaternary sands in the area of the Vistula River Valley,
- 3rd layer – Miocene sandy deposits (isolated from Quaternary aquifer in the area of High Plane and connected with them in the area of Vistula and Brda Rivers Valleys).

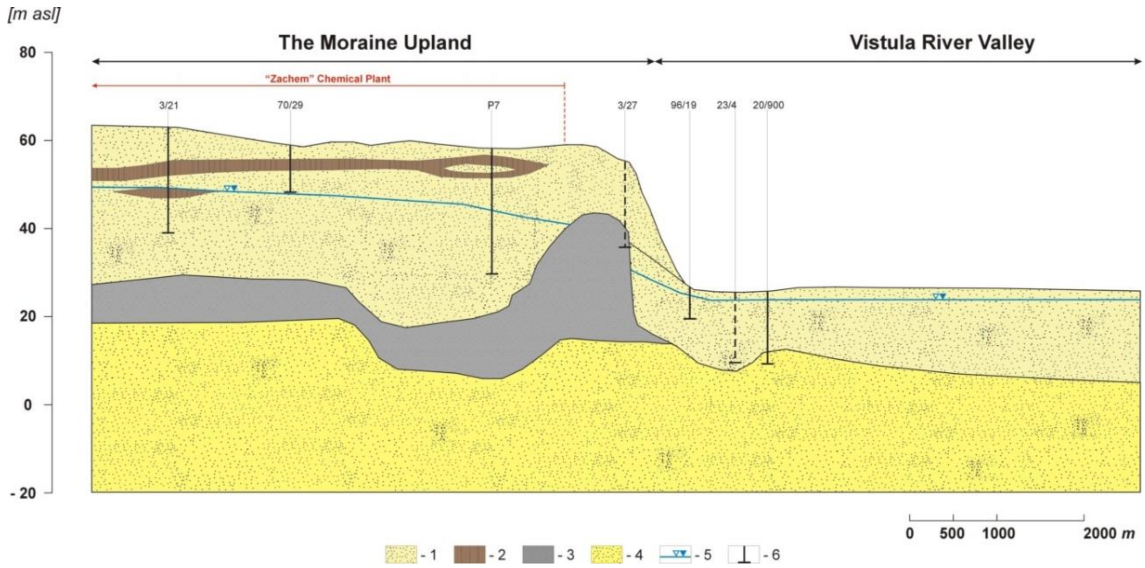

Fig 2. Geological cross-section of "Zachem" Chemical Plant in Bydgoszcz (based on Narwojsz 1987)
Legend: 1 – Quaternary sands, 2 – Quaternary boulder clay, 3 – Pliocene clay and silts, 4 – Miocene sands, 5 – groundwater table, 6 – borehole(well, piezometer)

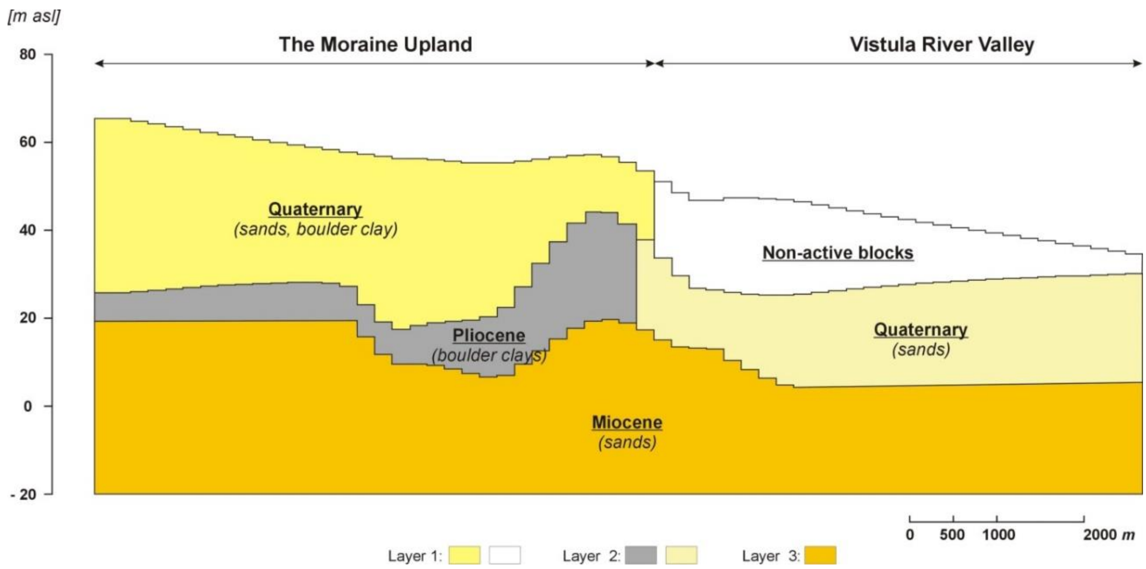

Fig. 3. Conceptual model of geological structure

Such detailed mapping of the geological structure based on a conceptual model allows to create a precise hydrogeological numerical model and to investigate the migration of chemical substances. From the viewpoint of the accuracy of modeling studies this methodology is more appropriate than the application of flat layers with constant thickness.

NUMERICAL MODEL

The hydrological model was created using the Visual MODFLOW program for the purpose of mapping the migration of chemical substances from the area of the "Zachem" Chemical Plant. Visual MODFLOW is currently the most popular and most widely used program for modeling in hydrogeology. It was developed by Schlumberger Water Services (formerly Waterloo Hydrogeologic). The creation of the numerical model is therefore the third and fundamental stage of modeling of chemical migration in industrial areas.

The model domain covers the area of a significant size of 8 km × 12 km, i.e. 96 km^2. The study area comprises both the chemical plant in Bydgoszcz and the land up to the Vistula and Brda riverbeds – this is the direction of pollution migration in groundwater from the above chemical plant. Discretization of model domain was conducted. The size of square calculation blocks is 200 meters. In total, there are 2400 blocks in one layer of the model area (60 columns and 40 lines) including the majority of active blocks.

The hydrogeological model of the analyzed area very well reflects the actual condition of hydrodynamic field, which was achieved based on field measurements of about 90 piezometers and wells. With respect to the measurement from December 2009 the differences between the actual and calculated elevations of groundwater table fall within ± 2 m for the vast majority of study sites. Larger differences occur only in about 15% of the boreholes, mainly in the area of very sharp decrease of the groundwater table at the border of the High Plane and Vistula River Valley. It is very difficult to show the accurate reflection of groundwater table morphology in this area, because a slight change in the location of a borehole gives a significant difference in the level of the groundwater table. Low values of two key statistical measures confirm good model fitness to the measured conditions: root mean square (RMS) amounts to only about 1.5 m and normalized RMS is only about 4.4%. The differences between the measured and calculated values are normally distributed (Czop 2010, Pietrucin 2013).
The main aim of creating a prognostic model was to map the directions of contaminant migration from the pollution sources in the area of the "Zachem" Chemical Plant in Bydgoszcz. Due to the complex hydrogeological conditions within this area and coexistence of both organic and inorganic chemical substances, the discussed problem is very difficult to resolve.

The simulation was performed by assuming a worst-case scenario of non-reactive pollutants' migration with the groundwater flow, i.e. no chemical reactions with the liquid (water) and solid (soil) phase. This approach to the problem allows to use the Modpath module. It was used to visualize the flow directions of contaminants and the maximal possible range of contaminant plume in groundwater (Figure 4).

The predicted ranges of contaminant plumes according to both organic and inorganic pollution migration in "Zachem" Chemical Plant should be regarded as preliminary and require further detailed studies.

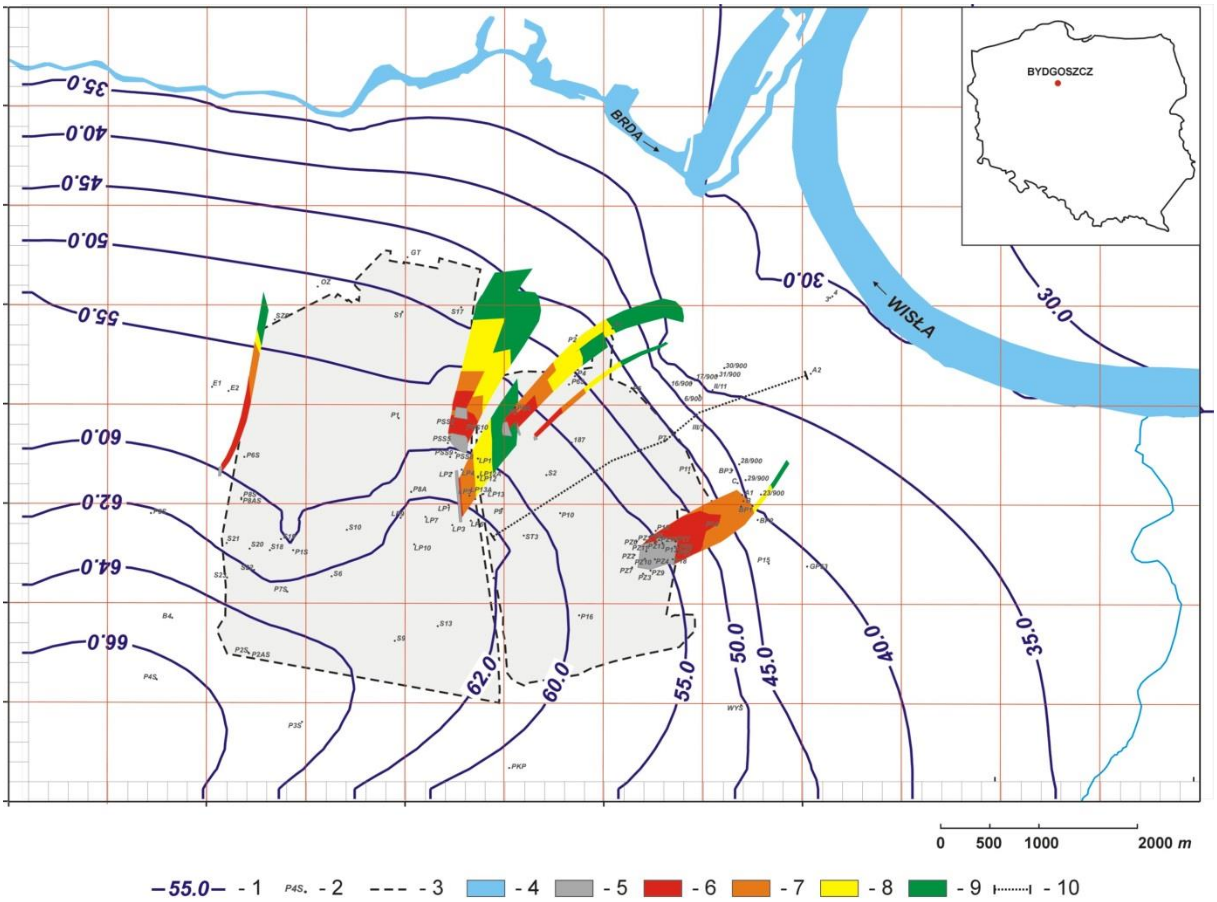

Fig. 4. Predicted ranges of contaminant plumes from pollution sources identified in the "Zachem" Chemical Plant in Bydgoszcz
Legend: 1 –groundwater table contour [m asl], 2 – hydrogeological borehole (well, piezometer), 3 – border of the "Zachem" Chemical Plant, 4 – surface water, 5- source of pollution, 6 – range of contaminant plume after 25 years, 7 – range of contaminant plume after 50 years, 8 – range of contaminant plume after 75 years, 9 – range of contaminant plume after 100 years, 10 – geological cross-section line (Fig. 3)

DETAILED STUDIES

The visualization of the contaminant flow directions and range of contaminant plume in groundwater is often mistakenly considered as the final stage of the modeling process. Authors take for granted that the border of the range is accurate and precisely mapped. After completion of a reliable conceptual and numerical models, the verification of the results should always require detailed research. Understanding of the research study area, geological structure and hydrogeochemical processes allows the authors to clarify the range of contamination. This task is relatively simple for one source of pollution and one contaminant plume but complicated and interesting conditions exist in mixing zones.

Organic substances originating from the identified sources of pollution in the area of the chemical plant (primary substance) migrate in groundwater in unchanged form or can be transformed by chemical reactions with other compounds (organic and inorganic) occurring within the contaminant plume, but new organic compounds (secondary substances) may therefore be formed in the contaminated groundwater. Because of diverse chemical composition of individual streams of contaminated groundwater and different Eh-pH conditions, chemical reactions (both degradation and the formation of new compounds) may occur in different directions. According to the world literature (Eisenhauer, 1968; Kuo et. al., 1977; Montgomery, 2000), soil and water pollutants in the area of chemical plants decompose into dozens of various substances (Figure 5). All of these transformations, due to their high complexity, are difficult to describe. Cross-reactions occur between organic and inorganic compounds and between a wide range of new products.

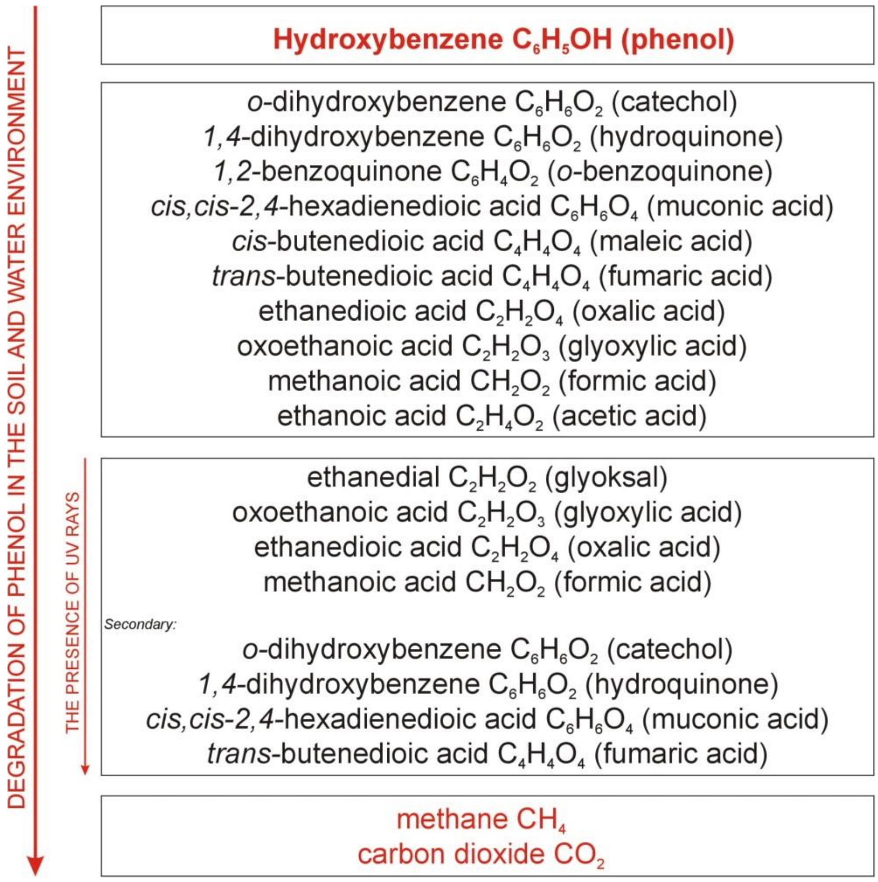

Fig. 5. Phenol degradation scheme in the soil and water environment

In the context of the contaminant plume there is also an important issue of determining the chemical composition of groundwater, taking into account the stratification of pollutants in the vertical profile of the aquifer. Such studies have been carried out at the “Zachem” Chemical Plant in the period from 2012 to 2013. Those studies were carried out under conditions of “low flow” sampling technique. Continuous measurements of variation in physicochemical parameters such as temperature, electrical conductivity, pH value, redox potential and dissolved oxygen were performed at the same time within the columns of individual boreholes (Witkowski 2009).

This technique allows for the spatial sampling of contaminant plume taking into account the stratification of the concentration of pollutants in the studied borehole: (x) samples along the length of contaminant plume from the pollution source in the direction of its drainage zone, (y) variation in the concentration from the center to the edge of plume and (z) vertical stratification in piezometer. These three monitoring directions of contamination spread in the aquifer are the most significant and allow for complete analysis and subsequent control of the contaminant plume propagation (Pietrucin 2013).

SUMMARY

Modeling of the chemical migration in groundwater in industrial, highly urbanized areas is very complicated. It also applies to the area of the discussed "Zachem" Chemical Plant in Bydgoszcz. This problem is even more complex under the conditions of overlapping impact of multiple and diverse pollution sources. Coexistence of organic and inorganic substances together with chemical reactions occurring in the aquifer in the vicinity of the studied chemical plant also cause a number of problems in this context. The only reasonable solution to this complex task is to broaden the numerical model with thorough research including accurate identification of the potential contamination. Then it is necessary to understand and map the geological structure which allows to create a target numerical model. Interpretation and critical assessment of the results justifies undertaking detailed studies. Those studies will verify ranges of contaminant plumes.

Modeling of chemical migration in the "Zachem" Chemical Plant in Bydgoszcz is one of the elements that allow for the development of an environmental reclamation plan. It is essential to purify the soil and water environment due to the real threat to the health and life of local inhabitants of Bydgoszcz and its nearby areas - Otorowo, Prątnowo, Łęgnowo. Due to very complex geology and hydrogeological conditions as well as extreme organic and inorganic contamination of groundwater, specialized remediation methods should be used in this area. These methods are designed for specific chemical compounds and individual contaminant plume.

Based on detailed analysis of chemical composition of groundwater in the context of inorganic substances and a wide range of organic compounds, particularly including the stratification of the water column in boreholes, it is planned to calculate subsequent numerical models of migration for reactive contaminants. The regional model allows to trace the directions of pollution spread in groundwater. In order to obtain a detailed analysis of the site, local models should be developed for each of the industrial waste dumps (e.g. "Zielona" industrial waste dump) or when their effects overlap - for their groups. The development and design of the optimum scenario for soil and water remediation can be based only on a reliable model. Preliminary costs of land restoration are estimated to be at least several hundred million PLN.

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