

# INCORE — CONTRIBUTION TO STUDIES OF THE POST-INDUSTRIAL URBAN AREAS POLLUTION; A CASE STUDY: BYDGOSZCZ OLD GASWORKS, POLAND

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Abstract. The INCORE (Integrated Concept for Groundwater Remediation) project was conducted within the 5<sup>th</sup> Framework Programme of the European Union. Its main purpose was to test in practice the method of plume backtracking for pollution source detecting. Observations of changes in concentration of alien chemical substances during the imission pumping tests (IPT) of boreholes set along a control plane allow for identification of plume parameters and possible source localisation. The test site in Poland was located in the Bydgoszcz town in the north-central Poland. In the area of the old gasworks, the polycyclic aromatic hydrocarbons (PAHs) and volatile chemicals of BTEX group were recognised as the main thread to groundwater quality. One control plane, consisted of 21 small dimensions boreholes, was set up perpendicularly to the groundwater flow direction. It was also parallel to the Brda river, draining the investigation area. The imission pumping tests were conducted along this control plane, and samples were collected for BTEX and PAH concentrations laboratory analysis. The concentrations of BTEX were determined within the range of less than detection limit up to some thousands  $\mu g/l$ , but in the most samples they exceeded the drinking water standards. Benzene and, in less quantities, toluene were found as dominant species. The PAHs concentration in many samples exceeded the value of 10,000  $\mu g/l$ , and compounds of smaller number of rings such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene were prevailing in their composition.

Key words: groundwater, pollution, old gasworks, PAHs, BTEX.

Abstrakt. Projekt INCORE (Integrated Concept for Groundwater Remediation) przeprowadzony został w ramach 5-tego Programu Ramowego Unii Europejskiej. Głównym jego celem było sprawdzenie w praktyce metod wstecznego śledzenia smug zanieczyszczeń w wodach podziemnych (*plume backtracking*) dla identyfikacji ognisk zanieczyszczeń. Parametry badanych smug zanieczyszczeń określano na podstawie zmiany stężeń substancji w czasie testowych pompowań imisyjnych (IPT) otworów hydrogeologicznych umieszczonych wzdłuż odpowiednio zaprojektowanych płaszczyzn kontrolnych. W Polsce do badań wytypowano obszar starej gazowni miejskiej w Bydgoszczy. Głównymi zanieczyszczeniami stwierdzonymi na tym terenie były wielopierścieniowe węglowodory aromatyczne (WWA) oraz węglowodory lotne z grupy BTEX. Testowe pompowania imisyjne były prowadzone w 21 małośrednicowych otworach badawczych, umieszczonych w płaszczyźnie kontrolnej prostopadłej do głównego kierunku spływu wód podziemnych, w badanej przypowierzchniowej warstwie wodonośnej i jednocześnie równoległej do koryta rzeki Bzury, drenującej teren gazowni. Analizy laboratoryjne pobranych próbek wód podziemnych wykazały zawartości węglowodorów lotnych w przedziale od poniżej granicy wykrywalności do kilku tysięcy mikrogramów w litrze. W większości pobranych próbek oznaczone ilości BTEX przekraczały dopuszczalne stężenia w wodach pitnych. Przekroczenia dotyczyły głównie benzenu i w mniejszym stopniu toluenu. Stężenia WWA w wielu próbkach przekroczyły wartość 10 000 mg/l, przy czym stwierdzono dominację związków o mniejszej liczbie pierścieni, takich jak naftalen, acenaftylen, acenaften, fluoren, fenantren i antracen.

Słowa kluczowe: wody podziemne, zanieczyszczenie, stara gazownia, WWA, BTEX.

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## INTRODUCTION

The main objective of the INCORE (Integrated Concept for Groundwater Remediation) Project, conducted within the 5<sup>th</sup> E.U. Framework Programme, was to establish the optimal method for groundwater study. This method should enable: (1) to carry out the scientific and economically effective exploration of the buried sources of soil and groundwater pollution in the urban areas that for many years were occupied by industrial plants, and (2) to assess the existing hazard to the environment and the human beings. The industrial plants, originally located outside the city limits (primarily on the river banks), are presently "absorbed" by the expanding urban agglomerations. These plants are situated inside towns, not infrequently near the housing estates. These areas, utilised by the industrial plants for decades, are characterised by the presence of various pollution sources as well as by the pollution of shallow groundwater.

The methodical INCORE concept, which consisted of measuring the total hazardous emissions in the whole post-industrial area and of backtracking the pollution plumes, was elaborated at the Tübingen University (Ptak, Teutsch, 2000). Based on this method, the studies have been conducted in the selected urbanised areas of Germany, Austria, Italy, France, and Poland, i.e. in the areas of the different groundwater conditions, with different number of existing measurement points, and of the different pollutants concentration ranges and sizes. They represented a cross-section of conditions that may be expected in other European industrial areas.

In Poland, a testing ground for the INCORE Project was selected in an area of Bydgoszcz town old gasworks, located close to the Brda River in the present Bydgoszcz city centre. Production of gas from the hard coal in the mid 19<sup>th</sup> and early 20<sup>th</sup> centuries was especially hazardous to the environment due to: (1) the small efficiency of gas and technological sewage pu-

rification facilities, and (2) the applied waste management methods, i.e. waste disposal within or near production sites, including burying, use of the solid wastes for ground levelling, and spilling the liquid wastes into the ground. The gas production at the Bydgoszcz town gasworks started in 1860 and ended in 1979 (Hoppe, Perlińska, 2000). During its history, the gasworks was destroyed and rebuilt many times. As a result of the World War II and the closure of gas production in 1979, many installations (including the underground ones) were heavily damaged. That was the main reason why within the gasworks area, not only the polluted soils around the individual facilities but also different randomly polluted sites may have occurred. The search query of the old plans and records indicated several other gas purification or underground waste disposal sites to those visible now, containing for example, post-distillatory tars, ammonia water, benzene etc.

A year before the beginning of the EU project, the PGI scientific group carried out a preliminary geologic and hydrogeological reconnaissance of the Bydgoszcz gasworks area what enabled the preparation of the pertinent INCORE project proposal. This study indicates that the greatest chemical hazard to the groundwater in the Bydgoszcz gasworks area is caused by the penetration of polynuclear aromatic hydrocarbons (primarily naphthalene) and volatile organic compounds of BTEX group (primarily benzene) derived from the tar wastes deposited underground (Bojakowska, Irmiński, 2002).

During this phase of investigation, soil samples collected from several other old gasworks in the Kujawy–Pomorze Province were additionally chemically analysed. The results indicated a major pollution of the post-gasworks sites with polynuclear aromatic hydrocarbons (Bojakowska, Sokołowska, 2003). The historical examinations, essential for the study of the old industrial locations, were performed in Bydgoszcz, too.

## SCOPE AND METHODS OF INVESTIGATION

After the dominant direction of the groundwater flow in the first Quaternary aquifer had been identified, 21 small diameter piezometers, up to 6 m deep on average and located about 10 m one from another, were drilled. These piezometers, located along the Brda river bank within the gasworks segment, made up a control plane (Fig. 1). During the drilling work, numerous new data on the pollution type and extent were obtained. Moreover, the expected range of filtration coefficient (k) was determined, and other parameters of aquifuges and water permeable beds were described, for example, the morphologically diversified top of Tertiary clays (variegated clays) covered with residual pavement. In addition, the erosional troughs, filled with pebbles and extending towards the Brda river (zones of privileged, more rapid water flow), were discovered. Some of the anthropogenic sediments and muds contained semi-fluid tars, apparently buried together with other wastes (cinders, debris) during the plant operation and the formation of artificial embankment on the river meander.

During the field work, 5 series of individual borehole pumping with sampling and simultaneous in-situ measurements of physico-chemical parameters (conductivity, pH, temperature and oxygen content) in a flow chamber were conducted. This way, an innovative method of immission test pumping (ITP) was used to indicate the flow channels, i.e. organic pollution plumes flowing through the control plane. The samples collected from each test pumping were transported on the same day to the Central Chemical Laboratory of the Polish Geological Institute. This is an accredited laboratory in groundwater analyses with a multiyear experience in the organic pollutants determination. The main reason for such a standard of conduct was the necessity of analyses of easily volatile compounds and the extraction of PAHs.

The analyses of BTEX (benzene, toluene, ethylobenzene,1,4-dimethylobenzene, 1,3-dimethylobenzene, naphthalene) in water samples were performed with a HEADSPACE (19395A) system — gas chromatograph (5890II), equipped with a mass spectrometer detector



Fig. 1. Direction of the groundwater flow (Sept. 30, 2002) and localisation of the control plane along the Brda river

(5971 GC/MSD Hewlett-Packard), and a HP-FFAP polar capillary column. The analysis was conducted with an internal standard (DWM-570 certified standard, ULTRA Scientific).

The following polynuclear aromatic hydrocarbons (PAHs) were determined in water samples: acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene. Each sample used for the determination of organic matter was desulphured and extracted by a liquid-solid extraction method using a Kuderna-Danish apparatus. The applied solvents included dichloromethane PAHs which were detected by a gas chromatograph equipped with a mass spectrometer detector (Hewlett-Packard GC/MSD, model 5890II/5971). Separation was done using a HP-5MS non-polar capillary column (1.: 25m, i.d.: 0.20 mm, film: 0.33 µm). The temperature was set at 70° to 300°C, with a rate of 10°C/min (to 200°C), then 2,5°C/min (200-300°C), and held for 7 min. The mass spectrometer detector worked at 280°C in a SIM (Single Ion Monitoring) mode. The following internal standards were used: PM-612 from ULTRA Scientific, and benzo(a)pyrene and perylene from Promochem.

#### **RESULTS AND DISCUSSION**

The concentration of BTEX compounds in the water samples collected from the test boreholes varied from below detection limits to several thousand  $\mu g/l$  (Table 1), in most of the samples exceeding allowable concentration limits for water. Of the BTEX compounds, benzene and some toluene are prevalent. Ethylobenzene and xylenes reveal considerably lower concentrations. The very high contents of BTEX, exceeding several thousands  $\mu g/l$ , were recorded in the water samples collected from boreholes G11–G18; the highest levels (above 10,000  $\mu g/l$ ) were noted in wells G14 and G12. The raised concentrations of these compounds (above 1,000  $\mu g/l$ ) were observed in the water derived from boreholes G3 and G4.

The PAHs contents in the examined water varied from several to several thousand  $\mu g/l$ , with 2-ring naphthalene prevalent. Of the remaining PAHs, 3-ring compounds were predominant. The determinations of PAHs in the water samples indicated that despite distinct variability in the concentrations of these compounds in individual wells, the PAHs spectrum in the water of neighbouring wells was similar. For example, the water samples collected from wells G1–G7 were characterised by the lowest concentrations of PAHs compared to those collected from other wells; the level of PAHs averaged about several  $\mu g/l$ . The water samples from wells G1–G4 primarily contained acenaphthene and acenaphthylene whereas those from wells G5–G7 — additionally fluorene and phenanthrene. The water samples from wells G8–G10 revealed far more PAHs: varying from several to tens µg/l, and their spectrum was completely different from that observed in the remaining wells. The PAHs spectrum of these wells was visibly distinguished by the presence of 4-, 5and 6-ring compounds. The water samples collected from wells G11-G18 showed the highest concentrations of PAHs exceeding several hundred µg/l, and from well G18-even several thousand µg/l. The PAHs spectrum of these wells is characterised by prevalent 3-ring compounds. The water samples from wells G19–G21 contained distinctly lower concentrations of PAHs, averaging tens of µg/l; their PAHs spectrum was similar to that of wells G11-G18, although with a relatively minor contribution of compounds with more ring in a molecule. Based on the similar content and spectra of PAHs in the water samples derived from wells grouped in such a way, the mean concentrations of different PAHs from all the pumping were calculated and adequately plotted.

The diverse concentrations and spectra of PAHs in the examined water are undoubtedly linked to the type of and distance from the pollution sources, and the different solubility of these compounds in water. Water from the wells located far from the pollution sources was characterised by the lowest PAHs contents; in addition, this water was represented by a 3-ring hydrocarbons showing relatively higher solubility in water. Water from the wells located near the pollution sources showed not only a higher level of PAHs but also a higher participation of compounds with more ring in a molecule.

## Table 1

Well	Concentration [mg/l]						
	benzene	toluene	ethylobenzene	1,4-dimethylo- -benzene	1,3-dimethylo- -benzene	1,2-dimethylo- -benzene	BTEX sum
G1	185	n.o.	n.o.	n.o.	n.o.	n.o.	186
G2	65	n.o.	n.o.	n.o.	n.o.	n.o.	66
G3	1,102	3	46	12	12	6	1,180
G4	904	8	48	14	12	17	1,003
G5	140	1	5	1	1	1	150
G6	34	2	1	1	2	1	41
G7	711	4	50	12	3	20	800
G8	6	n.o.	n.o.	n.o.	n.o.	n.o.	7
G9	1	n.o.	n.o.	n.o.	n.o.	n.o.	2
G10	104	19	10	12	21	27	193
G11	2,281	1,443	205	260	573	446	5,208
G12	4,624	3,194	321	370	958	644	10,110
G12`	3,840	2,605	288	323	822	553	8,430
G14	4,748	3,421	315	470	1,266	808	11,027
G15	1,894	1,316	223	284	728	476	4,921
G16	1,250	793	173	167	435	273	3,091
G17	2,594	1,510	351	266	678	407	5,806
G18	1,775	1,455	373	515	1,212	780	6,110
G19	31	9	101	27	27	52	247
G20	12	4	1	1	2	1	21
G21	1	2	1	1	2	1	8
G22	1	1	n.o.	0	2	1	6

### Average concentrations of BTEX in groundwater

n.d. - below limits

The determinations of benzene, toluene, ethylobenzene, xylenes and  $\Sigma 17$  PAHs in 110 samples enabled not only to create the detailed database but also to obtain curves showing the relationship between pollutants concentrations and pump-

ing time or the depression cone radius. Some of these curves are presented on Figure 2. This has let us to prepare maps of PAHs concentrations along a cross-section line (Fig. 3). Moreover, the inferred parageneses of organic compounds were de-



Fig. 2. Some of the concentration curves from ITP pumping



Fig. 3. Spatial distribution of BTEX and naphthalene concentrations detected during the different immission pumping from the groundwater outflows in the gasworks area

scribed. This has also enabled to conclude on the character and type of the pollution sources. The comparison of these elements (chemical composition, width and azimuth of pollution plumes) with the results of historical studies made possible to indicate sites commonly buried or built-up in the old industrial area. These sites have still been the sources of chemical substances hazardous to the environment and the humans.

The preliminary study indicated that in the area of the Bydgoszcz old gasworks, the migration pathways of pollutants to the reservoir, i.e. Brda river, are too short to make the pollutants natural attenuation and dispersion more effective. However, the final assessment of these possibilities, encompassing also the selection of optimal water purification methods, requires the implementation of the second investigation phase. The fact of full understanding and good co-operation between the three interested institutions, i.e. the property owner, the city administration and the research institute, should be emphasised. Thanks to that, the obtained results may be a starting point for a reclamation project of the old gasworks area. At least two institutions, i.e. the Gas Company and the Bydgoszcz Municipality, are interested in this project because the hazardous pollutants cross the plot boundaries jeopardising recreation areas outside the gasworks area, and additionally leading to degradation of Brda river water quality. Such problems require special management of the polluted groundwater by the city municipality (Boroń, 2003).

The presented data were prepared for the research group engaged in the INCORE Project, and carried out an assessment of the health risk. This study was performed by the Institute of Ecology of the Industrialised Areas in Katowice.

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