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MONITORING OF THE AQUATIC ENVIRONMENT OF AN INDUSTRIAL AREA WITH MULTIPLE SOURCES OF POLLUTION

Abstract: Chemical plants are important objects of hydrogeological research, due to their potentially large impact on the soil and water environment. The topic of this paper is one of the oldest chemical plants in northern Poland, owned by the 'Zachem' company and located in the city of Bydgoszcz. The plant is located on a 500 ha property. This area has isolated about a dozen landfills for different types of wastes. In order to make a proper estimation of the influence of a chemical plant on its environment we must first identify the geological and hydrogeological conditions, and also the character of its land-use. Field investigations must be preceded by in-depth historical studies of the plant's development and the technologies used within, and an identification of historical and present contamination sources. The author describes the current condition of the plant's groundwater monitoring and indicates the direction of modernization and further development. This paper presents the problems faced when designing a groundwater monitoring network for industrial areas.

Key words: chemical plant, groundwater monitoring, industrial dumps, migration of pollutants

Introduction

The monitoring of the aquatic environment of an industrial area is one of the most difficult problems in hydrogeology. The design of an optimal monitoring

network for a detailed assessment of water pollution should be preceded by a highly detailed appraisal of the geological structure and hydrogeological conditions in the study area. One of the criteria for assessing the nature of the hazard to groundwater and determining the possibility to limit the propagation of pollutants is a recognition of the relationship between pollutants and their sources. At the field work stage there should therefore be a detailed inventory of pollution sources located both in the industrial area and in the surrounding area. Industrial landfills, both those currently in operation and past ones (which can be identified through archival studies), constitute hazards for the environment. It is important to identify the unique profile of a chemical plant, both in terms of its production range and the technological methods it uses.

The area of the 'Zachem' chemical plant which is the subject of this research is located in northern Poland, and occupies about 500 hectares near Bydgoszcz, the largest city in the Kuyavian region. The whole area was covered with the continental glacier during the last north-Polish glaciation, which has soil, geomorphologic and also hydrological implications. There are accumulative forms of sandy, loamy and argillo-silty materials. To the north and east, the research area is bordered by the Vistula and Brda Rivers.

Hydrogeological conditions

In the area of the chemical plant, three multiaquifer formations were found: Cretaceous, Neogene and Quaternary.

The Cretaceous multiaquifer formation was identified mainly in the north-eastern part of the research area, and conducts groundwater through fine- and medium-grained sands.

The Neogene multiaquifer formation is composed of fine-grained sands from the Miocene age and is combined with Quaternary sands within the valley of the Vistula river, creating a combined Neogene-Quaternary aquifer. Recharge is from the Quaternary deposits by direct infiltration within the buried, sand-filled valley. This is confirmed by the chemical similarity of water from both multiaquifer formations. The local increase of sulphates and chlorides indicates probable aquifer contact within the buried, sand-filled valleys and contamination of Quaternary groundwater.

Due to the varied geological structure, the occurrence and flow conditions of Quaternary groundwater should be classed as complicated. Simply put,

two aquifers can be distinguished: the first and the main. Figure 1 presents the generalized geological structure.

The first (*upper) aquifer is mainly related to the presence of sands over the boulder clay which isolates the main aquifer. It reaches a maximum thickness of 5 metres, and the groundwater table is unconfined and strongly dependent on the amount of infiltration water. In a large part of the chemical plant the aquifer only occurs after periods of strong rainfall, or in wet years. This aquifer is also fed artificially in the area of wet landfills, through leaching plots and sewage leaks. The aquifer may be considered as seasonal.

The analysis of archives identifies three main areas of occurrence of the first aquifer. The largest area is in the north-east of the proglacial Vistula valley terrace where an additional source of recharge in the second half of the last century was leaching plots and ash landfills. Some water from this area flows directly north to the Brda river through a shallow, sand-filled, buried valley. The valley is developed on boulder clays and Neogene argiles. Excess water from the former ash landfill is discharged through a drainage ditch. Water from this aquifer drains into the area where the boulder clay discontinues, where it feeds the main aquifer, or in the area of erosional dissection Neogene deposits, where it forms a bog spring.
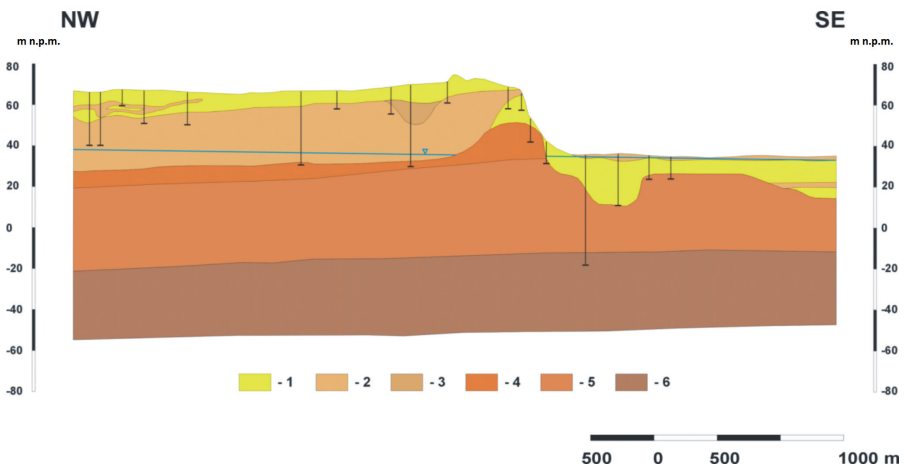
Fig. 1. Cross-section of the chemical plant (Narwojsz 1989), Quaternary: 1 – sand and gravel, 2 – boulder clay, 3 – mud and mudstone, Neogene: 4 – Pliocene argil and argillite, 5 – Miocene sand, 6 – Oligocene mud and mudstone

The second region where the upper aquifer occurs is the central area of the chemical plant where the aquifer was additionally recharged in the zone of sediment pound and a former aniline mud landfill. This water likewise feeds the main aquifer in the zones where the boulder clay discontinues. Detailed tracing of flow directions is difficult because of the large variability of the clay top and the relative thinness of the aquifer. Groundwater flow is affected by a large number of collectors and pipelines in a heavily industrialised area such as the chemical plant under discussion.

The third area of occurrence of the shallow aquifer is located in the historical leaching ponds in the north of the plant, where the aquifer combines with the top layers to form a Quaternary aquifer.

The main aquifer, with an unconfined or slightly confined groundwater table, is widely exploited in the chemical plant, and is formed of sands with a thickness of up to 80 meters within the buried valley. In the valley of the Vistula river it combines with Neogene sands, creating one Neogene-Quaternary aquifer. It is recharged by the infiltration of precipitation and from the first aquifer situated above. Groundwater flow is affected by the main operating drinking water intake for the chemical plant, barrier wells catching plumes of migrating pollutants, zones with increased conductivity (buried valleys) and places without permeable sediments.

General characteristics of the chemical plant

The chemical plant is one of the largest producers of organic chemicals in the Polish market. It was established on the site of a former German explosives factory built during World War II (Pietrucin 2012). These explosives were originally produced for the mining industry. Then, production was adapted to both military and civilian needs, producing Trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), Trinitrophenylmethylnitramine (tetryl). It also produced dinitrotoluene (DNT), nitrobenzene, aniline, products from recycled PVC, dyeing intermediates, dyes, pigments and phenol. The plant's production featured both acid denitration and nitrational acids. In the early 1960s, experimental isocyanate systems, bisphenol A and polycarbonate production were all trialled, and studies were carried out for the production of a polyurethane complex. In the next decade, the plant invested in the production of flexible polyurethane foams, brine electrolysis installations, phosgene, DNT, toluenediamine (TDA), toluene diisocyanate

(TDI), epichlorohydrin (EPI) and rigid foam and PUR foam fittings for the automotive industry. The chemical plant production profile has evolved over the decades, catering to the needs of the market and the political and economic situation of the country. In the context of industrial history, the plant was subject to investment stagnation in the last century, due to Polish economic troubles (www.zachem.com.pl 2012).

The basic and most important products manufactured in the plant are e.g., toluene diisocyanate (TDI), allyl chloride, epichlorohydrin (EPI), hydrochloric acid, sodium hydroxide and sodium hypochlorite.

Until recently, one of the branches of production was manufacturing, and products produced on a significant scale included polyurethane foams. These compounds (polyurethane PUR or PU) are polymers which are prepared using additional polymerization, multifunctional isocyanates, amines and alcohols.

In polyurethanes, the main distinguishing feature from other polymers is the presence of urethane groups [-O-CO-NH-] in their main chain. Quantitatively, the most important application of polyurethane is in foams. Foams are used in the furniture industry (mattresses and upholstery), in the automotive industry (upholstery, rigid foam bumpers, interior parts, shock absorbers), and in the construction and textile industries (sponge-lined fabric, warmer fabric). The last use of these materials is bath sponges, a variety of insulating materials, sealing kits, binders and glues.

Analysing the composition of the produced compounds, a strong link can be seen between the type of production and contaminants getting into the Quaternary aquifer groundwater.

At this stage, it is important not to forget the chemical plant's ecological activities. Since the middle of last century, technologies have been periodically improved and investments have been made in environmental protection. In the late nineties, a manufacturing restructuring program was developed with a particular emphasis on ecology. At the time, installations with potential hazards for the environment (e.g., phenol, aniline, nitrobenzene and a number of dyes) were closed. Unfortunately, a coherent program of action is lacking. The collaboration between many groups of hydrogeologists which resulted in the existence of the groundwater monitoring network is not restoring the actual quality of the Quaternary aquifer.

Inventory of pollution sources

One factor which particularly distinguishes this industrial area is the creation, over the decades, of a number of pollution sources over a relatively small area. Large sources of pollutants existing for many years, such as municipal landfills, settling or sedimentation ponds significantly increase the load of pollutants infiltrating through the vadose zone to the groundwater. The extent of the industrial infrastructure is having a potentially negative impact on the environment. The whole industrial area is generally regarded as environmentally hazardous. A more detailed analysis of the ground often reveals the presence of several, often overlapping, contaminant plumes, as well as zones of relatively good quality water.

In the course of the inventorisation of the chemical waste dumps in the chemical plant, 13 sources of pollution were catalogued: 3 currently being exploited, and 10 historical. Most of them have only fragmentary or non-informative documentation. During the inventory of industrial waste dumps the analysis has led to the location of landfills, the identification of their year of establishment, the nature of their use and also the types of waste deposited and details of the method of their disposal. This knowledge allows us to determine the occurrence and regionalization of groundwater pollution, identify the degree of groundwater contamination and determine the reasons for its occurrence, as well as to classify the types of pollution and the relative scale of the risks and dangers. The inventoried industrial waste dumps are summarized in Table 1.

Table 1. Inventoried dumps in the chemical plant area

No.	Industrial waste dumps	Foundation year	Explanations
1	General Works landfill	1956	Inactive
2	Ash and brain mud landfill (EC II)	–	Inactive
3	Sediment pound of deposits after EPI neutralization	1977	Inactive
4	Aniline mud dump site	1950	Inactive
5	3 aniline mud pounds	1950	Inactive

Table 1. contd.

No.	Industrial waste dumps	Foundation year	Explanations
6	Mud holes (WT-12)	1962	Inactive
7	Landfill holes in the area of synthesis I and II (Lisia landfill)	1972	Inactive
8	Sludge pounds from the industrial water intake station	1940– 1945	Active
9	Paved sludge drainage place		Inactive
10	Combustion site (Glinki/Dąbrowa)	–	Inactive
11	Combustion site (Zielona)	–	Active
12	Combustion site (Żółwin)	1950	Inactive
13	Central tank of averaging sewage	1977	Inactive
14	Isolated sediment waste landfill	–	Active

Analyses of the types of industrial waste have identified high concentrations of pollutants detrimental to groundwater quality. Selected components are summarized in Table 2, including both organic and inorganic pollutants. The concentrations of compounds and limit values for drinking water have been taken into account. Groundwater samples were collected from the piezometers in the chemical plant's monitoring network.

The pH values of groundwater samples range from slightly acidic to alkaline. The waters are strongly contaminated with organic compounds such as phenols, aniline, nitrobenzene or polycyclic aromatic hydrocarbons. The concentrations of all these components vary over an extended range, wherein extremely high values are reached: 61.2 mg/dm^3 for nitrobenzene, 81 mg/dm^3 for aniline and 820.1 mg/dm^3 for phenols.

Table 2. Groundwater pollutants in the area of the chemical plant

Component	Unit	Concentration		
		Min (1)	Max (1)	Limit value (2)
pH reaction	–	6.4	9.5	–
PAH's	µg/dm³	n.d.	1.35 (fluoroethene + pyrene)	0.1
Aniline	µg/dm³	n.d.	81000	–
Nitrobenzene	µg/dm³	n.d.	61180	1.0
Phenols	µg/dm³	0.088	820120	–
Nitrates	$mgNO_3/dm^3$	0.02	100	–
Sulfates	$mgSO_4/dm^3$	28.4	1947.8	250
Iron	mgFe/dm³	0.4	40	–
Calcium	mgCa/dm³	61.6	1222.4	–
Magnesium	mgMg/dm³	6.6	168	125
Chlorides	mgCl/dm³	8.7	6745	250
Sodium	mgNa/dm³	n.d.	9040	200

Comparing the results with acceptable standards for drinking water, the limit for PAH content was exceeded nearly 14 times and for nitrobenzene over 60,000 times. Of the inorganic compounds it is worth noting the high content of sulphates (1,947.8 mg/dm³), which exceeded water quality standards by about 8 times and the level of calcium (1,222.4 mg/dm³). The concentration of chlorides in the Quaternary groundwater (6,745 mg/dm³) exceeds the limit by about 27 times, while the sodium content of up to almost 10 g per litre of water (9,040 mg/dm³) exceeded the drinking water standard about 45 times. Such high concentrations of the aforementioned parameters require the mobilisation of remedial environmental action.

Due to developments in our knowledge and technical capabilities, it is feasible to attempt to restore the environment to a satisfactory condition. These activities cannot take place without a thorough diagnosis of the

state of pollution of the soil and water environment, including the range of contaminant plumes and the specific distribution of individual pollutants.

Migration of pollutants

In hydrogeology, as in all sciences, there is a need to use models. According to Motyka (1989) 'each model is a formalized structure used to map the set of phenomena that have a connection to each other'. Models can be divided into tangible (map, pattern volume) and intangible (conceptual). Any description of a phenomenon or process (the conceptual model) is subjective. It is a representation of the actual process consistent with the author's knowledge and suppositions. It is also adapted to the fit the purpose for which the model is intended (Motyka, Postawa 2004).

An accurate diagnosis of the migration of pollutants in an aquifer provides valuable information on the shape and extent of a contaminant plume. To this end, a mathematical model of the chemical plant area was created using the Visual MODFLOW program. In the first stage, a conceptual model was developed (Fig. 2) mapping the natural state of the geological structure in a simplified (but as accurate as possible) schematic. The distinctive structure of the Vistula River Valley with its steep slopes, and also the hydraulic contact of Quaternary multiaquifer formations with the Miocene aquifer should both be noted.

An increased level of chlorides Cl$^-$ relative to the hydrogeochemical background can be used to track the migration of pollutants in the groundwater. The mathematical model presented here was performed for the migration of chlorides. Chloride ions do not participate in the processes of oxidation and reduction, and it practically does not participate in the processes of adsorption-exchange. It only creates complex compounds to a very limited extent. It is the fastest migrating ion in groundwater (Hem 1970; Perelman 1971; Macioszczyk 1987). It can be used to assess the velocity of groundwater flow, and as a reference for comparing the migration of water (Motyka, Postawa 2004).
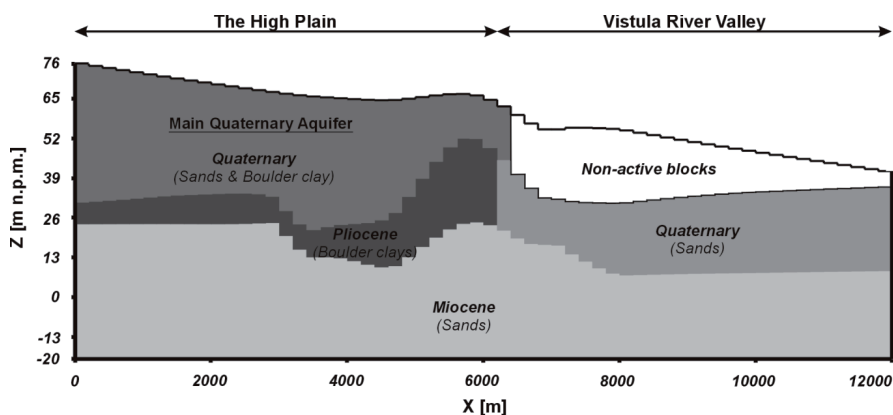
Fig. 2. Conceptual model of chemical plant base (Czop 2010)

The Quaternary deposits of the high plain and also of the Vistula River Valley are generally shown in the conceptual model as aquifers. The Quaternary deposits in the high plain area also have a diversified hydrogeological character: sands are permeable and boulder clays are impermeable. The use of real data from monitoring research played an important role in the construction of the conceptual model of the chemical plant. The direction of movement of contaminant plumes was also the tracer for the evaluation of groundwater pathways. The Pliocene is represented by impermeable deposits. Knowing the location of some of the waste dumps in the chemical plant, their contents were investigated and the migration of contaminants in the aquifer was traced. The result of this simulation is shown in the map below (Fig. 3). (Monitoring data from selected piezometers.)
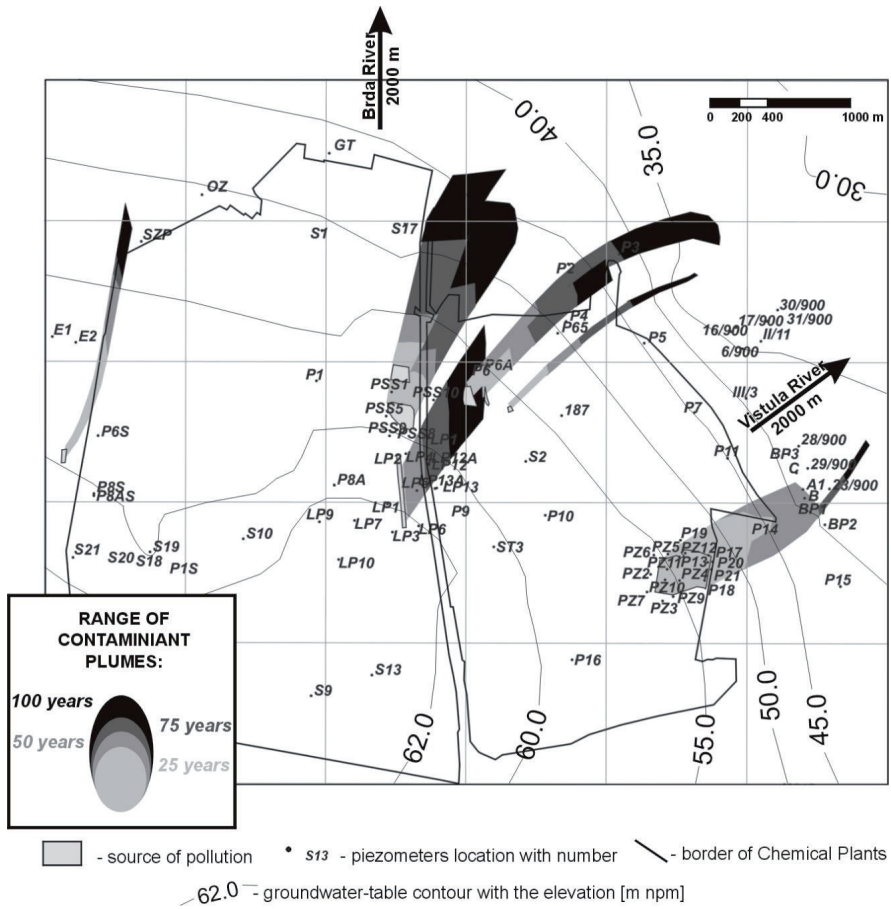
Fig. 3. Migration directions of contaminant plums (Czop 2010)

Numerical data from modeling was fitted to the real data from groundwater table measurements with an accuracy of about 4%. Values for residuals ($\Delta H = H_{CALCULATED} - H_{MEASURED}$) range from -4 m to +4 m, but the bulk of them are within ±2 m (Fig. 4).
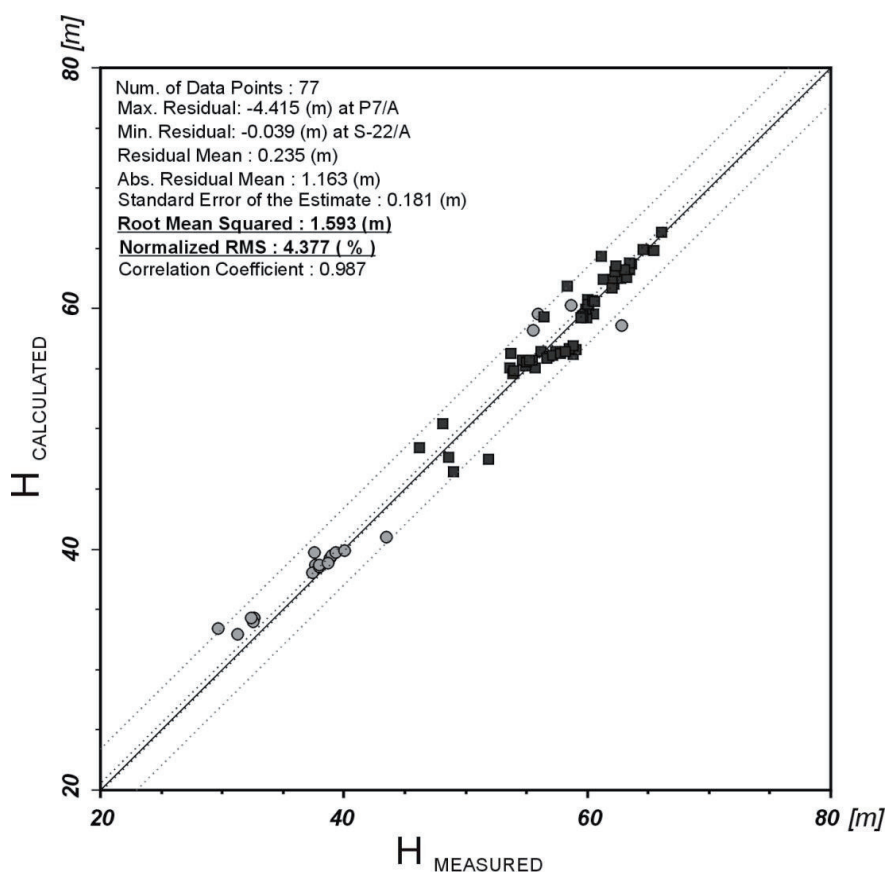
Fig. 4. Mathematical model calibration (Czop 2010)

The absolute residual mean for the model of the chemical plant is only about 1.2 m. The results fall into a normal distribution.

From a hydrogeochemical point of view, the most interesting area is the mixing zone in a contaminant plume. Here a number of chemical reactions take place which are difficult to monitor. Across the contaminant plume both organic and inorganic substances were found. The presence of inorganic substances in difficult oxidation-reduction stages, with varying Eh parameters, results in a lot of speciation. An example of this is sulphur, which is found in several speciations; as S^{2-}, H_2S, S^0 and SO_4^{2-}. Organic substances in the course of migration occur in an aquatic environment in the form of primary products and various reaction products (derivatives). Secondary products

(derivatives) can be both organic or inorganic. Chemical reactions can take place between organic compounds, primary substances, decay products and also between the same derivatives, creating new products in the aquatic environment. Due to the overlapping of contaminant plumes, cross-reactions can occur between organic substances (primary and secondary compound products) and inorganic substances (of different speciations).

Awareness of the hydrogeochemical complexity of the problem allows us to trace the results of chemical analyses of water samples more fully than can be done through archival materials. Knowledge of storage times and decay products also allows us to predict which of the organic compounds were originally deposited in a current or historical industrial waste landfill. During the design of a groundwater monitoring network of industrial areas with multiple sources of pollution, all the problems cited in the article must be taken into account. This includes a detailed geological structure survey with an emphasis on the morphology of the bottom of the aquifer and impermeable interlayers. Subsequently, it is important to undertake hydrogeological studies and detailed studies of archival material relating to industrial waste landfills. After identifying contaminants and their sources, correlated with the chemical plant's production, the design not only of the location of piezometers in a monitoring network, but also of a sampling methodology, can begin. In such complex geological-hydrogeological conditions, spatial sampling of contaminant plumes is extremely important. It is therefore necessary to remember to take samples along the length of a contaminant plume from the landfill in the direction of its drainage zones (x), as well as to determine the variation in concentration from the center to the edge of plumes (y). Vertical sampling must take into account the stratification of concentrations of the substance in the piezometers (z) – Figure 5.

Stratification results in variations in the concentration of a parameter (the concentration of contaminants) within the contaminant plume. All three directions must be taken into account when monitoring the spread of contaminants in the aquifer in order for a full analysis, and then control of, the propagation of contaminant plumes to be possible. During sampling, the author recommends the use of the 'low flow' technique; pumping with a small yield of approximately 0.5–1.0 l/min. This technique, however, is possible only in the case of a fully-filtered observational borehole. The boreholes in the area of the studied chemical plant are of just such a construction.

Thus, it is possible to sample the water column with an accuracy of 1 m (in the 'z' direction).
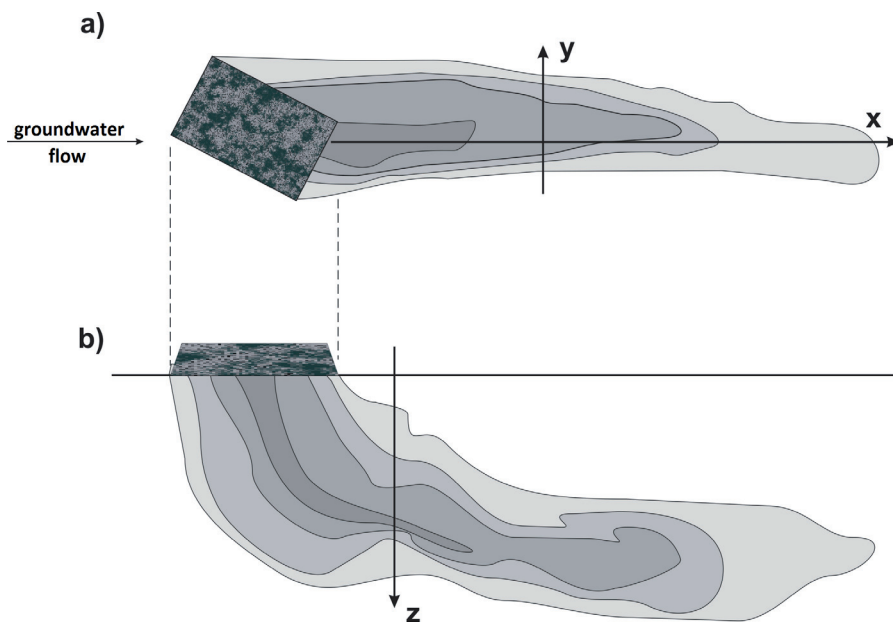

Fig. 5. Scheme of three-directional sampling a) plan, b) cross-section

Summary

There are two aspects to the issue of monitoring of the aquatic environment in industrial areas. The first is a reconnaissance of the area, including geology, water conditions and local drainage zones. Seemingly simple geological conditions can turn out to be complicated because of an impermeable interlayer seriously disturbing the flow directions of quaternary groundwater. The second aspect is that of sampling, which includes a full recognition of contaminants and chemical plant production. The assessment of groundwater pollution is based on research, including archival materials, and a thorough analysis of the development of the industrial (Fig. 6).

The most problematic parts of a chemical plant are the mixing zones of contaminant plumes. An understanding and ability to explain the chemical reactions taking place in this area are the key to the proper design of a groundwater monitoring network. Furthermore, it is important to pay

attention to the sampling of the dispersion of contaminants in the aquifer, taking into account the three directions (x, y, z).
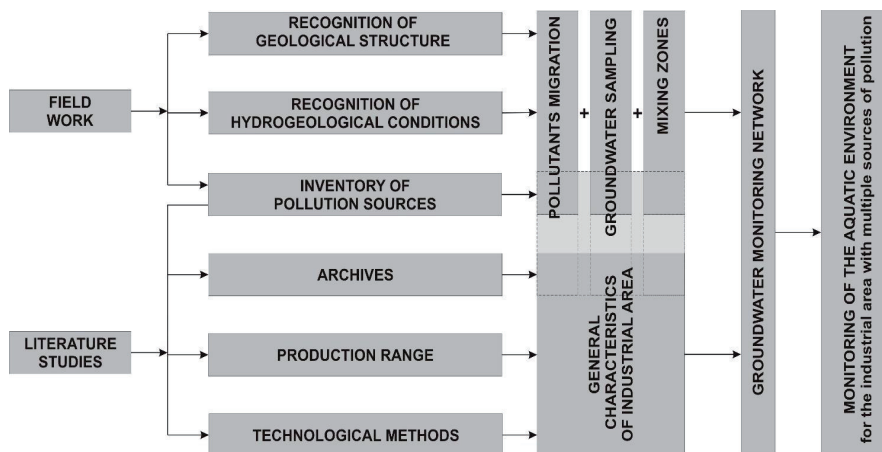

Fig. 6. Scheme activities to establish monitoring of the aquatic environment for the industrial area with multiple sources of pollution

It is necessary to coordinate research to assess the degree of contamination of groundwater in the area of a chemical plant. Creating an optimal monitoring network is possible only after fulfilling the several requirements raised in this article. The functionality of such a network should also take into account any future remedial actions to be taken in the chemical plant.

Acknowledgements

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