

## INTRODUCTION

Geochemical mapping of Poland carried out in 1990–1995 has provided evidence that the Silesia-Cracow area is the most polluted region (Lis, Pasieczna, 1995a). Many years' mining and processing of mineral deposits along with increasing demand on raw mineral resources resulted in the large-scale migration of people into this region, causing growth of cities and development of the Upper Silesia agglomeration, which has become the largest and the most populated area in Poland.

The level of environmental pollution of the region (especially by heavy metals and other toxic elements and compounds), harmful to the fauna, flora and human health, is similar to that found in other Europe's regions of long-lasting hard coal mining and processing of ore deposits. Regional studies (Lis, Pasieczna, 1995b, 1997) enabled characterising of the areal extents and magnitudes of the most significant pollutants. Mapping works on 'Detailed geochemical map of Upper Silesia, scale 1:25 000' (SMGGŚ) started in 1996. The elaboration is represented by a number of atlases prepared for successive map sheets. It provides information useful for both environmental management and making decisions by local authorities.

Geochemical mapping at the scale of 1:25 000, carried out in the Mysłowice Map Sheet M-34-63-A-d area is the continuation of detailed serial mapping works initiated by a pilot project of the Sławków Map Sheet (Lis, Pasieczna, 1999). The project was ordered by the Ministry of the Environment and financed by the National Fund for Environmental Protection and Water Management.

The map sheet covers the eastern part of Mysłowice (districts: city centre, Słupna, Brzęczkowice, Morgi, Brzezinka, Larysz, Kosztowy, Krasowy, Hajdowizna and Dzieńkowice), western districts of Jaworzno (Długoszyn, Dąbrowa Narodowa, Łubowiec, Pszczelnik and Jeleń) and the southern part of Sosnowiec (districts: Niwka, Modrzejów and Jęzor). The whole area is located within the catchment of Przemsza River that starts in the Jęzor district (its historical name is The Triangle of Three Emperors (Trójkąt Trzech Cesarzy) where the Czarna Przemsza and Biała Przemsza rivers join. In its lower course, the Przemsza River is the border between Mysłowice and Jaworzno.

This region is an industrial (mining, energy and machinery industry), anthropogenically altered area. Forested areas occur mainly in the north-eastern part of the sheet.

Hard coal mining has always been the dominant industry in the Silesia region. Historical mines were located mainly along the Przemsza River valley due to favourable conditions for river transport. Power industry as well as zinc and iron smelting accompanied hard coal mining activity. The traditions of power industry in the Jaworzno region date back to the 19th century. In 1995, industrial restructuring resulted in establishing the Jaworzno III Power Plant company wholly owned by the State Treasury, gathering all the Jaworzno power plants.

The Mysłowice Sheet area is also a region of historical smelting industry. Significant development of smelting industry in this region took place in the 18th century. Iron was smelted from local bog ore deposits. Zinc and lead ores were supplied to Mysłowice from mining areas near Bytom (Mysłowice..., 2009). Zn–Pb ores mining was also carried out on site near Długoszyn and Rudna Góra (Szuwarzyński, Panek, 1977). The Leopoldine, Hustine, Stanislaus, Dar Jana, Eduard and Teresa smelters and the Kunegunda rolling mill were located in Mysłowice (as far as Kosztowy and Dzieńkowice).

Some regions of the sheet also have high natural values. The original landscape at sites of opencast mining of raw materials was highly altered and the areas became habitats of specific and valuable flora. These are the Krasowy and Dzieńkowice quarries (after limestone extraction) and the Wygonie-Kępa and Długoszyn quarries (after ore-bearing dolomite extraction). Water ponds and large reservoirs as well as the banks of river valleys are the habitats of rushes and mature forests, which are important for the occurrence of local biodiversity.

Information on the chemical condition of soils, aqueous sediments and surface water in the Mysłowice Map Sheet area presented as geochemical maps can be useful in land use planning, assessing local plans, making decisions concerning environmental constraints, giving water-legal permits, assessing groundwater hazards and discharging duties imposed upon district governors by the Environmental Protection Law, i.e. conducting regular soil quality tests.

The internet version of the atlas is available at <http://www.mapgeochem.pgi.gov.pl>.

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## CHARACTERISTICS OF THE MAP AREA

**Geographical and administrative setting.** The map sheet area belongs to the Silesian Voivodeship and includes parts of the cities (urban districts) of Mysłowice, Jaworzno and Sosnowiec. South-western part of the map sheet lies within the borders of Mysłowice, its eastern part belongs to Jaworzno, and the northern region, in the interfluvium of the Czarna Przemsza and Biała Przemsza rivers, belongs to Sosnowiec.

According to the physiogeographic subdivision (Kondracki, 2000), the Mysłowice map sheet area belongs to the Silesian Upland. Lower-order units include the Jaworzno Hills that cover most of the area and the Katowice Upland extending in its north-western part.

**Relief and geomorphology.** Jaworzno Hills are a belt of tectonic horsts composed of Triassic limestones and dolomites overlying Carboniferous rocks. These are individual hills and ridges separated by depressions filled with sands commonly of large thicknesses. The characteristic element of the landscape in the south-eastern part of the map sheet is the Imielin Hills separated by the Przemsza River valley incised to a depth of 70 m (Klimaszewski ed., 1972). In general, the relief is diversified in this area and the elevations vary from 240 m a.s.l. in the Przemsza River valley to 307.1 m a.s.l. in the Rudna Góra region.

Katowice Upland is characterised by a series of flat-topped ridges. The hills have gentle slopes and reach elevations of 260 to 325 m a.s.l. They are composed of Carboniferous deposits represented by sandstones, claystones and siltstones. A significant element of the landscape is the Morgi-Larysz ridge with 320–325 m of elevation a.s.l., and the Brzęczkowice ridge of undulated top consisting of five culminations from 260 to 280 m of elevation a.s.l. (Studium..., 2008).

Over most of the area, the original relief was considerably altered due to many-years' mining of hard coal, filling sands, clay deposits, limestones and dolomites (Chwastek *et al.*, 1990). The changes in land surface give rise to mining collapse areas, barren rock piles and open-pit extraction sites. Large areas of the map sheet are covered by anthropogenic soils (Rzepecki, Suchanecki, 1995) whose thickness often exceeds 2 m.

In the southern part of the map sheet, there are abandoned carbonate rock quarries. They cross-cut the Krasowy and Wygonie-Kępa hills and the slope of the Przemsza River gorge (Program..., 2008). Another form developed as a result of land alteration is the large settling ponds of the Jaworzno III Power Plant, situated in the Przemsza River valley.

The largest river draining the area is the Przemsza, which is supplied in the west by the Rów Kosztowski River, and in the east from the Wąwolnica Stream. The Przemsza River was regulated in 1928–1935. It is a cement-based stone-bed river. The river bed of its tributary, Biała Przemsza, is lined with concrete slabs and sealed by waterproof foil.

A number of small no-name streams flow throughout the area. Most of them are seasonal watercourses filled with water only during heavy rainfall. Natural and artificial water reservoirs are dominant elements of the hydrographical system. These are represented by settling ponds of the closed down coal mine KWK Jan Kanty and settling ponds of the Jaworzno III Power Plant. Overflow lands and wetland areas formed in subsidences due to underground coal mining are observed in forests and wastelands.



**Land use.** Land use of the map sheet area is diversified. Urban development of both compact and dispersed building cover approximately 20% of the total area (Plate 2), and occur mainly in the western and north-eastern part of the map sheet. Industrial areas, accounting for about 6% of the total area, include the Jaworzno III Power Plant, former Jaworzno II power plant, coal mine KWK Mysłowice-Wesoła, close down coal mine KWK Niwka-Modrzejów and other industrial institutions. Almost 50% of the area is covered by forests and other green areas. These are semi-natural forests and moderately altered despite close proximity to harmful industrial plants. The remaining area is represented by agricultural land, grazing land, barrens (Plate 3), water reservoirs, domestic roads and railways.

**Economy.** Mining and power supply are the main industry sectors in this region. The beginning of hard coal mining in the Mysłowice region dates back to the mid-19th century, and even to the 16th century in the Jaworzno area (Jaros, 1984). In Mysłowice, shallow-seated hard coal seams were mined at those times in the Larysz (Karlssegen Mine) and Brzęczkowice (Theodor and Leopoldine mines) districts, as well as at sites of the later Mysłowice (Louise Mine at Słupna) and Niwka-Modrzejów mines. The Mysłowice coal mines played an important role on the regional, Upper Silesian scale. In the early 20th century, they produced over 10% of the total production of all Upper Silesian coal mines (Mysłowice..., 2009).

In 1833, the Jerzy Mine was founded in Niwka. In the period of 1909–1912, a new mine shaft was constructed to be the main shaft of the Modrzejów Mine. Since 1945, the mine has been named the Niwka-Modrzejów Mine. The Jan Kanty Mine was founded in 1920 in Jaworzno, it was called Dachs during World War II. In 1945, the mine was joined with the Jaworzno Mine, and since 1954 it has been called the Komuna Paryska Mine. In 1999–2000, the Niwka-Modrzejów and Jan Kanty mines were closed down after depletion of resources.

The Mysłowice Mine was established in 1887. An important event in its history was the introduction of a hydraulic filling on a commercial scale for the first time in the world's mining in 1901. The KWK Wesoła Mine was founded in 1942, and in the period of 1967–1989 it was called KWK Lenin. Currently, hard coal is mined by the KWK Mysłowice-Wesoła Mine belonging to the Katowice Coal Holding company (Katowicki Holding Węglowy).

The beginning of the Jaworzno power industry is associated with the construction of small power plants that existed since the late 19th century (PKE..., 2009). Currently, the Jaworzno III Power Plant is the largest energy-producing company totalling 1345 MW.

In 1930, the Jaworzno power plant supplied electricity not only to the city of Jaworzno but also to Kraków, Olkusz administrative district and seven administrative communes of the Chrzanów district. In the next years, successive power plants were built and modernized. In 1995, the Jaworzno III Power Plant was established as a result of restructuring operations that combined all the Jaworzno power plants into one company. This is now one of the most modern and environment-friendly companies in Poland. It has a physical-chemical sewage treatment system, modernized electrofilters, and dry ash collection and flue gas desulphurization systems.

Thanks to pro-ecological investments and operations leading to the use of raw building material (gypsum), which is a by-product in gas desulphurization, it became profitable to locate Knauf Jaworzno III and ORTH-Gipse plaster and drywall production companies in Jaworzno.

In Sosnowiec, filling sand has been extracted since 1952. Production was carried out by an enterprise for production of filling materials for coal mining industry (Przedsiębiorstwo Materiałów Podsadzkowych Przemysłu Węglowego), subsequently by the Maczki-Bór sand mine. Land reclamation processes have recently been carried out over its working pits, using coal mine waste (Bieczek, 2007).

One of the most prominent companies in Mysłowice is the heating and power plant (Zakłady Energetyki Ciepłej). Mysłowice Brzezinka hosts the following institutions: electromechanical heating equipment company (Zakłady Urządzeń Elektromechanicznych Zelmech), chemical materials processing company (Zakłady Przeróbcze Surowców Chemicznych Mikrogran), mining equipment factory (Wytwórnice Sprzętu Górniczego Dehank), electrotechnical equipment company (Mysłowickie Zakłady Sprzętu Elektrotechnicznego Polam-Elpor) (in bankruptcy) and Transgór transportation company. Drilling machines are produced by a drilling equipment company (Zakłady Mechanicznych Urządzeń Wiertniczych) in Sosnowiec. Jaworzno (in the Wąwolnica Stream valley) hosts part of the Organika-Azot chemical plant, located to the east of the map sheet border. This plant was established in 1917 and is one of Poland's oldest chemical companies. It produces pesticides, herbicides, fungicides, insecticides and other sanitary preparations. During the

initial period of operation, the company produced nitric acid, cyanic compounds, potassium chloride and detonating fuse. Since the 1930s, the company has produced copper sulphate, trichloroethylene, calcium cyanide and ferrocyanides (Proksa, 2008). Just after the World War II, the company produced pesticides (mainly DDT).

In the map sheet area, there are also renovation and construction services, mining-supporting companies, and software and computer producers and services. Retail and service activities and transportation sectors are developed as well.

## **GEOLOGY AND MINERAL DEPOSITS**

Carboniferous, Triassic and Quaternary deposits compose the surface geological structure of the map sheet area. The area which is a part of the Upper Silesia Coal Basin (USCB) is situated in a transition zone between the Main Saddle and Main Trough. The characteristic feature of the Main Saddle is the occurrence of middle Upper Carboniferous deposits right at the surface. Both the Main Saddle and the Main Trough are cut by numerous faults and tectonic grabens, and the beds are locally folded (Biernat, Kryszowska, 1956; Biernat, 1970; Bukowy, 1970; Kowalska, 2004).

Lower **Carboniferous** deposits are known from boreholes and mining excavations. Upper Carboniferous (Westphalian) deposits are exposed locally on the surface – in the eastern part of Mysłowice, in the northern area of the map sheet and in the Szczotki district of Jaworzno. They are represented by the Orzesze and Łaziska beds (Plate 1). Carboniferous beds dip southwest and southwards at a small angle (5–15°).

The Orzesze Beds comprise shales and mudstones with siderites, sandstone interbeds and hard coal seams of variable thickness and quality. Thickness of the Orzesze Beds varies from 280 to 700 m. They are characterised by several tens of metres thick clay shale layers used for ceramics production (Biernat, 1970). The Łaziska Beds (about 200 m in thickness) are dominated by thick-layered medium- and coarse-grained sandstones and conglomerates. Claystones are subordinate and occur as thin interbeds accompanying hard coal seams.

The **Triassic** is represented by its lower and middle lithostratigraphic units: Buntsandstein and Muschelkalk. The Triassic deposits outcrop in some regions in the south-eastern part of the map area (Dzieńkowice, Jeleń, Kosztowy) and near Szczotki and Długoszyń in Jaworzno. The beds lie almost horizontally.

The Lower Triassic (Buntsandstein) consist of continental deposits; red and variegated sands and clays, overlain by Roethian marine carbonates: cavernous limestones (thickly crystalline, often dolomitic) of thicknesses up to 10 m (Biernat, 1970). The Lower Triassic is exposed patchily near Długoszyn and Szczotki.

The Middle Triassic (Muschelkalk) is composed of platy and wavy limestones and marls of the Gogolin Beds overlain by Diplopora dolomites and ore-bearing dolomites contain zinc and lead mineralization (Kurek *et al.*, 1994, 1999). Middle Triassic outcrops occur near Długoszyn, Dzieckowice and Jeleń and locally in the south-western part of the map area (Plate 1).

**Quaternary** deposits (Pleistocene and Holocene) form a discontinuous cover ranging in thickness from 52 m in the Przemsza River ice-marginal valley to one or several metres in the remaining area. The oldest Pleistocene deposits are represented by tills, sands, gravels and boulders of the South Polish Glaciations. Glacial and glaciofluvial sands and gravels of the Odranian Glaciation cover most of the area.

Eluvial sands and silty tills (resembling loess) are observed near Dąbrowa Narodowa in Jaworzno and near Kosztowy-Osiedle Zawadzkiego in Mysłowice. In the Jaworzno region, eolian sands are frequent, forming 10-m high dune belts.

Holocene deposits (muds, clays and sands) fill river valleys.

**Mineral deposits.** The map area is abundant in proved hard coal deposits and stone materials (Triassic dolomites and limestones, Carboniferous clays and Quaternary ceramic clays and sands).

Parts or wholes of the Mysłowice, Wesoła, Kazimierz-Juliusz, Jaworzno, Dzieckowice, Brzezinka, Ziemowit, Niwka-Modrzejów, Jan Kanty and Modrzejów **hard coal** deposits are situated in the map sheet area (Jochemczyk *et al.*, 2002).

Some of the Mysłowice and Wesoła hard coal deposits, exploited by the KWK Mysłowice-Wesoła hard coal mining company, are located in the west of the map area. Coal is mined there from the Saddle and Ruda beds. Steam coal (ash content 8.89%, average sulphur content 0.78%, average heating value 26 584 kJ/kg) is mined from the Mysłowice coal deposit. The Wesoła coal deposit has the following parameters: ash content 12%, total sulphur 0.6%, heating value 26 700 kJ/kg, thickness from 1.0 to 12.5 m. Coal seams are accompanied by coal-bed methane deposits extracted from the Wesoła deposit and used by a local heating station (Program..., 2008).

The Jan Kanty and Niwka-Modrzejów hard coal deposits are situated in the north-east of the map area. There is also a small hard coal deposit of Kazimierz-Juliusz in this region. Due to the recent closing down of some mines, the hard coal resources were re-classified to off-balance resources (Wołkiewicz *et al.*, 2009). In 2008, the Modrzejów hard coal deposit was documented within the Jan Kanty and Niwka-Modrzejów coal deposits wholly located in the map sheet area. It contains steam coal of the following parameters: ash content 8.24%, heating value 26 757 kJ/kg total sulphur content 0.56%. The total thickness of coal seams varies from 1 to 8.4 m.

The ZG Sobieski hard coal mine (former KWK Jaworzno mine) extracts coal from the Jaworzno coal deposit, whose large portion is situated to the east and south beyond the borders of the map sheet, and from the Dzieńkowice coal deposit wholly located in the Mysłowice Sheet. Coal of the Ruda, Orzesze and Łaziska beds, 1 to 3 m in thickness, is mined from the Jaworzno coal deposit. This is steam coal of average heating value 23 000 kJ/kg, ash content 7% and total sulphur content 2.5%. ZG Sobieski is one of the mines affected by the largest influx of mining water to the mining pits. The amount of water which cannot be used for technological purposes is transferred to the Przemsza River (Zakład..., 2005; Kurek, Preidl, 2008). The Dzieńkowice coal deposit (total area of 188.4 ha) has been exploited since 2004 and produced steam coal of the following parameters: ash content 16%, total sulphur content 1.77%, heating value 22 321 kJ/kg.

In the south-west of the map sheet, there is part of the Ziemowit hard coal deposit.

There is also the proved Brzezinka hard coal deposit in the map area, containing steam coal of the following average parameters: ash content 14.28%, total sulphur content 0.96%, heating value 24 968 kJ/kg. It includes several coal seams of comprising the Ruda, Orzesze, Saddle and Łaziska beds. Thicknesses of the coal seams are variable, ranging from 1 to 14.9 m (Jochemczyk *et al.*, 2002).

**Zinc and lead deposits.** Near the Długoszyn and Rudna Góra small ore bodies were completely exploited by open pit mining in historical times (Szuwarzyński, Panek, 1977). Traces of ancient mining have been preserved to date as post-mining wasteland.

**Raw rock materials.** The following deposits are situated within the map area: northern portions of the Imielin Północ and Imielin-Rek Triassic limestone and dolomite deposits, Jeleń broken and block stone deposit, Brzezinka I and Dąbrowa Narodowa clay deposits for ceramic industry and Jaworzno-Podłęże natural aggregate deposit. The Imielin

Północ and Imielin-Rek deposits are under exploitation, whereas the Jeleń deposit has been abandoned.

Ceramic clay deposits include clay shales and clays from the Carboniferous outcrop belt, and Quaternary tills and ice-dammed lake clays. Extraction of the Brzezinka I clays was abandoned, whereas the deposits at Dąbrowa Narodowa are still undeveloped.

The Jaworzno-Podłęże natural aggregate deposit comprise eolian dune sands and alluvial sands of the Przemsza River.

## HUMAN IMPACT

Due to well developed infrastructure, mining and energy industry, many years' activity of processing factories and improper communal management, the natural environment of Mysłowice, Jaworzno and Sosnowiec is highly degraded (Jochemczyk *et al.*, 2002; Stan środowiska..., 2008).

**Atmospheric air.** Atmospheric air is polluted by emissions from industrial sources, dumps, road transportation, communal economy and individual furnaces.

The results of state monitoring indicate that permissible concentrations of most of pollutants are not exceeded. The monitored parameters of the air quality (sulphur dioxide, nitrogen dioxide, nitrogen oxide, lead, ozone) fall within class A. Benzene concentrations are contained within class B, whereas benzo(a)pyrene and PM 10 dust concentrations fall within class C (Program..., 2008; Stan środowiska..., 2008). PM 10 dust concentrations exceeding standard levels are observed mainly during heating seasons. In 2004–2007, daily permissible levels of phenol, cadmium and tar substances were exceeded only occasionally (Program..., 2003, 2008).

The point sources of atmospheric air pollution are furnaces of individual houses which emit mainly coal dust.

The most polluting factories are the Jaworzno III Power Plant, the heating plants of Mysłowice-Wesoła and ZG Sobieski mines as well as the heating plant (Zakład Energetyki Ciepłej) operating in the area of closed down KWK Niwka-Modrzejów mine. The Jaworzno III Power Plant emits into the air approximately 8 million Mg/year of carbon dioxide, 35 420 Mg/yr of sulphur dioxide and 1134 Mg/yr of carbon oxide. Fly ash and slag dump sites of the Jaworzno III Power Plant are also the serious sources of pollution. Gases and fly ash dust

originating from steam coal combustion contain a number of elements, among others: arsenic, beryllium, cobalt, chromium, mercury, lead, vanadium and zinc (Kabata-Pendias, Pendias, 1999; Hławiczka *et al.*, 2001; Pacyna, Pacyna, 2001; Olkusi, 2007).

Air quality is also affected by pollutants emitted by other industrial factories located both within and beyond the borders of the Mysłowice Map Sheet. Another serious source of pollution is combustion of fuel oil by vehicle engines with emission of hydrocarbons, nitrogen dioxide, carbon oxide and metal compounds along the main transportation routes.

Atmospheric air is also contaminated by far-reaching emissions coming from the industry located in the western areas of the Upper Silesian agglomeration.

**Surface water and groundwater.** Permanent mining activity, urbanization and industrialization of the sheet area caused both changes in the hydrographic network and water quality degradation. Dewatering of hard coal mines resulted in the formation of depression cones and changes in the surface water and groundwater recharge system. The necessity of quick drainage of urban areas gave rise to the regulation of the rivers, straightening of their courses and changes in their beds. Most of the rivers flow in concrete built river-beds or artificial channels (Czaja, 2005). Vast depressions and sinkholes are distributed throughout the terrain. Streams and springs periodically cease flows, and the surface water quality is not satisfactory. Chemistry of these waters is characterised by considerable salinity and large contents of sulphates and heavy metals. Saline waters from hard coal mines commonly show mineralization above 3 g/dm<sup>3</sup>. The concentrations of salts can occasionally reach a level of 150 g/dm<sup>3</sup> (Gabzdyl, Pozzi, 2001). The greatest volume of pollution comes from mine dewatering systems in active and closed hard coal mines. The waters from these mines are typically of very poor quality (classes II and III). The largest amounts of saline waters come from the Mysłowice-Wesoła, Niwka-Modrzejów, Jan Kanty and ZG Sobieski mines.

Disposal of communal and industrial liquid sewages and surface runoff carry phosphorus and organic compounds to the surface waters, resulting in their eutrophication.

Mining saline water, communal sewage and water from sewage treatment plants are discharged into the Przemsza and Biała Przemsza rivers. The Przemsza River also collects water from settling pond of the Jaworzno III Power Plant. Water quality of the Biała Przemsza River at its confluence with the Przemsza River falls within class IV, whereas the waters of the Czarna Przemsza and Przemsza rivers were classified in 2006 within class V

(Program..., 2008). The water of the Wąwolnica Stream, collecting sewage from the Organika-Azot chemical factory in Jaworzno, is polluted with pesticides and cyanides.

The above-described pollution sources of surface water also cause degradation of groundwater. An area of poor quality groundwater occurs in the north-eastern part of the map sheet. Its boundary runs from Mysłowice in the west to Maczki in the east (Rózkowski, Siemiński, 1995; Rózkowski *et al.*, 1997).

In the south of the map area, there is a proved Triassic major aquifer (MGB Chrzanów) with a 100-m thick water-bearing formation (Kawalec, Patorski, 1998) and class Ib water quality (Wagner, Chmura, 1997). This is a fissured-karst aquifer highly vulnerable to contamination. It belongs to the high groundwater protection area (OWO), and in its central part it represents the highest groundwater protection area (ONO) (Kleczkowski, 1990).

**Soils.** Chemical degradation of soils results from industrial activity, transportation, eluates and dusts from waste dump sites, industrial sewage discharge and atmospheric dust accumulation. In some regions, there is a high concentration of metals due to the activity of metallurgy, machinery and hard coal mining industries, including historical mining and smelting of iron and Zn–Pb ores. In the south of the map sheet, the concentration of metals is also associated with the natural geochemical background in areas of ore-bearing rock outcrops.

In urban areas the soils are contaminated by salts (sodium, calcium and magnesium chlorides) due to snow-clearing services. Their alkalization is caused by admixture of calcareous rubble and accumulation of dust containing calcium and magnesium compounds. In river valleys, the soils are polluted by floods in rivers, especially those of contaminated water.

Both natural and anthropogenic factors cause reduction of soil fertility. As a result, the reduction in the quality and amount of humus, changes in soil structure and acidity and removal of alkaline cations are observed.

Soil investigations performed in 2001 in allotment gardens areas of Mysłowice showed significant concentrations of heavy metals and polycyclic aliphatic hydrocarbons exceeding permissible limits (Plan..., 2003, 2008; Program..., 2008b).

The topsoil in Jaworzno contains cadmium, zinc and lead, especially in areas of outcropping Triassic carbonate rocks (Program..., 2005). In the vicinity of the Organika-Azot



chemical company in Jaworzno, the soils are contaminated with mercury and other heavy metals, as well as by pesticides and cyanides (Program..., 2005; Pasieczna ed., 2008b).

In many areas, the soils are mechanically and chemically disturbed. Mechanical modification of soil structure takes place due to settlement activity, sealing, hardening, compacting, soil cover removal, mixing with rubble, cement, glass and metals, soil groundwork (by heat transport networks and asphalt and cobblestone covers) and soil displacement during earth work (ditches, embankments, flattening works). The specific forms of soil degradation include disturbance of hydrogeological conditions in post-mining depressions and overflow lands due to mining activity.

## **MATERIALS AND METHODS**

The 2007–2010 researches included studying published and archival materials, selecting sampling sites in topographic maps at the scale of 1:10 000, collecting samples, coordinate surveying at sampling sites, chemical analyses of samples, setting up field and laboratory databases, preparing a vector topographic map, statistical calculations, constructing geochemical maps and a geological map, and finally interpretation of results. The sequence of investigations is shown in Figure 1.

### **FIELD WORKS**

Soil samples were collected at a regular grid of 250x250 m (16 samples per 1 km<sup>2</sup>). The total number of soil sampling sites was 1330 (Plate 2). At every site, two samples were collected from two depths: 0.0–0.3 (topsoil) and 0.8–1.0 m (subsoil). If the parent rock was found shallower in the soil profile the subsoil sample was collected at a smaller depth. Soil samples (ca. 500 g) were collected using a 60-mm hand probe, put in linen bags labelled with numbers, and pre-dried on wooden pallets at a field storage site.

Samples of aqueous sediments and surface water were collected from rivers, streams, melioration ditches, canals, settling ponds, pools and ponds. The distance between watercourse sampling sites was about 250 m. 500 g sediment samples (of possibly the finest fraction) were taken from water reservoir shores using a scoop. They were subsequently placed in 500 ml plastic containers labelled with numbers.

Surface water samples were collected at the same sites as aqueous sediment samples. Specific electrical conductivity (EC) and acidity (pH) of water were measured on site. EC was measured using a conductometer with automated temperature compensation, assuming the reference temperature of 25°C. Water samples were filtered on site using 0.45 µm Millipore filters and acidized with nitric acid in 30 ml bottles. The bottles were also labelled with numbers.

All the sampling sites were indicated in topographic maps at a scale of 1:10 000 and numbered. Locations of the sampling sites were defined with GPS, using a device equipped with an external antenna and a computer which can record not only coordinates but also additional information (pH and EC of water samples, data on land development and land use, type of soil and aqueous sediment). The coordinates were taken with an accuracy of  $\pm 2 - 10$  m. The coordinates of soil sampling sites were put into the memory of the GPS equipment, before going out in the field, and the sites were subsequently found using the satellite positioning system. For database safety reasons, all the field data were also noted on special sampling cards (Fig. 2).

## LABORATORY WORKS

**Sample preparation.** The soil samples were air-dried and sieved through a 2 mm nylon sieve. Each topsoil sample (0.0–0.3 m) was split into three portions: one of them was submitted for chemical analysis, the second one was analysed for grain-size and the third one was archived. Each subsoil sample (0.8–1.0 m) was sieved and split into two portions: one of them was submitted for chemical analysis and the other one was archived (Fig. 1). The soil samples for chemical analyses were pulverized in agate planetary ball mills to a grain size  $< 0.06$  mm.

Aqueous sediment samples were air-dried and then sieved through a 0.2 mm nylon sieve. The  $< 0.2$  mm fraction was divided into two portions: one of them was used for chemical analysis and the other was archived (Fig. 1).

All the archive samples are stored at the Polish Geological Institute-National Research Institute in Warsaw.

**Chemical analyses** were carried out at the Central Chemical Laboratory of the Polish Geological Institute-National Research Institute in Warsaw.

Soil and aqueous sediment samples were digested in aqua regia (1 g of sample to final volume of 50 ml) for 1 hour at the temperature of 95°C in the aluminium heating block thermostat.

Contents of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in the soil and aqueous sediment samples were determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES) method. Mercury content was measured using a cold vapour atomic absorption spectrometry (CV-AAS) method. Soil pH was measured by water extractions using a pH-meter. Organic carbon content was measured using a coulometric method. Determination of B, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, P, SiO<sub>2</sub>, SO<sub>4</sub>, Sr, Ti and Zn in surface waters was performed by an ICP-AES method. Contents of Ag, Al, As, Cd, Cl, Co, Cu, Li, Mo, Ni, Pb, Rb, Sb, Tl and U were analysed using an inductively coupled plasma atomic mass spectrometry (ICP-MS) method. The applied analytical methods and the detection limits of measured elements are shown in Table 1.

Quality control in the determinations was performed through analysis of duplicate samples (about 3% of all samples), analysis of reference materials with certified content of elements studied (2.5% of all samples) and analysis of laboratory control samples confirming correct instrument calibration (10% of all samples). 'Reagent blank samples' and 'preparation blank samples' were used. Purity of reagents and vessels was controlled with 'reagent blank samples'. 'Blank samples' (*sea sand extra pure Merck*) were used to monitor for possible contamination introduced during the sample preparation procedure.

For the solid samples, analytical precision is below 25%. For the surface water samples, analytical precision is about 15–25% (depending on the element's concentration).

Grain size analyses of topsoils (0.0–0.3 m) samples were carried out at the Hydrogeology and Engineering Geology Laboratory of the Polish Geological Institute-National Research Institute in Warsaw, using a laser particle size analyzer. Advantages of the laser technique include the following: small sample volume (<1 g), quick measurement and high determination accuracy with regard to some grain sizes (Dębicki *et al.*, 2002).

The comparisons of the results of grain size analyses obtained using a sieve-sedimentation method (according to the international classification of FAO and USDA) and the laser technique show significant differences in the proportions of individual fractions (Kasza, 1992; Issmer, 2000). Thus, direct use of laser method results does not allow soil

classification according to pedological criteria. However, the data are very useful for interpretation of geochemical analyses.

The results of grain size analyses (recalculated to percentage ranges) are presented in the maps with regard to the following grain size classes: sand fraction 1.0–0.1 mm, silt fraction 0.1–0.02 mm and clay fraction <0.02 mm (Plates 4–6).

## DATABASES AND GEOCHEMICAL MAP CONSTRUCTION

**Base topographic map.** The 1:25 000 scale topographic base map was constructed using the most up-to-date 1992 coordinate system topographic map at the scale of 1:50 000, Katowice Map Sheet M-34-63-A (vector map VMap L2). The topographic map contains the following vector information layers: relief, hydrography (including dividing into rivers, streams, ditches and stagnant water reservoirs), road communication network (with road classes indicated), railway network, land development (including classification into rural, urban and industrial development), forests, industrial areas (industrial objects, mine shafts, mine excavations, mine dumps and tailing ponds).

**Geological map.** Geological map was constructed on the basis of Detailed Geological Map of Poland, 1:50 000, Katowice Map Sheet (Biernat, Krysowska, 1956). Individual elements of the geological map were digitized to create their vector images which were subsequently combined with the topographic base, producing a geological map at the scale of 1:25 000 (Plate 1).

**Database management.** Separate databases were prepared for: topsoil (0.0–0.3 m), subsoil (0.8–1.0 m), aqueous sediments and surface water.

Soil databases contain the following information: sample number, sampling site coordinates, site description (land development, land use, soil type, sampling site location – district, commune and locality), date of collection, sampler name and analytical data.

Aqueous sediment and surface water databases contain the following information: sample number, sampling site coordinates, site description (land development, land use, water body type, sediment type, sampling site location – district, commune and locality), date of collection, sampler name and analytical data.

**Statistical calculations.** Information from the databases were used to create subsets for statistical calculations according to different environmental criteria, e.g. concentrations of

elements in soils of industrial areas, forest soils, urban soils and in aqueous sediments and water of individual water bodies, as well as for geochemical map construction. Statistical calculations were made for both whole datasets and subsets created for soils, aqueous sediments and surface water. In the case of some elements with the content lower than the detection limit value for the given analytical method, half of the detection limit value was taken. The arithmetic and geometric means, median, minimum and maximum values were calculated. These data specified for individual elements, pH and EC are shown in Tables 2–5 and presented in the geochemical maps.

**Map construction.** The following maps were produced for the Mysłowice Sheet (Plates 2–63): land development, land use, contents of organic carbon and grain size of topsoil (sand, silt and clay fractions ); acidity of topsoil and subsoil; contents of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in topsoil, subsoil and in aqueous sediments; acidity, specific electrical conductivity and contents of Ag, Al, As, B, Ba, Ca, Cd, Cl, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, SiO<sub>2</sub>, SO<sub>4</sub>, Sr, Ti, Tl, U and Zn in surface water; topsoil classification indicating appropriate soil use.

Land development, land use and topsoil classification indicating appropriate soil use are presented as dot maps (Plates 2, 3 and 63).

To show the distribution of grain size classes (Plates 4–6) and the contents of elements in soils, contour maps were constructed because of their clarity and legibility. The geochemical contour maps were produced using the Surfer software and the *Inverse Distance to a Power method*. The classes of contents of elements were created most often using geometric progression.

Soil acidity (Plates 7 and 8) is presented according to the soil science classification (acidic, neutral and alkaline soils).

The geochemical maps of soils were constructed using the analytical dataset created for the Mysłowice Sheet and the datasets of 1:25 000 scale neighbouring sheets. Thus any disagreements at the sheet borders were avoided. After interpolation the Mysłowice Sheet was extracted from mono-element maps and combined with the topographic base map.

The geochemical maps of aqueous sediments and surface water were elaborated separately for the Mysłowice Sheet area only. They were constructed as dot maps with the circle diameters corresponding to individual classes, most often according to geometric progression.

While constructing the map of soil classification (Plate 63), indicating appropriate soil use, the results of geochemical analyses were referred to the permissible levels of metals, defined in the Regulation of the Ministry of the Environment (Rozporządzenie..., 2002), according to the recommendation that 'soil or land is considered polluted if the concentration of at least one substance exceeds the permissible limit value'.

Based on the contents of individual metals analysed (specified in the Rozporządzenie..., 2002), each soil sample was categorized into class A, B or C. In the case of equal permissible limit values for classes A and B (for arsenic, barium and cobalt), the soil was categorized into class A, which is more advantageous to the user and enables multifunctional land use.

For publication purposes, the geochemical maps were constructed by combining the maps into pairs: the topsoil map is presented together with the aqueous sediment map, and the subsoil map is shown with the surface water map. This method of presentation provides the possibility of direct comparison of geochemical images of various media. Taking into account the comfort of potential users, the maps (with a bar scale shown) have been printed out in a slightly smaller format (A3). This operation did not cause omitting any important details of the maps. The whole report or its individual plotter printed maps are available for those who are interested in 1:25 000 scale maps.

## **RESULTS**

### **SOILS**

The soils of the Mysłowice Map Sheet were formed by natural processes and modified by anthropogenic processes of industrialization and urbanization. The parent rocks are Carboniferous, Triassic and Quaternary deposits. Accumulation of chemical elements in these soils occurred as a result of geological (outcrops of rock formations, geochemical barriers) and anthropogenic (mining water and sewage discharge, eluates from post-mining waste dump sites and settling ponds, coal combustion, and iron and non-ferrous metal smelting) processes.

The most common soil types are *Podzols* developed on sands, sandstones, tills and their eluvium as well as on various silty deposits. *Podzols* are the most popular in coniferous forest areas. *Rendzinas*, developed on limestones and dolomites, occur in the south-eastern part of the map area. River valley bottoms are covered with alluvial soils (*Fluvisols*)

characterized by the presence of mineral-organic layers deposited during high water levels. In some areas of river valleys and topographic lows, peat soils (*Histosols*) are observed.

**Grain size.** Almost all chemical and physical properties of soils result either directly or indirectly from their mechanical composition. By determining the grain size of soil particles, we can infer about the soil origin and its vulnerability to contamination. This is one of the most important parameters controlling migration ability of elements within the soil profile. The grain size is also the basic indicator of soil fertility (Kocowicz, 2000). Each mechanical fraction, i.e. particle groups of defined sizes and often similar physico-chemical properties, affects porosity, compactness, plasticity, sorption types and soil resistance to degrading factors (Prusinkiewicz *et al.*, 1994).

Grain size composition of soil is one of the factors determining content of chemical elements. Soils rich in the clay fraction ( $<0.02$  mm) and silt fraction ( $0.1\text{--}0.02$  mm) are characterized commonly by greatest content of many elements and their low migration ability under hypergenic conditions. The standards and recommendations on permissible limits of elements in soils commonly take account of this soil property, allowing higher limiting concentrations for clay fraction-rich soils and lower limiting concentrations for sand fraction-rich soils (Kabata-Pendias *et al.*, 1995).

The following grain size groups have been distinguished within the topsoil of the study area:  $1.0\text{--}0.1$  mm,  $0.1\text{--}0.02$  mm and  $<0.02$  mm, according to the Polish Standard BN-78/9180-11 recommended by the Polish Society of Soil Science (Prusinkiewicz *et al.*, 1994). There is a close relationship between the soil grain size and parent rock lithology. The most abundant are sandy soils developed on Pleistocene glaciofluvial sands and gravel, weathered sandy tills, aeolian sands and outcrops of Carboniferous sandstones (Plates 1 and 4). Many of the soils contain over 75% of the  $1.0\text{--}0.1$  mm fraction. There are also soils containing over 90% of sand fraction in the western districts of Jaworzno and in the region of the Bobrek and Biała Przemsza river valleys (Plate 4). These soils are characterized by a small proportion of the silt ( $<5\%$ ) and clay ( $<5\%$ ) fractions.

The soils of Mysłowice and Sosnowiec are developed on outcrops of Carboniferous clastic deposits and are enriched in the silt fraction ( $0.1\text{--}0.02$  mm). The clay fraction content commonly ranges between 10 and 25%, occasionally exceeding 20% (Plate 5). The soils of the southern areas of the sheet, developed on Triassic carbonate-marly deposits, are also enriched in the silt fraction.

Most of topsoil in Jaworzno contain below 5% of the clay fraction (Plate 6). A higher content of the clay fraction (5–10%) is observed in the soils developed on Carboniferous rocks in Mysłowice. Soils rich in the clay fraction (>15%) occur also in the reclaimed area of a settling pond of furnace waste at the Jaworzno III Power Plant.

**Acidity.** Both topsoil and subsoil are acidic, which is related to the land use, in combination of parent rock lithology. Acidic and highly acidic forest soils (average pH <5.7) cover most of the area. They developed mainly on glaciofluvial sand-gravelly deposits and sands. Patches of highly acidic soils are also observed in some forest areas in the south of the map sheet. Extremely low pH values (<5) are found in forest topsoil in the vicinity of the Jaworzno III Power Plant. It can be associated with long-lasting emissions of sulphur dioxide and nitrogen oxides by the plant, resulting in environmental acidity when they react with water. Due to acidic pH, plant nutrients are washed out and toxic aluminium is released. High content of aluminium in aqueous sediments and surface water of this region (Plates 11 and 12) is probably related to the very low pH of the soil.

Neutral and alkaline soils occupy urban and industrial areas (Tables 2 and 3). The vast area of alkaline soils (pH >7.4) occurs in the centre of Mysłowice and in the Sosnowiec districts of Niwka and Modrzejów (Plate 7). The soils of the Dąbrowa Narodowa district of Jaworzno are neutral and locally alkaline. In some districts, pH value exceeds 8, which can be result of long-lasting industrial emission of alkaline dust particles.

Alkaline subsoil (0.8–1.0 m) were observed in areas predominantly controlled by the Triassic carbonate geology in the southern part of the map sheet, in urbanized areas of Mysłowice and Sosnowiec in the north of the sheet and in the vicinity of the former settling pond of furnace waste of the Jaworzno III Power Plant (Plate 8).

**Geochemistry.** Physico-chemical conditions of soil-forming processes led to chemical changes of soils in relation to their parent rocks; however geochemistry of the parent rocks is noticeable. Spatial distribution of elements inherited from the parent rocks enables determination of geochemical background variability and identification of anomalies in elements' contents.

The analysis of elements' contents in soils indicates a strong relationship in the distribution of aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, titanium and vanadium with the bedrock lithology. The low values of these elements were found in soils developed on glaciofluvial sands in Jaworzno and in the southern districts



of Mysłowice (Kosztowy and Furmaniec). These soils are chemically poor and acidic, which favour leaching of elements.

In the areas of Triassic carbonate outcrops (Długoszyn, Pszczelnik, Rudna Góra, Kosztowy, Dzieńkowice), the soils (especially subsoils) are rich in calcium, iron and manganese. The calcium and magnesium contents in topsoil of these areas exceed 1%, locally reaching a level of several percent. High calcium and magnesium values are profitable to the environment because they increase alkalization and enable bonding of heavy metals.

In the eastern districts of Mysłowice, the soils that developed on Carboniferous clastic deposits contain more aluminium, cobalt, chromium, iron, manganese, nickel, phosphorus, sulphur, titanium and vanadium than the soils developed from Quaternary sandy deposits. The values slightly exceed those typical of the regional background level (Lis, Pasieczna, 1995b).

Distribution of total organic carbon (TOC) shows a very specific pattern in the sheet area. Low TOC contents (<3%) were found in soils developed on Quaternary sandy deposits and Triassic carbonates. The soils that developed on Carboniferous rocks and Quaternary tills commonly contain 3–6% TOC, whereas its content in the anthropogenic soils from the vicinity of the Jaworzno III Power Plant is over 12%, with the maximum of 50.40% (Table 2). Maximum TOC contents are observed at hard coal storage sites of the power plant.

Enrichment of the soils in some elements (arsenic, barium, zinc, cadmium, lead, mercury, copper, strontium and silver), observed particularly in topsoil, is related to the anthropogenic factors. The most chemically altered soils due to industrial activity occur around objects and settling ponds of the Jaworzno III Power Plant, in the Wąwolnica Stream valley in Jaworzno and in the city centre, Brzezinka and Brzęczkowice districts of Mysłowice.

The barium concentration in subsoil in these areas seldom exceeds 240 mg/kg, whereas topsoil analysis shows large areas of the content exceeding 240 mg/kg. The average barium contents are also considerably greater in topsoil (Table 2 and 3). The main source of barium is probably dust from hard coal combustion (Rózkowska, Ptak, 1995a).

Soils strongly polluted by metals cover the area of Mysłowice city centre, where the following anomalies were detected: >1000 mg/kg of zinc, >80 mg/kg of strontium, >100 mg/kg of lead, >0.20 mg/kg of mercury, >20 mg/kg of copper and >4 mg/kg of cadmium. The dispersed waste after the historical zinc smelters and closed down Kunegunda zinc rolling mill are the probable source of these anomalies (Falecki, 2010).

Near the factories of Zelmech, Mikrogran, Polam-Elpor and mining equipment factory (Wytwórnia Sprzętu Górniczego) in Mysłowice Brzezinka, increased concentrations of the following metals were noted: silver (up to 10.2 mg/kg), copper (>40 mg/kg), lead (>100 mg/kg), strontium (>80 mg/kg) and zinc (>500 mg/kg). All of them are undoubtedly related to dust emission and municipal sewage discharge.

Worth noting are metal anomalies observed in both topsoil and subsoil of the Brzęczkowice area. The arsenic, cadmium, lead and zinc contents reach the level of up to 230 mg/kg, 50 mg/kg, 3000 mg/kg and 28 900 mg/kg, respectively. The anomalies were found in the area of historical Leopoldine zinc smelter located near the present A4 motorway and Katowice–Tychy road junction, close to the former hard coal mine of the same name (Falecki, 2010). Three small zinc smelters operated in this area, including Hustine, Stanislaus and Dar Jana. Zn–Pb ore was transported to these smelters from the Tarnowskie Góry and Olkusz regions. It is worrisome that this polluted area is currently used as allotment gardens.

Historical activity of the Eduard and Teresa zinc smelters in the Kosztowy district gave rise to anomalous concentrations of arsenic, cadmium, copper, lead and zinc in soils. In the vicinity of the former Cordulla zinc smelter in Dzieńkowice, increased cadmium, zinc and lead contents are observed.

A copper anomaly (up to 4180 mg/kg at a depth of 0.8–1.0 m) was found in the Larysz at the site of the former waste dump (between Konopnickiej and Ptasia streets). Beside copper the soils show increased arsenic, barium, cadmium, mercury and lead contents. The most likely source of contamination in this area is a landfill for outdated pesticides.

The strongest mercury anomaly (with the maximum of 15.95 mg/kg in topsoil) is observed in the factory area and the Jaworzno Organika-Azot's landfill of chemical waste in the Wąwolnica Stream valley. The factory has produced pesticides for over 60 years. The contamination is also observed at the depth of 0.8–1.0 m, reaching its maximum of 36.15 mg/kg. Mercury is certainly sourced from its compounds used for pesticide production. Chemical waste was dumped at the Rudna Góra landfill located in a former sand pit. The landfill is not lined and part of its waste was used in building escarpments along the Wąwolnica Stream (Siłowiecki, Czarnomyski, 2010). Before the World War II, the landfill was being filled mainly with slag and bottom ash. During the World War II, cyanide-containing cyclon B production waste was dumped here. After the War, pesticide production waste containing mercury, arsenic and organochlorine compounds were dumped at this site.

In the 1970s through 1980s, the factory produced e.g. DDT and lindane – agricultural insecticides whose production and agricultural use has recently been banned in most countries.

The soils developed in the area of former settling ponds of the Jaworzno III Power Plant show a specific composition. Near the settling ponds located at Dzieńkowice and to the north of the Jaworzno III Power Plant, the soils are enriched in aluminium, barium, calcium, cobalt, chromium, copper, iron, magnesium, nickel, phosphorus, sulphur, strontium, titanium and vanadium. These elements most probably come from the mineral matter of hard coal dumped in the form of ash (Rózkowska, Ptak, 1995b).

The distribution of phosphorus indicates its origin from anthropogenic sources. High phosphorus contents ( $>0.03\%$ ) correlate well with the distribution of calcium. The areal extent of phosphorus enrichment is larger within topsoil than subsoil. The source of the element are chemically-synthesized fertilizers (once used in areas which are mostly barren lands now) and municipal sewage.

Proportion of areas of topsoil contaminated by cadmium, zinc and lead is presented in Table 6. Over most of the map area (83.31%), the topsoil contains  $<4$  mg/kg of cadmium. Lead contents of  $\leq 100$  mg/kg was found in 68.72% of the soils, whereas zinc contents of  $\leq 500$  mg/kg was found in 84.21% of the soils.

The topsoils contaminated by cadmium ( $>16$  mg/kg), lead ( $>500$  mg/kg) and zinc ( $>2500$  mg/kg) occupy only 1.28–2.18% of the map sheet area. The contaminated subsoil area is much smaller.

The heavy metal contamination of soils is a problem for the local authorities and should be discussed with respect to the appropriate land use. To fit the geochemical data to the local authorities' needs the topsoils of the Mysłowice Sheet were classified applying current guideline values (Table 7) established by the Polish Ministry of the Environment (Rozporządzenie..., 2002). The guideline values are based on the average of particular elements in soils for Poland as a whole and also on the assessment if the content of a particular element may have negative influence on the ecosystem or on human health. Guideline values are applied for three-level scale: A (protected areas), B (agricultural, forest and residential areas) and C (industrial areas).

The total classification was calculated using the rule that the sample is classified to a particular soil use group if the content of at least one element exceeded the permissible limit

value. With respect to concentrations of metals, 21.95% of the topsoils were included into group A, 35.04% of the topsoils were classified into group B and 43.01% of the topsoils into group C (Table 7). The only soils meeting requirements of multipurpose use are those categorized into classes A and B. Class C soils occur mostly in compact settlement and industrial areas of Mysłowice, Jaworzno and Sosnowiec (Plate 63). The map shows the recommended land use according to guidelines provided in Rozporządzenie... (2002). Much of the soils are currently improperly used and require at least monitoring or reclamation. Concentrations of metals in soils of some forest, agricultural, grassland and garden areas are so high that the land should be used for industrial purposes.

### AQUEOUS SEDIMENTS

Chemical composition of aqueous sediments (rivers, streams, ditches and stagnant water reservoirs) excellently describes the environment pollution because they retain most of mobilized heavy metals and other elements (due to both natural and anthropogenic processes). Toxic effects of polluted sediments on aqueous ecosystems have been widely documented for many years (Calmano, Förstner, 1995; Wolska *et al.*, 1999; Burton, Landrum, 2003).

**Biała Przemsza River and its catchment.** The map area covers only the lower river course; however the chemical composition of alluvial deposits is altered by anthropogenic processes within the whole drainage basin. In its middle and upper course, strongly contaminated sediments are transported into the Biała Przemsza River by its tributaries: Sztola, Kanał Główny and Kozi Bród.

Alluvial sediments of the Biała Przemsza River are polluted by silver, arsenic, cadmium, chromium, lead, sulphur and zinc, and to a lesser extent by mercury. They also contain considerable amounts of calcium, magnesium, manganese and strontium. The sediments contain up to 13 mg/kg of silver, up to 391 mg/kg of arsenic, up to 127 mg/kg of cadmium, up to 17 100 mg/kg of lead, up to 3.990% of sulphur and up to 24 800 mg/kg of zinc (Table 4). These elements are derived from the sewage discharges by the ZGH Bolesław mine and smelting company as well as mine water from the Olkusz and Pomorzany Zn–Pb ore mines, located beyond the eastern boundary of the map sheet. The sewage is discharged to the Biała Przemsza River through the Roznos Canal and Biała and Sztola rivers (Labus, 1999). No significant decrease in the average concentrations of cadmium (24 mg/kg), lead (962 mg/kg) and zinc (3774 mg/kg) are observed in the Biała Przemsza River alluvial

deposits as compared with the results of measurements from the period of 1999–2000, which gave the following values: 88 mg/kg of cadmium, 322 mg/kg of lead and 3200 mg/kg of zinc (Bojakowska, Sokołowska, 2001).

Chromium in the sediments (up to 467 mg/kg) originates from industrial sewage discharged to Kozi Bród River from the Szczakowa tannery.

Sediments of the Main Canal (Kanał Główny) that drains the reclaimed part of the Szczakowa sand mine contain barium, cobalt, iron, manganese, nickel, strontium and zinc. Enrichment of the sediments in these metals can be associated with the sorption of elements by iron hydroxides commonly occurring in poor fens that develop as a side- effect of reforestation in post-mining areas.

**Bobrek River and its catchment.** Pollution, observed in alluvial sediments of the lower course of the Bobrek River, comes from the whole drainage basin area. The riverheads of the Bobrek are situated at Groniec in the central part of the Strzemieszyce Sheet. The uppermost section of the river's course drains the area covered with peat and muddy clay soils characterized by a high sorption potential. Alluvial deposits of the Bobrek River and its tributaries in this region are enriched in aluminium, arsenic, cadmium, chromium, mercury, iron, manganese, strontium, vanadium and zinc. There are also high contents of barium (500–1000 mg/kg). Most of the metals come from sewage discharged by the terminals of iron smelting industry railway located at Groniec (Pasieczna ed., 2008a). Barium is also derived from barite processing at iron ore crushing plants (situated within the terminals) and supplied to the ArcelorMittal iron smelter. The source of some of the elements enrichments is surface runoff in the riverheads of the Bobrek where anomalies are observed in soils.

In its upper section, the Bobrek River is supplied by the Rakówka and Jamki streams and the canal running from the coking plant in Dąbrowa Górnicza. Sediments of the watercourses contain chromium, copper, iron, manganese, nickel and strontium. These elements mostly come from industrial sewage of Dąbrowa Górnicza.

Sediments of the Bobrek River downstream of Rakówka Stream mouth contain increased contents of silver due to sewage discharges from the Saint Gobain Glass factory using silver compounds for mirror production (Pasieczna, ed., 2008a). Sediments of the right-bank tributaries of the Bobrek River draining the areas of Mikrohuta metal company in Dąbrowa Górnicza, closed down KWK Porąbka-Klimontów hard coal mine, Enmech

mechanical factory and the hazardous waste landfill of Slima Electric Motors company are highly polluted by metals.

Alluvial deposits of the Bobrek River in the Mysłowice Sheet are contaminated by silver (up to 6 mg/kg), cadmium (up to 8 mg/kg) and mercury (up to 0.35 mg/kg). They are also enriched in chromium, copper and phosphorus (Table 4). The anomalies are associated mainly with municipal and industrial sewage discharges.

**Przemsza River and its catchment.** The Przemsza River and its upper section called the Czarna Przemsza River drain the most industrialized and urbanized area of the Upper Silesia region. Numerous hard coal mining waste dumps are located within the drainage basin. Some of them are characterised by a high concentration of pyritic sulphur, which causes eluates acidification and mobilization of metals. Iron and steel smelters discharge sewage containing non-ferrous metals, iron, aluminium, calcium and manganese oxides, sulphur, oils, cyanides and many other substances. There are several hundreds of sewage outlets into the river and its tributaries, including municipal sewage from the largest cities of the region. The Przemsza River and its tributaries (Brynica, Bolina, Pogoria) are regulated and embanked rivers. Their sediments are the ones most affected by human impact. In terms of hydrological conditions, the Przemsza River is characterised by a moderate gradient and a stable flow throughout the year (Panek, 2008).

Within the map area, alluvial sediments of the Przemsza River contain anomalous values of metals: 2–5 mg/kg of silver, 15–40 mg/kg of cadmium, 50–90 mg/kg of chromium, 100–300 mg/kg of copper, 2–4% of iron, 1–2.5 mg/kg of mercury, 400–800 mg/kg of manganese, 20–50 mg/kg of nickel, 300–1500 mg/kg of lead and 1000–6000 mg/kg of zinc. They are also enriched in phosphorus and sulphur, and locally in arsenic, strontium and vanadium.

Pollution of the alluvial deposits results mainly from primitive exploitation of Zn–Pb ores, which started in the 13th century in the Przemsza River drainage basin. Zinc smelting has developed since the 18th century in this area. In the early 19th century, about 80 zinc smelters operated in Upper Silesia region (Molenda, 1960, 1963, 1970; Jaworska-Cygorijni, 1989). Zn–Pb ore dressing processes favoured migration of fine-grained ore fragments into sediments, which were subsequently contaminated and transported downstream. Fine-grained particles accumulated in river channel facies are still the source of metals in contemporary alluvial sediments (Klimek, 1993).

At present, metal contamination is sourced mainly from industrial sewage discharges of iron smelters (Cedlera, Bankowa, Będzin, Buczek and ArcelorMittal) and the Będzin heat and power plant, as well as from suspension after flotation of Zn–Pb ores in the Biała Przemsza River drainage basin. The Brynica River transports sewage from industrial areas of Sosnowiec, Katowice, Czeladź and Bytom. The Rawa River collects sewage from the city centre of Katowice and supplies the Brynica. The eastern areas of Katowice are crossed by the Bolina River degraded by sewage from the Szopienice smelter of non-ferrous metals and other industrial factories.

Anomalous concentrations of metals are observed in the small watercourse discharging sewage into the Przemsza River from the industrial zone of Mysłowice Brzezinka. The following metal amounts were found in this area: cobalt – 30 mg/kg, chromium – 990 mg/kg, copper – 4000 mg/kg and nickel – 747 mg/kg.

Sediments of the Łęg reservoir are enriched in aluminium, cobalt, mercury, nickel, titanium and vanadium.

**Rów Kosztowski River and its catchment.** Geogenic elements in deposits of the drainage basin are represented by aluminium, barium, calcium, cadmium, magnesium, nickel, phosphorus, sulphur, titanium and vanadium. Their contents remain within the limits of regional geochemical background. Sediments of the right bank tributary of the Rów Kosztowski contain anomalously high amount of iron (up to 35.97%) and manganese (up to 4000 mg/kg). These elements probably originate from historical sites of extraction and smelting of iron from bog iron deposits.

The Rzutna wetlands are an environment favourable for accumulation of oxides and hydroxides of metals in bog iron deposits on fluvial terraces and river channel slopes.

The chemical composition of the deposits in the drainage basin is also affected by anthropogenic factors. In the upstream area, chromium- and copper-rich sewage is discharged from the Mysłowice Brzezinka industrial zone.

**Wąwolnica River.** In the south-eastern part of the map area, there is the mouth of a stream transporting sewage from the Organika-Azot chemical plant in Jaworzno. The sediments of Wąwolnica and its left bank tributary contain the following concentrations of individual elements: arsenic – 2379 mg/kg, copper – 450 mg/kg, iron – 21%, phosphorus – 1.40%, lead – 2900 mg/kg, sulphur – 9.27% and zinc – 1700 mg/kg. There is also a slightly increased contents of silver (2–4 mg/kg). However, the sediments are most severely

contaminated by mercury (up to 16.36 mg/kg) that poses a hazard to plants and animals. The sediment contamination is caused by long-lasting production of various chemical substances in the Organika-Azot chemical plant. In the 1930s, the plant produced copper sulphate, calcium cyanide, ferrocyanides and other products. After the World War II, the technological processes were based on the mercury electrolysis method (Proksa, 2008) and lead compounds were used for pesticide production.

## SURFACE WATER

**Biała Przemsza River and its catchment.** Water acidity of the Biała Przemsza River at its mouth is 5.5–7.9; electric conductivity is 0.24–1.46 mS/cm (Table 5). EC values commonly range between 0.80 and 0.90 mS/cm.

The characteristic composition of elements in water is related to the exploitation and treatment of zinc-lead ores: arsenic ( $3\text{--}4\text{ }\mu\text{g/dm}^3$ ), cadmium ( $0.8\text{ }\mu\text{g/dm}^3$ ), lead ( $30\text{--}55\text{ }\mu\text{g/dm}^3$ ), zinc ( $400\text{--}550\text{ }\mu\text{g/dm}^3$ ) and molybdenum ( $2\text{ }\mu\text{g/dm}^3$ ). Water enrichment in these elements is observed throughout the whole river course, downstream from sewage discharge outlets of the ZGH Bolesław zinc smelter and Zn–Pb ores mines of the Olkusz region. A severe hazard is also thallium concentration ( $11\text{--}13\text{ }\mu\text{g/dm}^3$ ) originating from the same source. Surface water of the Silesia-Cracow region is commonly enriched in thallium. Its concentration varies from 0.16 to  $3.24\text{ }\mu\text{g/dm}^3$  (Paulo *et al.*, 2002), whereas the geochemical background of surface water of Poland is  $0.006\text{ }\mu\text{g/dm}^3$  (Salminen ed., 2005). Thallium and many of its compounds (especially sulphates) have been classed as very toxic substances, whose concentrations in the environment are particularly hazardous to organisms.

The average contents of calcium, magnesium and iron in surface water of the study area are small:  $107.1\text{ mg/dm}^3$ ,  $33.3\text{ mg/dm}^3$  and  $0.04\text{ mg/dm}^3$ , respectively.

The greatest accumulation of pollutants within the drainage basin is observed in stagnant water reservoirs. In the reservoir located near the KWK Jan Kanty hard coal mine dump at Szczotki, the following values were measured: nickel –  $37\text{ }\mu\text{g/dm}^3$ , boron –  $1070\text{ }\mu\text{g/dm}^3$ , lithium –  $340\text{ }\mu\text{g/dm}^3$ , and manganese –  $2140\text{ }\mu\text{g/dm}^3$ . The fish pond and the small pool situated in the northern part of Dąbrowa Narodowa are extremely polluted water reservoirs. The concentrations of silver and copper are  $0.66\text{ }\mu\text{g/dm}^3$  and  $17.4\text{ }\mu\text{g/dm}^3$ , respectively. There are also high contents of cobalt, iron, manganese and lead.



Extreme concentrations of aluminium ( $170\,000\ \mu\text{g}/\text{dm}^3$ ), cadmium ( $65\ \mu\text{g}/\text{dm}^3$ ), cobalt ( $470\ \mu\text{g}/\text{dm}^3$ ), iron ( $155\ \text{mg}/\text{dm}^3$ ), manganese ( $18\,500\ \mu\text{g}/\text{dm}^3$ ), sulphates ( $3200\ \text{mg}/\text{dm}^3$ ), titanium ( $23\ \mu\text{g}/\text{dm}^3$ ) and uranium ( $8\ \mu\text{g}/\text{dm}^3$ ) were observed in surface water of two reservoirs located near the KWK Jan Kanty hard coal mine dumps at Szczotki. These values were not taken into consideration when calculating the statistical parameters of the elements in the drainage basin water.

**Bobrek River.** Water of the lower reach of the Bobrek River show both relatively constant pH values (7.4–7.6) and high electric conductivity (3.03–3.27 mS/cm). It is worth noticing that just the electric conductivity value  $>1\ \text{mS}/\text{cm}$  itself classifies the water as very highly polluted (Witczak, Adamczyk, 1994). The water contamination is related to industrial sewage discharge along the whole stream course. In the upstream and middle reaches, the watercourse is contaminated by sewage discharged from the Przyjaźń coking plant and ArcelorMittal iron smelter in Dąbrowa Górnicza, by saline water and brines flowing from the KWK Porąbka-Klimontów and KWK Kazimierz-Juliusz hard coal mines, and by flows from the watercourses draining the area of mining waste dump in the Maczki-Bór sand mine, the site of disposal of post-flotation waste, coke, brown coal fly ash, flue gas desulphurization waste, furnace waste and crushed rocks (CTL Maczki-Bór..., 2008).

In the lower course of the Bobrek River, sewage contaminated by the following elements are discharged to the river from the KWK Niwka-Modrzejów hard coal mine: boron ( $470\text{--}490\ \mu\text{g}/\text{dm}^3$ ), chlorine ( $600\text{--}640\ \text{mg}/\text{dm}^3$ ), potassium ( $50\ \text{mg}/\text{dm}^3$ ), lithium ( $50\ \mu\text{g}/\text{dm}^3$ ), molybdenum ( $9\ \mu\text{g}/\text{dm}^3$ ), sodium ( $370\text{--}390\ \text{mg}/\text{dm}^3$ ), rubidium ( $800\ \mu\text{g}/\text{dm}^3$ ), sulphates ( $250\ \text{mg}/\text{dm}^3$ ), strontium ( $1200\ \mu\text{g}/\text{dm}^3$ ) and thallium ( $0.40\text{--}0.60\ \mu\text{g}/\text{dm}^3$ ). The river water also contains considerable amount of arsenic, barium, cobalt, copper, nickel, phosphorus and antimony. They are probably supplied with water of the right bank tributaries contaminated by municipal and industrial sewage discharged by the Mikrohuta smelter in Dąbrowa Górnicza and Enmech mechanical company in Sosnowiec.

**Przemsza River and its catchment.** Due to similar water chemistry, the characteristics of the drainage basin are presented together with those of the mouth of the Czarna Przemsza River.

In areas situated beyond the northern border of the map sheet, the Czarna Przemsza River is discharged by contaminated waters of its tributaries: Pogoria, Potok Zagórski, Brynica and Bolina as well as by direct municipal and industrial sewage discharges. The main

source of industrial sewage are the Będzin heat and power plant, Buczek and ArcelorMittal iron smelters and KWK Sosnowiec hard coal mine. Within the limits of the map sheet, the Czarna Przemsza and Przemsza rivers are affected by municipal sewage from Mysłowice, Sosnowiec and Jaworzno, saline mining waters from the KWK Niwka-Modrzejów and KWK Mysłowice-Wesoła hard coal mines, sewage from the Jaworzno III Power Plant and very highly polluted water of the Wąwolnica Stream.

Water acidity ranges from 7.0 to 7.7. The maximum value (pH 9.0) was noted in the small stagnant water reservoir in the Brzęczkowice residential district.

The pH of the Łęg reservoir varies between 7.5 and 7.9 and a forest lake located east of it is filled with acidic water of pH 4.7–6.0.

Specific electric conductivity is commonly between 2 and 3 mS/cm, indicating high mineralization of the water. The highest EC value (21.56 mS/cm) was measured in the canal carrying sewage to the Czarna Przemsza River near the Kazimierz III mine shaft belonging to the Niwka-Modrzejów hard coal mine.

The Czarna Przemsza and Przemsza waters are contaminated mainly by elements originating from coal mine brines, including: boron, chlorine, potassium, lithium, magnesium, sodium, rubidium, sulphates, strontium and uranium. In some areas considerable amounts of metals are also observed. The water of a canal carrying sewage to the Czarna Przemsza near the Kazimierz III mine shaft contain up to  $0.47 \mu\text{g}/\text{dm}^3$  of silver, up to  $1523 \mu\text{g}/\text{dm}^3$  of barium and up to  $494 \text{ mg}/\text{dm}^3$  of calcium. The Przemsza and Łęg reservoir water contain considerable concentrations of thallium ( $5\text{--}10 \mu\text{g}/\text{dm}^3$ ), whereas the water of the system of ditches and the reservoir located near the Jaworzno III Power Plant are enriched in aluminium ( $400\text{--}1600 \mu\text{g}/\text{dm}^3$ ), cadmium ( $2\text{--}6 \mu\text{g}/\text{dm}^3$ ), cobalt ( $4\text{--}9 \mu\text{g}/\text{dm}^3$ ), iron (up to  $25 \text{ mg}/\text{dm}^3$ ) and manganese ( $1000 \mu\text{g}/\text{dm}^3$ ).

Extremely high concentrations of metals (cadmium, cobalt, chromium, copper, molybdenum, and nickel), chlorine, potassium, sodium, rubidium and phosphorus are observed in the waters of the watercourses and the settling pond in Mysłowice Brzezinka. The concentrations are as follows: cadmium  $9.6 \mu\text{g}/\text{dm}^3$ , cobalt  $82.4 \mu\text{g}/\text{dm}^3$ , chromium  $3000\text{--}4000 \mu\text{g}/\text{dm}^3$ , copper  $400\text{--}600 \mu\text{g}/\text{dm}^3$ , molybdenum  $20\text{--}40 \mu\text{g}/\text{dm}^3$ , nickel  $2000\text{--}5500 \mu\text{g}/\text{dm}^3$ , zinc  $31\,000\text{--}33\,980 \mu\text{g}/\text{dm}^3$ . These metals probably come from eluates from ancient waste dumps and industrial sewage discharged from the Brzezinka industrial zone, where chemical and machinery industries developed.

A positive trend is the decreasing concentrations of metals over the last several years. For example: the presently measured zinc concentration varies from 30 to 315  $\mu\text{g}/\text{dm}^3$ , whereas in the period of 1994–1996 the value was 820–19 700  $\mu\text{g}/\text{dm}^3$  (Pistelok, Galas, 1999).

**Rów Kosztowski Stream and its catchment.** The water has pH ranging from 6.8 to 7.9, and their average electric conductivity is 0.67 mS/cm. The EC value measured in stagnant water reservoirs in the upstream of the river (near the old brick pit in the Larysz district) is 2.73 mS/cm.

The water shows increased concentrations of elements characteristic for saline mine waters (barium, boron, chlorine, lithium, sodium, strontium, rubidium), phosphorus and metals (cobalt, iron, manganese, antimony), which can originate from both drainage of Carboniferous deposits in the upstream area and municipal and industrial sewage discharges.

**Wąwolnica Stream.** Its water show acidity varying from 6.8 to 7.5 and specific electric conductivity between 0.93 and 1.99 mS/cm.

The increased contents of boron, chlorine, potassium, lithium, magnesium, sodium, sulphates and strontium are associated with eluates from waste dumps of the KWK Jaworzno hard coal mine located east of the map sheet border. Near the Organika-Azot chemical factory in Jaworzno, the Wąwolnica and its left bank tributary water contain considerable amounts of arsenic, cobalt, iron and manganese. The metals come from eluates of the Central Landfill Site (Centralne Składowisko Odpadów) of the Organika-Azot chemical factory in Jaworzno, which produces metals-containing pesticides.

## CONCLUSIONS

1. Anthropogenic pollution of the environment come from the following sources: hard coal mining, large-scale coal combustion at power plants, effects of post-mining and furnace waste dumps and settling ponds, historical mining and processing of Zn–Pb ores, iron and non-ferrous metals smelting, chemical and machinery industries and transportation.
2. Chemical composition of soils' parent rocks finds its reflection in geochemistry and grain size. The soils that developed on glaciofluvial and fluvial sands contain small contents of aluminium, barium, calcium, cobalt, chromium, iron, magnesium,

manganese, nickel, phosphorus, strontium, titanium and vanadium. It refers to both topsoil (0.0–0.3 m) and subsoil (0.8–1.0 m). The soils that evolved from the Triassic carbonates are conspicuous by increased contents of calcium, magnesium and manganese and are enriched in most of the analyzed elements. The soils that developed from the outcrops of Carboniferous rocks are enriched in the silt and clay fractions as well as in aluminium, barium, cobalt, chromium, iron and nickel.

3. The soils of areas composed of the Triassic carbonates and its historical extraction are polluted with cadmium, lead and zinc. These metals are concentrated mainly within the topsoil. The areas of anomalies diminish at the depth of 0.8–1.0 m, however their intensity simultaneously increases.
4. Soils acidity is variable and constrained largely by land use. The soils of compact settlement and industrial areas are commonly neutral, whereas forest soils are acidic.
5. Contamination of aqueous sediments and surface water is related to human impact. It is sourced from mining waters of active and closed down hard coal mines, industrial and municipal sewage and eluates from mine waste dumps.
6. Aqueous sediments are polluted mainly by metals derived from contemporary and historical smelting, metallurgy industry (chromium, zinc, cadmium, cobalt, copper, nickel, lead, mercury, silver and iron) and chemical industry (mercury, arsenic).
7. The surface water is characterised by high variability in the contents of individual elements, acidity and electric conductivity. Salinity of most of the watercourses is due to the inflow of mineralized mining water. Water discharged from hard coal mines contaminates the watercourses with barium, boron, chlorine, potassium, lithium, molybdenum, sodium, strontium, sulphates, rubidium, thallium and antimony.
8. The most polluted water bodies are stagnant water reservoirs located near mine waste dumps.

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