

INTRODUCTION

Geochemical mapping of Poland (Lis, Pasieczna, 1995a, b) has proved that the most polluted soils, aqueous sediments and surface water occur in the Silesian-Cracow region. In the area of the discovered anomaly of heavy metals, mapping works on 'Detailed geochemical map of Upper Silesia (SMGGŚ)' scale 1:25 000 started in 1996 with a pilot project of the Sławków Map Sheet (Lis, Pasieczna, 1999).

Geochemical mapping, scale 1:25 000 carried out on the Bieruń Stary Map Sheet M-34-63-C-a area is the continuation of detailed cartographic survey conducted by the Polish Geological Institute–National Research Institute. The project was ordered by the Ministry of the Environment and financed by the National Fund for Environmental Protection and Water Management. The purpose of the study was to identify pollution of the area degraded due to long-lasting hard coal mining, power industry, smelting and other industries.

Economic activity in the region has rich and long tradition. In the 14th century when forge existed in this area, using local bog iron deposits. Linen manufacturers operated in Łędziny. The Mleczna River water was dammed up to operate forges in Jaroszowice (famous for their production of excellent scythes and gun barrels). Forests were grubbed out and charcoal was produced. Opencast hard coal mining started in 1657 at coal seams outcrops in the forests of Jaroszowice and in Łędziny (Polak, 2000). In the mid-19th century, hard coal production became the main industry in this region, reaching its acme in the late 20th century. Currently, hard coal is exploited by the KWK Ziemowit mine in the Łędziny.

The land use of the sheet area has a mixed character, rural-urban with a significant contribution of industrial facilities and transportation routes. Its western area is part of the Tychy urban district, the north-western area belongs to the Katowice and Mysłowice urban districts, and the south-eastern area covers part of the Bieruń Stary and Łędziny urban communes and a small part of the Bojszowy commune, which belong to the Bieruń-Łędziny powiat.

The large industrial centre of the area is the Tychy Subzone of the Katowice Special Economic Zone (PT-KSSE) situated in Tychy town and Bieruń commune. International and Polish companies (mainly of the motorcar industry) operate within this zone.

The land use is characterised by the predominance of forest complexes in the north of the map area. To preserve natural forests protected areas have been created recently. One of

the most important protected area is the Murcki reserve preserving old-growth forest (200-year beeches), threatened bird and plant species (*Streptopus amplexifolius*, *Daphne mezereum*) and amphibian hatchings. The wetland area in the north-east is the ecological site of Płone Bagno. It has been established in order to protect a bog forest with a part of peat bog, which is a regional-scale unique natural plant population with sites of rare plant species occurrence. (Lasy..., 2010).

Information on the soils, aqueous sediments and surface water quality in the Bieruń Stary Map Sheet 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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CHARACTERISTIC OF THE MAP AREA

Geographical and administrative setting. The Bieruń Stary Sheet M-34-63-C-a covers the area of about 82.5 km² within the coordinates of 19°00'00"–19°07'30" eastern longitudes and 50°05'–50°10' northern latitudes. It is situated in the Silesian Voivodeship. Western part of the sheet area belongs to the Tychy urban district divided into the following districts: Czulów, Zwierzyniec, Wygorzele, Zawisć, Jaroszowice and Urbanowice. The north-eastern part of the map area belongs to the urban districts of Katowice and Mysłowice. The south-eastern portion of the map sheet covers part of the Bieruń Stary and Łędziny urban communes and a small fragment of the Bojszowy commune. The study area is situated at the southern periphery of the Upper Silesian Agglomeration, which is the most populated region of Poland with strongly developed industry and transportation systems.

The map area is located at the border the Silesian Upland and Podkarpacie regions. Its north-eastern part – Pagóry Jaworznickie Hills belong to the Silesian Upland, whereas the south-western part – the Pszczyna Plain, which is a lower-order unit of the Oświęcim Kettle Hol, belongs to the Podkarpacie region (Kondracki, 2000).

Relief and geomorphology. The relief of the map area is clearly dependent on tectonic structures of the basement. The Pagóry Jaworznickie Hills are a belt of tectonic horsts composed of Triassic limestones, marls and dolomites overlying Carboniferous rocks. Near Łędziny, the horsts form a hilly ridge of approximately 270–300 m a.s.l. of elevation with a summit of Klimont mountain (302.4 m a.s.l.). The terrain slopes southwards in steps, towards the Oświęcim Kettle Hol. Individual hills and ridges separate vast, locally wetland valleys filled with glaciofluvial deposits. Their bottoms are at the height of 240–250 m a.s.l.

The eastward-sloping Pszczyna Plain lies at the height of 230–260 m a.s.l. Its basement is composed of Carboniferous deposits overlaid by Neogene clays covered by 40 m thick Quaternary tills and sands.

The present-day landscape of the area is highly altered by human-made infrastructure. It includes railway and road embankments and viaducts of the eastern bypass of the Upper Silesian Industrial Region, crossing the central part of the map sheet area from east to west, and of the international road E75 running from north to south along the western boundary of the map sheet (Plate 1). A number of old road embankments (of the Zwierzyniecka,

Borszacka, Wygorzelska, Łędzińska and Szyjowa roads) and remains of old dumps can be found in the forests of the northern part of the map area.

Barren rocks dumps of the KWK Ziemowit coal mine in Łędziny and terrain depressions that was formed as a result of underground coal mining-induced subsidence have also transformed the landscape significantly.

The map area covers the left-bank drainage basin of the Gostynia River, which is a tributary of the Vistula River. Most of the area is drained by the Mleczna River (and its left tributary the Przyrwa – Potok Ławecki Stream) that flows into Gostynia River beyond the southern border of the map sheet. The Gostynia River and its tributary the Tyszanka River (also called Potok Tyski) carry water from the south-western part of the map area. Most of the watercourse channels are regulated and commonly isolated with concrete slabs. There is a number of small, unnamed watercourses (streams, canals and drainage ditches) throughout the whole area. Most of them are ephemeral watercourses carrying water only during wet periods.

Natural and artificial water reservoirs are the important hydrographic elements of the landscape. The largest artificial water reservoirs are as follows: the mining water reservoir of the KWK Ziemowit hard coal mine in Łędziny, the Potok Nowotyski reservoir and settling ponds of communal and industrial sewage treatment plant in the Urbanowice. Inundated areas that were formed as a result of underground coal mining-induced subsidence are observed in some places. The largest natural reservoir is the Łysina Lake. It plays the flood-prevention and recreational functions.

Land use. Non-built up or rural areas (82% of the total area) predominate in the region. Urban areas account for approximately 12%, whereas industrial areas 6% (Plate 2). Industrial development areas are situated at the Tychy Subzone of the Katowice Special Economic Zone (PT-KSSE) between Bieruń and Tychy (Katowicka..., 2010), and at the KWK Ziemowit hard coal mine in Łędziny.

In terms of land use, forests occupy the largest area (over 34%) in the north of the map sheet. Agricultural lands (23%) and barren lands (18%) dominate in the central part. The remaining area is dominated by grassland, water reservoirs, roads and railways (Plate 3).

Economy. Industrial infrastructure of the region has developed mainly during the last 45 years and therefore it is more modern and functional than similar industrial facilities in other Silesian cities and towns. Industrial works have been located on the outskirts of the

cities, outside the areas of post-mining deformations, and are well connected by transportation routes.

The basic economic activity of the area is hard coal mining that started with a large number of small shallow coal mines in the mid-19th century, but developed on a large scale in the late 20th century. In the western part of Łędziny, there is the mining area of the KWK Ziemowit hard coal mine with the Piast mine shaft. There are also numerous coal trade and freight forwarder companies, a waste management company and planting and maintenance services of green areas, as well as many small trade and service businesses. A large logistics and warehouse complex is under construction.

The Czulów ventilating shaft of the KWK Murcki-Staszic hard coal mine, which main facilities lie beyond the northern boundary of the map sheet, is situated in the north-western part of the map area.

A new industrial centre of the region is the Tychy Subzone of the Katowice Special Economic Zone (PT-KSSE), partly situated within the boundaries of the Tychy city and partly in the Bieruń commune. PT-KSSE covers the area of 143.32 ha. A number of international and Polish companies employing over 10 thousand employees operates there (Katowicka..., 2010). Warehouses and accompanying facilities (social and office buildings, transformer stations, water and sewage systems and roads are located there too. Over 150 investors operate in this area and over 80 companies of various industry sectors have already started their production there (Katowicka..., 2010). The most broadly represented sectors are components, spare parts and equipment for motor vehicle industry. The remaining sectors include printing, packaging, plastics, food, electrical, metallurgical, glass and mining equipment machinery industries.

In the Tychy area, there is also the power and heating plant that started to operate in 1963 using hard coal fuel (Elektrociepłownia..., 2010). Much of the zone is occupied by the Fiat motor vehicle company plants, founded in 1971–1973, and associated cooperatives. There are also other supporting services within the zone, such as accounting offices, law chambers, customs agencies and freight forwarder companies (Katowicka..., 2010).

Paper mills, established in 1887, operate in Tychy-Czulów. A dairy plant is located in Bieruń.

Worth noting is historical intense fish farming in the southern part of the map sheet area. Fish farming traditions date back to the 14th/15th centuries in the Bieruń region. The

Wielki Staw Bieruński and Staw Jaroszowicki ponds covered the area of 600 ha and were surrounded by large dams (Marcinek, 1993). Traces of one of them have been preserved in Bieruń until the present. The ponds were completely dried up in 1809–1825.

GEOLOGY AND MINERAL DEPOSITS

The map area is situated in the eastern part of the Main Trough of the Upper Silesian Coal Basin (USCB). Its geology is characterised by the presence of several structural stages. The basement of the USCB is composed of crystalline rocks overlain by Cambrian and Devonian sedimentary formations (Buła, Kotas, 1994; Buła, Żaba, 2005). These are in turn overlain by four structural stages separated by stratigraphic unconformities: Late Paleozoic with Carboniferous deposits, Mesozoic with Triassic deposits, Neogene and Quaternary.

The oldest well-explored rock formation is the coal-bearing Carboniferous series composed of sandstones, siltstones, clay shales and coal seams. Its top is at the depth of from several to a few tens of metres. Rock strata gently dip commonly at the angle of $<10^\circ$ and are cut by 50–170 m throw faults. In the area of economic interest (to the depth of 1000 m), there are the Łaziska Beds of the Kraków Sandstone Series and the underlying siltstone series of the Orzesze Beds (Krysowska, 1967). The siltstone-shale Orzesze Beds contain sandstone interbeds, siderite concretions and several tens of thin coal seams. The Łaziska Beds are represented by arkosic and calcareous sandstones, and conglomerates with subordinate clay shale interbeds and relatively thick coal seams. The Łaziska Beds are outcropped near Łędziny and Urbanowice, forming horst-like hills that rise above the top of Quaternary deposits.

The Mesozoic structural stage is represented by the Lower and Middle Triassic formations composing the hills near Łędziny, Bieruń Stary and Cielmice (Plate 1). The Lower Triassic includes also a 30-m thick package of Roethian marine dolomites and limestones underlain by a few metres thick continental sands and variegated clays. The Middle Triassic is represented by platy and conglomeratic limestones with marl interbeds, included in the Gogolin Beds. They attain the thickness of up to 30 m, but they are erosionally truncated in many places.

The Triassic and Carboniferous strata are divided into a number of tectonic blocks. In the study area, Krysowska (1967) distinguished sublongitudinal structures of the Dąb-

Urbanowice Sink and Zapór Graben, and the obliquely arranged Blich and Przyrwa grabens and the Jakub Fault between Cielmice and Bieruń Stary.

The **Neogene** is composed of Miocene marine deposits distributed in topographic lows throughout the whole map area, but not outcropping on the surface. The deposits are represented by marly clays, sandy claystones, gypsum and limestones (Krysowska, 1967). Their thickness, locally exceeding 100 m, is variable and constrained by relief variations of the top of the underlying Carboniferous and Triassic formations.

The **Quaternary** is represented by glacial, glaciofluvial and alluvial deposits covering most of the study area (Plate 1). Thin Odranian Glaciation tills occur in patches mainly in the vicinity of Czulów, Zwierzyniec, Wygorzele, Jaroszowice and Bieruń Stary. Pleistocene glaciofluvial sands and gravel form a relatively uniform, 10–40-m thick cover. Holocene sands, muds and peaty muds compose accumulation terraces in river valleys.

Mineral deposits. Parts of the Murcki, Wesoła, Łędziny, Ziemowit, Kobiór-Pszczyna and Piast hard coal deposits are situated within the map sheet area (Strzemińska *et al.*, 2005).

Opencast **hard coal** extraction was carried out from the 17th to 19th centuries on the outcrops of the Łaziska Beds in the Jaroszowice and Łędziny forests (Polak, 2000). In 1842, a 3 m thick coal seam was discovered near Łędziny and exploited in the Radość Henryka shallow underground coal mine. The mine was then renamed to Matylda in 1893, and again renamed to Piast after World War I. Since the 1970s, the mine has been a part of the KWK Ziemowit coal mine and has operated until the present time (Informator..., 2008).

Technically mineable coal seams (currently to the depth of 1000–1200 m) are represented by the Łaziska and Orzesze beds. The Łaziska Beds contain thicker water-containing coal seams, more strongly contaminated by sulphur. The coal seams of the Orzesze Beds are thin. They locally contain considerable amount of ash and are rarely qualified for exploitation.

Power coal seams, 2–6 m in thickness and with heating value of 20.4–21.2 MJ/t, are mined in the KWK Ziemowit coal mine in Łędziny. Its mining area extends beyond the eastern boundary of the map sheet. The average ash content in the coal is 14.4%, the content of total sulphur is 1.55%. In total, 48 hard coal seams have been proved in the Łaziska and Orzesze beds of this area. Thickness of the documented interval varies from 423 to 1000 m, and the average total thickness of coal seams is 56 m (Strzemińska *et al.*, 2005). Associated mineral deposits include 0.5 cm–15 cm thick intergrowths of tonsteins and coal-bed methane.

Mining waste of the KWK Ziemowit coal mine is used for land reclamation of the Maczki-Bór sand pit in Sosnowiec as well as for covering dumps and post-mining deformations. Mining water is discharged to the Przyrwa Stream through a settling pond located West of Łędziny. Part of the water is later used for industrial processes and as drinking water.

In the north-western part of the map sheet, there is a hard coal deposit exploited by the KWK Murcki coal mine. Its mining facilities are located in the Katowice Map Sheet area. The Łędziny and Kobiór-Pszczyna coal deposits have been still undeveloped.

Miocene **clays** are extracted for the local brick production.

HUMAN IMPACT

Natural environment of the region has been degraded mainly due to long-lasting hard coal mining accompanied by discharges of saline mining waters, post-mining subsidence and loss of stability of buildings above unsupported underground excavations (Chwastek *et al.*, 1990; Program., 2001, 2003). Changes in the landscape and chemistry of the surface environments are also caused by other industry sectors accompanied by the infrastructure (buildings, railways, overhead power lines) and by the effects of communal, industrial and mining waste landfills.

Atmospheric air. The air is polluted mainly by emissions from industrial and transportation sources, dumping sites, ventilation mine shafts, heating plants, furnaces of individual houses and by far-reaching dust emission from Upper Silesian Industrial Region and Ostrava-Karvina Region in the Czech Republic. The direction and speed of wind are essential for the pollution volume. Locally increased air pollution is observed mainly during the heating season. Large forest areas in the northern part of the map area improve the air quality.

Most of gas emission and dust originate from industrial coal combustion in the Tychy-Urbanowice power and heating plant and the Łaziska Power Plant. Gases and fly dusts emitted from coal combustion contain the following elements: arsenic, beryllium, cobalt, chromium, mercury, lead, vanadium and zinc (Kabata-Pendias, Pendias, 1999; Hławiczka *et al.*, 2001; Pacyna, Pacyna, 2001; Olkuski, 2007).

The Tychy-Urbanowice power and heating plant has consistently introduced modern combustion technology and emission filtering systems since 1994. They allow to fulfil the permissible limits recommended by the Integrated Pollution Prevention and Control.

Heating stations of the Fiat motor company, plastics manufacturing company, dairy plant and paper mill have a smaller contribution to the air pollution. The air quality is also influenced by emission from printing, metallurgy and chemical companies as well as from a bituminous mass plant and other plants.

Significant emissions originate from individual houses heated by coal and coke. Due to economic reasons, many of the residents use low quality coal. Its combustion causes a distinct increase of PM dust in the atmospheric air during the heating season. In Łędziny and Bieruń, only about 16% of the energy demand is covered by using gas boilers (Program..., 2003).

Due to the well-developed road infrastructure, emission from car engines is a significant source of air pollution in this region. The car exhaust contain carbon oxide, nitrogen oxides and hydrocarbons.

Piles of barren rocks and landfills affect the air quality through secondary dusting and gas emissions. The Tychy-Urbanowice communal landfill is a source of landfill gases (carbon dioxide, methane, ammonia and aromatic hydrocarbons), whereas the sewage treatment plant located close to the landfill is a source of biogas emission (Program..., 2003). The air quality is also affected by emissions from the large transportation company of Bertani (emitting carbon oxide and dioxide, sulphur dioxide, nitrogen oxides and dusts) and the Nitroerg explosives company in Bieruń Stary, emitting components specific for this type of activity (Blarowski *et al.*, 2003).

Air quality monitoring is conducted only in Tychy. It includes standard automatic measurement and passive measurement of benzene concentration. In 2008, dust content fell within the permissible limits, however benzo(α)pyrene concentrations exceeded the limits (Raport..., 2009). The results of air monitoring show a constant trend of improving air quality in the Silesian Voivodeship over the last several years.

Surface water and groundwater. The long-lasting hard coal mining, urbanization and industrialization of the region have caused changes in the hydrographic network and a deterioration of water quality. Vast topographic lows and depressions are observed at the surface. Watercourses and springs periodically disappear, and the surface water quality is

unacceptable. Saline mining waters commonly show mineralization of above 3 g/dm^3 , but the concentrations of salts can occasionally reach 150 g/dm^3 (Gabzdyl, Pozzi, 2001).

The drainage of a few multiaquifer formations through mine excavations has led to the cones of depression forming, that cause changes in the conditions of surface and ground water recharge. A vast combined cone of depression covering the northern and eastern parts of Tychy, Łędziny and Bieruń has developed. Simultaneously, the Carboniferous coal-bearing deposits have undergone dewatering down to the depth of 100–300 m (Program..., 2003).

The Mleczna River valley is the area of significant subsidence and water inflow in some places, accompanied by degradation of forests. Near the Żogalik Pond, there is a subsurface outflow of water and overgrowth of an abandoned and drying stream.

Sewage systems serve less than half of the population of the sheet area, and the degree of sewage purification is insufficient (Blarowski *et al.*, 2003). The existing sewage treatment plants commonly do not meet the requirements of both Polish and EU standards. A mechanical-biological sewage treatment plant was built in Łędziny in 2003 (Hołodunów district). It serves the northern part of the town (Łędziny..., 2010). A project for constructing a new sewage treatment plant for the southern area of the town is under preparation.

The Gostynia and Mleczna rivers are among the most polluted rivers in the Silesian Voivodeship. Their water is characterised by excessive contamination with respect to both sanitary conditions and physicochemical properties, and contain chemical compounds from sewage and mining waters discharged in the upstream areas of their catchments and from other sources situated throughout the map area.

The Gostynia River receives sewage from the Łaziska Górne town (including the Łaziska power and heating plant), Tychy (through the Potok Tyski Stream), in its lower course also from Łędziny and Bieruń. A significant source of pollution in Tychy is the sewage treatment plant located in Urbanowice, collecting both communal and industrial sewage (including those from gully emptiers). This is a mechanical-biological sewage treatment plant, chemically assisted for phosphorus removal.

The upstream section of the Mleczna River and its left-bank tributary the Przyrwa Stream receive sewage from the southern districts of Katowice and Mysłowice. The Mleczna River also receives sewage from the Czulów sewage treatment plant that collects sewage from a paper company. Mining waters from the KWK Ziemowit hard coal mine are mechanically purified in a settling pond in Łędziny near the Przyrwa Stream. At the first stage, the mining

water is pumped into the reservoir. After purification from suspended particles with the use of coagulants, the water is gradually discharged into surface water streams and partly intended for power units cooling in the Łaziska Power Plant.

Additional contamination of surface water is caused by eluates from mining wastes that undergo weathering processes at the ground surface. Leaching of mineralised waters (often acidic) from dumps leads to the release of sulphates and sulphuric acid. In the acidic environment, heavy metals are mobilized, and even aluminosilicates disintegration and release of aluminium occur.

Soils. Degradation of soils occurs as a result of emissions of dust, industrial gases and motor fumes, dumping of wastes and improper agriculture. Due to the use of mineral fertilizers, sewage precipitates and pesticides, harmful metallic elements, nitrogen, organophosphate compounds, chlorinated hydrocarbons, and other substances are introduced into the soils.

These factors result in the decrease in humus content, change in soil acidity, moisture and structure, leaching of nutrients, and, in consequence, in the decrease of soil productivity. The soils in the study area are commonly either excessively moistened in subsidence troughs or dried up within the cone of depression. Fertilization with sludge from the Tychy sewage treatment plant contributes to the pollution of the soils by heavy metals and unwanted organic compounds.

Soils of the western and northern parts of the Bieruń-Łędziny powiat are categorized into class A, allowing plant cultivation without significant restrictions (Blarowski *et al.* 2003). But in some regions, the soils are polluted with heavy metals. In the river valleys, high acidity is observed.

Chemical contamination by heavy metals is the result of activity of industry, vehicle repair services and transportation. Local contamination of the soils is caused by dumping of outdated pesticides and fluorescent lamps as well as and mining wastes.

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 vector topographic sheet, 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 km²). The total number of soil sampling sites was 1326 (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 ladle. 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 marked at topographic maps at the 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 as type of soil and aqueous sediment). The coordinates were taken with the accuracy of ±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 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 (H₂O) was measured 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, SiO₂, SO₄, 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 ICP-MS method. The applied analytical methods and the detection limits of measured elements are shown in Table 1.

The control of 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 topsoil (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, Oświęcim Map Sheet M-34-63-C (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, Oświęcim Map Sheet (Biernat, Kryszowska, 1955). Individual

elements of the geological map were digitized to create their vector images which were subsequently combined with the topographic base, producing the 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 and 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 Bieruń Stary 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, SiO₂, SO₄, Sr, Ti, Tl, U, Zn in surface water and 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 Bieruń Stary Sheet and the datasets of 1:25 000 scale neighbouring sheets. Thus any disagreements at the sheet borders were avoided. After interpolation from mono-element maps the Bieruń Stary Sheet was extracted and combined with the topographic base map.

The geochemical maps of aqueous sediments and surface water were elaborated separately for the Bieruń Stary 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.

RESEARCH RESULTS

SOILS

The most common soil types are *Podzols* and *Cambisols* developed on glaciofluvial and glacial deposits. *Phaezems*, *Rendzinas* (on hills near Łędziny) and *Histosols* occur locally (Miler-Janczyk *et al.*, 2004).

Both natural soil-forming processes and anthropogenic factors affect the soil quality. Economic activity, and industrialization and urbanization processes have resulted in soil degradation (changes in the soil profile and physicochemical properties).

Grain size. Almost all chemical and physical properties of soils are either directly or indirectly related to their mechanical composition. Determination of the grain size of soils provides information about their origin and vulnerability to contamination. This is one of the most important parameters controlling mobility of chemical elements within the soil profile. Grain size is also the main indicator of soil use values (Kocowicz, 2000). Each of the mechanical fractions of soils, i.e. groups of particles of defined size and often of similar physico-chemical properties, affects porosity, firmness, plasticity, sorption types and resistance of soils to degrading factors (Prusinkiewicz *et al.*, 1994). Grain size of soils is also an important factor controlling contents of individual elements.

Soils rich in the clay (<0.02 mm) and silt (0.1–0.02 mm) fractions are characterized commonly by the highest concentrations of many elements and their lower migration ability under hypergenic conditions. The standards and recommendations on permissible concentrations of metals in soils commonly take account of the 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: 1.0–0.1 mm, 0.1–0.02 mm and <0.02 mm, according to the Polish Standard BN-78/9180-11 (1997) recommended by the Polish Society of Soil Science.

Grain size variability of topsoil is clearly dependent on the parent rock lithology. Over most of the area, the sand fraction (1.0–0.1 mm) proportion exceeds 75% (Plate 4), and the highest content (>90%) is observed in the soils developed on sand-gravelly glaciofluvial deposits (Plate 1) in the north of the map area. The abundance of the sand fraction in the soils developed from tills indicates that they have been strongly washed out.

Enrichment in the silt fraction (0.1–0.02 mm) was observed in the soils of the central part of the map area (Wygorzele–Klachowiec–Urbanowice–Jaroszowice) and of the Pagóry Łędzińskie hills (Plate 5). The soils of these areas developed on tills as well as Carboniferous deposits and Triassic carbonates contain >10% (locally >15%) of the silt fraction.

The clay fraction (<0.02 mm) content does not exceed 10% (Plate 6) in most of the soils. The value increases only near mine shafts of the KWK Ziemowit hard coal mine in Łędziny, where it exceeds 10% in the soils developed on Carboniferous clastics.

Acidity. Both the topsoil and subsoil are acidic. The lowest pH values (<5) were noted in the topsoil of forests in the north of the map area. Acidic soils also occur in the south-eastern part of the map sheet (partly covered with forests) and in river valleys filled with alluvial sediments. A patch of acidic soil (pH<6.3) developed on tills at the depth of 0.8–1.0 m is clearly observed between the Tyszanka and Mleczna rivers.

Neutral soils (pH 6.8–7.4) cover larger areas at the depth of 0.8–1.0 m, occurring mainly in the central-eastern and western parts of the map sheet (Plates 7 and 8).

Small areas within both the topsoil and subsoil are characterised by alkaline soils (pH>7.4). They occur on the outcrops of Triassic carbonates (near the Łędziny and Cielmice) and along the western boundary of the map sheet on Carboniferous rocks and glacial tills. Some of the soils of urban areas are characterised by pH>8, which can be the result of alkaline dust admixture emitted by industrial plants.

Geochemistry. Chemical composition of parent rocks is the most important factor affecting the chemistry of soils. The main geochemical features of parent rocks are best legible in deeper sections of the soil profile. A spatial distribution of elements inherited from the parent rocks often allows recognizing geochemical background variability and identifying natural anomalies.

Analysis of the chemical composition the soils of the Bieruń Stary Sheet indicates the clear relationship between the spatial distribution of a number of elements (aluminium, barium, calcium, cobalt, chromium, nickel, phosphorus, strontium, titanium and vanadium) and the geological structure of the basement. The elements tend to accumulate in the silt fraction of the soils. Average contents of these elements (expressed in median values) are similar to the geochemical background values in the Silesian-Cracow region (Table 2). The soils that developed on tills are commonly enriched in most of components, as compared with the soils that developed on Quaternary glaciofluvial sandy deposits. Low contents of elements

in Quaternary glaciofluvial sandy deposits is related to poor chemical composition and acidity of sandy deposits that favours leaching of many components.

Easily noticeable are the high contents of aluminium, iron, chromium, titanium and vanadium, corresponding to the intersection image of till outcrops (especially at the depth of 0.8–1.0 m). The areas occupied by soils rich in these elements are larger in the topsoils than in the subsoils.

The highest enrichment in heavy metals, sulphur and phosphorus is observed in alluvial soils and is related to anthropogenic sources.

The Gostynia River valley alluvial soils show high values of aluminium (>1.60%), barium (>240 mg/kg), phosphorus (>0.120%), chromium (>20 mg/kg), cobalt (>8 mg/kg), nickel (>10 mg/kg) and vanadium (>40 mg/kg). Considerable enrichment of the same set of chemical elements is characteristic feature of alluvial soils in the Mleczna and Przyrwa Stream valleys. They are also enriched in iron (>4%) and manganese (>800 mg/kg). The source of these elements is water and sediments containing anthropogenic and lithogenic components collected from all over the drainage basins and deposited during floods. A favourable environment of high sorption sediments (organic muds, clays and peats) is crucial for the concentration of metals.

The organic carbon content in soils developed on Quaternary tills, fluvial muds and older basement rocks commonly ranges between 1.50 and 3%. The values >3% of organic carbon were observed in alluvial soils of the Gostynia River valley and in forests of the northern part of the map area. In some forests, the soils contain >24% of organic carbon and are also enriched in cadmium (>2 mg/kg), mercury (>0.10 mg/kg), lead (>100 mg/kg) and sulphur (>0.080%). This anomaly was probably formed at the site of waste dumping from settling ponds and tailings piles of the KWK Mysłowice-Wesoła coal mine, which facilities are located close to the northern boundary of the map sheet.

Distinct anomalies of some elements (with two regions of maximum concentrations for both the topsoil and subsoil) were noted in alluvial soils of the Mleczna River valley in the central part of the map sheet area, where fish ponds existed in the 19th century (Absalon, Wac, 1992). The topsoils and subsoils are abundant in arsenic, barium, cadmium, cobalt, chromium, iron, manganese, nickel and phosphorus. Iron and other metals could originate from the historical extraction and processing of bog iron deposits in the Lasy Murckowskie

forests (Ratajczak, Skoczylas 1999) and from forges that operated in this area from the mid-17th century (Oficjalna..., 2010).

The soils developed on the outcrops of Triassic carbonates (at the Wzgórza Łędzińskie hills and near Cielmice) are conspicuous by the abundance of calcium and magnesium (>1%). The distribution maps of these elements, reflecting the relationship with the chemistry of the bedrock, are more clearly expressed for subsoils. These soils also show enrichment in iron, manganese, chromium, cobalt, vanadium and titanium, which can be related to dispersed ore mineralization and limonite accumulation.

Anthropogenic contamination of the soils was observed in several sites.

Arsenic contamination (>20 mg/kg) was reported for alluvial soils of the Gostynia River, Przyrwa Stream and Mleczna River valleys. A local anomaly (up to 537 mg/kg arsenic) was noted in the alluvial topsoil in Bieruń Stary, which is also strongly polluted by copper (up to 724 mg/kg), lead (up to 6876 mg/kg) and zinc (up to 23170 mg/kg) and enriched in barium, calcium, iron and sulphur. The anomalies occur in the lower parts of drainage basins of unnamed watercourses flowing to the Mleczna River from the area of the KWK Piast hard coal mine (located beyond the eastern boundary of the map sheet) and draining the Triassic carbonates in their upstream areas and Quaternary muds in their downstream parts. The concentrations of these elements probably originate from anthropogenic sources.

In the immediate proximity to the Urbanowice sewage treatment plant, the topsoil reveals strong anomalies of silver (up to 11 mg/kg), barium (up to 670 mg/kg), cadmium (up to 12 mg/kg), chromium (up to 76 mg/kg), copper (up to 298 mg/kg) and mercury (up to 7.2 mg/kg). The anomalies are slightly less extensive at the depth of 0.8–1.0 m.

Strong chemical degradation of both the topsoil and subsoil is observed in the area of Czulów paper mill (operating since 1887) and in its closest proximity. The most serious problem is mercury and copper pollution. The concentrations of these elements in the topsoil are 457 mg/kg and 20.23 mg/kg, respectively. In the subsoil, the copper concentration is 4047 mg/kg, the mercury concentration is 4.70 mg/kg, and the anomalies cover larger areas. The soils are additionally polluted by arsenic (>40 mg/kg), barium (>240 mg/kg), lead (>250 mg/kg) and sulphur (>0.160%).

In the Urbanowice industrial area and in the area of Fiat motor company plants, the soils are enriched in barium and calcium that originate probably from dust emitted by the power and heating plant during industrial coal combustion (Rózkowska, Ptak, 1995a, b). Dust

emissions from other factories of the region cause an insignificant increase in the contents of cobalt, copper, nickel and vanadium in their surroundings. A considerable enrichment of the topsoil in sulphur is mainly due to emissions of sulphur dioxide from the Łaziska Power Plant and Tychy power and heating plant.

The parts of the sheet area contaminated to a different extent by cadmium, lead and zinc were estimated (Table 6). Most of the mapped area topsoil contains <4 mg/kg of cadmium, <100 mg/kg of lead and <100 mg/kg of zinc, whereas the subsoil commonly contains <1 mg/kg of cadmium and <25 mg/kg of lead.

Copper, arsenic and mercury anomalies occur only locally and do not bring any serious hazard to the soil environment.

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 Bieruń Stary 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 estimation of the degree of contamination by metals was carried out for the topsoil, classifying them with respect to soil use into the groups A, B and C based on permissible limit values (Rozporządzenie..., 2002). 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 exceeds the permissible limit value. With respect to contents of metals, 37.63% of the topsoils were included into group A, 43.97% into group B and 18.40% into group C (Table 7). The classification (Plate 63) indicates recommended land use according to guidelines provided in Rozporządzenie... (2002). Much of the soils are currently improperly used and require at least monitoring or local reclamation. Concentrations of metals in the soils of some forest, agricultural, grassland and garden areas are so high that the land should be used for industrial purposes only.

The only soils that meet requirements of multi-purpose use are those categorized into classes A and B. Class C soils occur mostly on alluvial deposits, in industrial areas of the