

INTRODUCTION

Geochemical mapping at the scale of 1:25 000 at the Myślachowice Sheet M-34-63-B-d is the continuation of detailed mapping works initiated between 1996–1999 by the pilot sheet “Detailed geochemical map of Upper Silesia – Sławków Sheet M-34-63-B-b” (Lis, Pasieczna, 1999). The project was ordered by the Ministry of the Environment and it was financed by the Polish National Fund for Environmental Protection and Water Management.

The area of the Myślachowice Sheet is located in the southern part of the Cracow-Silesia Upland. The main sources of geologic-anthropogenic anomalies in the sheet area are outcrops of ore-bearing Triassic dolomites hosting zinc-lead ores as well as their historic and current exploitation and treatment. Additional chemical changes of the natural environment and landscape degradation are caused by mining of hard coal-bearing Upper Carboniferous sediments in the southern part of the map area.

Mining, power supply and chemical industries are located in the southern part of the map area (Trzebinia and Myślachowice towns).

Some part of the Myślachowice Sheet (Żabnik Stream valley) is under protection because of high natural values – special peat flora occurrence.

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

The following specialists contributed to this work:

- **J. Lis, A. Pasieczna** – concept and project proposal, project leadership, supervision and coordination of research, databases, compilation of geochemical maps, interpretation of results;
- **P. Dobek, T. Kolecki, P. Kaszycki, T. Szyrak, J. Szyborska-Kaszycka** – sample collection;
- **P. Pasławski, K. Jakimowicz-Hnatyszak, E. Włodarczyk** – leadership and coordination of analytical works;
- **Z. Dobieszewska, M. Cichorski, J. Duszyński, Z. Prasol, K. Stojek** – mechanical preparation of samples for analyzes;
- **I. Witowska, E. Maciolek** – chemical preparation of samples for analyzes;
- **E. Górecka, I. Jaroń, G. Jaskólska, D. Karmasz, J. Kucharzyk, B. Kudowska, D. Lech, M. Liszewska, E. Maciolek, A. Maksymowicz** – chemical analyzes;
- **W. Wolski, Z. Frankowski, P. Dobek** – grain size analyzes;
- **A. Pasieczna, H. Tomassi-Morawiec, A. Bliźniuk** – statistical calculations;
- **M. Głogowska, A. Dusza-Dobek** – characteristics of the map area;
- **M. Głogowska** – geology and mineral deposits;
- **A. Dusza-Dobek, A. Witkowska** – human impact.

CHARACTERISTICS OF THE MAP AREA

Geological and administrative setting. The area of Myślachowice Sheet belongs to the north-western part of the Małopolska voivodeship. It covers Chrzanów district (northern part of Trzebinia and Chrzanów communes) and Olkusz district (southern part of Bukowno commune). Only tiny western part of the map area is located within the Silesia voivodeship (Jaworzno district).

The area under study belongs to the Cracow–Częstochowa Upland, which consists of Silesia Upland and the Olkusz Upland (Kondracki, 2000).

The area is located within the Biała Przemsza River catchment (Kurek et al., 1994). Only its south-eastern part is located within the Chechło River catchment.

At the Myślachowice Sheet area mining activity brought harmful, usually irreversible, changes of the terrestrial and aquatic environments – contamination of soil, ground water and surface water as well as pollution of the atmosphere, creating huge heaps from hard coal mining and changes of the hydrological systems (man-made changes of watercourses, rising of groundwater table and streams restoration).

Relief and geomorphology. In the north-western part of the Myślachowice Sheet there is Biskupi Bór trough filled with Quaternary sands up to about 300 m a.s.l. Horst-like Garb Tarnogórski, located in the north-eastern part, is built up of the Middle Triassic limestones and ore-bearing dolomites (Plate 1). The eastern part of the Myślachowice Sheet is built up of Triassic carbonates, Permian conglomerates and Carboniferous clastic rocks creating hills (part of Olkusz Upland). Hills (elevations), located at the south-western edge of the map area, are as high as 370 m a.s.l. and mostly built up of Triassic and Jurassic carbonates. Some depressions are filled with Pleistocene deposits. The relief of Myślachowice Sheet area is strongly antropogenically changed. Open-pits of sand were built around Biskupi Bór village. Numerous collapse sinks were formed above the Siersza hard coal mine excavations in the central and south-eastern part of the map sheet.

Common changes of relief are historical open-pits of zinc-lead ores at the area of shallow occurrence of Zn–Pb ore-bearing dolomites.

At the Górka place the quarry of limestones and marls is left. Within the neighbouring of Siersza power plant there are hard coal mine and furnace waste dumps currently under recultivation. Their altitude is 20–30 m above ground level.

Land use. Non-built up areas cover 80.34% of the Myślachowice Sheet area, village areas 11.78%, urban areas 5.48% and industrial areas 2.40% (Plate 2). Industrial and urban areas are located mainly in the southern and central part of the map sheet. Essential role in the land use is played by forests covering 62.16% of the area and wastelands 29.35% (Plate 3). Cultivated fields cover only 1.80% of the map area.

Economy is based mainly on industry. Mining of hard coal and zinc-lead ores has a multi-centurial tradition. Sand open-pits have been operating since the first half of the 20th century. Main industrial sectors are: chemical, power supply and mining. Most of the industrial plants are located in Trzebinia town: Siersza power plant, Trzebionka Mining Company (Zn–Pb ores mine), Górka Cement factory, producing aluminous cements, Szczakowa sand mine.

Economy of the area has been changing for last years because of closing down the big industrial plants. Not so long ago mining industry was dominant (exploitation of hard coal, zinc-lead ores, limestones, marls and sands) in the sheet area. Closing down the Siersza hard coal mine, and planned closing down of Trzebionka Zn–Pb ores mine, will cause serious economic changes. Moreover, the Trzebinia Metallurgy Factory and the Górka Refractory plant in Trzebinia are being closed down as well.

There are also numerous small companies representing food and clothing industries as well as trade and services.

GEOLOGY AND MINERAL DEPOSITS

Geological structure of Myślachowice Sheet area consists of three structural units (Kurek et al., 1994): Early Paleozoic (Carboniferous), Permian–Mesozoic (Permian, Triassic and Jurassic) and Cenozoic.

Carboniferous deposits are exposed in a few outcrops in the southern part of the map area (Plate 1), and are further studied with mine excavations and drillings. The Carboniferous deposits are folded and cut by faults (Nieć et al., 2002). The Lower Carboniferous is built up by limestones and clastic deposits. They are overlaid by Namurian

and Westfalian clastic complex with Łaziska and Libiąż Beds in the top (built up mainly of sandstones with thick hard coal beds). Thickness of Libiąż Beds does not exceed 100 m while Łaziska Beds are more than 350 m thick (Kurek et al., 1994). The Upper Carboniferous hard coal-bearing beds are weathered and thermically changed (Lipiarski, 2001).

Permian rocks are exposed in the south-eastern and central part of the map sheet area. These are clays (up to 35 m thick), Myślachowice carbonate conglomerates (up to 50 m thick), porphyric-carbonate conglomerates (several meters thick) and volcanic Filipowice tuffs (reaching 30 m of thickness).

Triassic. Lower Triassic (up to 30 m thick) comprises Buntsandstein continental gravels, conglomerates, sands, sandstones, claystones and mudstones as well as Roethian marine deposits: dolomites, marls and cavernous limestones up to 30 m thick. They are overlaid by the Middle Triassic (Muschelkalk) carbonate marine deposits about 100 m thick which are: limestones and marls of Gogolin Beds, Zn–Pb ore-bearing dolomites (reaching up to 40–70 m) and Diplopore dolomites. The Upper Triassic includes claystones, mudstones and limestones (from several to 170 m thick) exposed in the south-western part of the map sheet.

Jurassic rocks occur in the southern part of the map area. The Middle Jurassic includes sandstones, conglomerates, marls and limestones. The Upper Jurassic deposits are limestones and marls, up to 10 m thick, overlaid by platy and spongian-tuberolite limestones, 60–90 m thick.

The **Neogene** sediments of insignificant occurrence are dominated by gravels and muds.

Quaternary deposits create a cover of diversified thickness, reaching up to 70 m at the old valley of the Biała Przemsza River and up to 20 m at the remaining area. Glaciofluvial sands and rock debris of the bedrock are dominant. Eolian sands and loesses occur at some places, and muds and peats occur in the bottom of stream valleys.

Mineral deposits. The area of Myślachowice Sheet is exceptionally rich in mineral resources. **Hard coal** in this area has been exploited since the end of the 18th century. The first mine, called Albrecht, was established in 1804 and it exploited hard coal bed exposed on the surface (Pietraszek, 1961). In the middle of the 19th century several hard coal mines were opened – some of them were active until the World War II. In 1949 they were merged into the Siersza hard coal mine group (mining area of 40.3 km²). The main subject of exploitation were the Łaziska Beds, hosting low calorific hard coal, containing high amount of sulphur (2–5%) and ash (4–40%) (Nieć et al., 2002). Due to economical reasons Siersza hard coal mine group was closed down in 1999.

Zinc-lead ores (particularly oxidized ores), galena and accompanying sulphates (used for production of alum) as well as iron ores (limonite), occurring with Zn–Pb ore-bearing dolomites were exploited in the area of sheet since the Middle Ages (Szuwarzyński, 1978, Strzelska-Smakowska, 2006).

Currently zinc-lead ores are being extracted at Trzebionka mine from the Balin-Trzebionka ore deposit, whose main part is located beyond the southern border of the map sheet (Przeniosło, ed., 2004). Zn–Pb sulphide ores, hosted by ore-bearing dolomites, are exploited there at the depth of 190–260 m. The ore deposit consists of several plate-like ore bodies built up of sphalerite and galena aggregates with mean values 3.5% of Zn, 1.4% of Pb and admixture of iron sulphides. Zinc sulphide contains cadmium, silver, cobalt, copper, thallium and arsenic; galena hosts rather silver and arsenic (Harańczyk, 1962; Cabała, 1996), and iron sulphides are the main hosts for arsenic and thallium (Paulo, Strzelska-Smakowska, 2000). Particular ore bodies thicknesses ranges from about 3 m to dozens of meters (locally over 30 m) and their horizontal size ranges from several tens of meters to several kilometers (Szuwarzyńska et al., 2001).

Rock raw materials were exploited not long ago in numerous open-pits. Jurassic limestones and marls were exploited at Górká deposit until 1954 for the needs of the local cement plant. Open-pit remaining after its exploitation is filled with water and waste of Górká refractory factory (Motyka, Szuwarzyński, 1998) affecting the environment because of high alkalinity of water.

Exploitation was also abandoned at the Trzebinia-Siersza deposit, where clays and muds were extracted for construction materials production.

In the northern part of the map sheet there is a big area of Szczakowa sand open-pit covering 10 km² (Preidl et al., 1995) exploiting Quaternary sands (Bednarczyk, 2001). Simultaneously with sand exploitation the area is being recultivated by forestation.

Weathered and poorly cemented carbonate conglomerates (Myślachowice conglomerates) were exploited locally as an aggregate (Nieć et al., 2002).

HUMAN IMPACT

The natural environment in the area under study is severely degraded due to long time mining of Zn–Pb ores, hard coal and rock raw materials as well as activity of power supply and processing industries.

Atmospheric air pollution. The air conditions are determined by far-reaching emissions derived from: fuel combustion (coal dust, sulphur dioxide, nitrogen dioxide, carbon dioxide and carbon oxide), vehicles (hydrocarbons, carbon oxide, dust, lead compounds), production processes (hydrocarbons, fluorine, industrial dust, hydrogen sulphides) and communal dumps.

High amount of pollution emitted to the atmosphere derives from the Siersza power plant (Ocena., 2005), Trzebionka Mining Company, and Trzebinia Oil Refinery (located 1 km south of map sheet border). Atmospheric air is also polluted by emissions from the neighbouring Silesia voivodeship.

Surface water and groundwater pollution. The biggest hazards for surface water and groundwater are caused by industrial plants (including Zn–Pb ore mine) as well as their post-production wastes:

- Siersza hard coal mine (under liquidation) – mine waste dump in Trzebinia;
- post-production wastes dump from Górká Refractory plant in Trzebinia;
- settling pond of Górká Refractory plant contaminated with caustic liquors and dangerous wastes;
- Górbet refractory company in Trzebinia;
- Siersza power plant – furnace waste dump and mine waste dump (closed down);
- communal dump in Trzebinia (operating);
- Balin-Okradziejówka communal dump (under liquidation).

The biggest amount of industrial sewage is produced at Trzebionka Mining Company – zinc-lead ore mine (7.461 mln m³/yr) and Siersza power plant (3.348 mln m³/yr) (Raport..., 2005). In other industrial plants far less amounts of sewage are produced, which are disposed to communal sewerage.

Disposing mine waters into the rivers causes increase of salinity as well as content of sulphates and heavy metals in surface water. Disposal of brines into the river net brings also disturbances in natural supply of rivers and streams and rebuilding of riverbeds. Other sources of pollution are housing and various branches of industry, which cause increase of water mineralization, their biological degradation and eutrophication. On the other hand, regulation of riverbeds and construction of flood-control systems can lead to destruction of water ecosystems and landscape degradation.

The main watercourse in the area under study is Kozi Bród Stream receiving cooling water from Siersza power plant and communal sewage from Trzebinia town.

Water from Szczakowa open-pit sand mine as well as from mine and furnace waste dump of Siersza power plant are disposed into Jaworznik Stream – right-bank tributary of Kozi Bród Stream.

At the north-eastern edge of the map sheet there is the Sztola River. It is its upstream (not polluted yet). However, several kilometers down, there are some water discharge sites of the Bolesław Mining and Metallurgy Company which pollute the river with zinc, lead and other metals (Lis, Pasieczna, 1999; Raport..., 2005).

Mining activities brought harmful, usually irreversible, changes of aquatic environments in the studied area – contamination of ground and surface water, and changes in hydrological systems (man-made changes of watercourses, formation of undercut areas and depression cones; Rózkowski et al., 1997).

Soil pollution. Chemical degradation of soils is related to industrial activity, transportation, mining activity and storage of industrial wastes. High values of zinc, lead and cadmium were found in previous studies at soils from the map sheet area (Raport..., 2005), which are related not only to exploitation of Zn–Pb ores but also to naturally increased geochemical background of soils developed from ore-bearing dolomites.

Many basic features of studied area have changed significantly as a result of closing down large industrial plants in recent years. Up to recently the exploitation of hard coal and Zn–Pb ores dominated there, but now the coal mines are closed down and during next several years also the Zn–Pb ore mine will be closed down. Reducing this activity will result in lower pollution of natural environment, but the abandoned industrial areas and non-recultivated waste dumps could be menace themselves.

MATERIALS AND METHODS

Studies done in years 2003–2005 comprised study of published and archival materials, choosing sampling sites at topographic maps at a scale of 1:10 000, samples collection, coordinate surveys at the sampling sites, laboratory works, set up of field and laboratory databases, elaboration of a vector topographic map 1:25 000, statistical calculations, construction of geochemical maps and geological map, and interpretation of results. Mentioned herein works are shown on Figure 1.

FIELD WORKS

Soil samples were collected at the regular grid 250x250 m (16 sites per 1 km²). The total number of soil sampling sites was 1332. At every site collected two samples from two depths: 0.0–0.3 m (topsoil) and 0.8–1.0 m (subsoil). In case of shallow deposited parent rocks the subsoil sample was collected from shallower depth. Soil samples (of about 500 g) were collected by means of a hand probe and were initially dried at the field storage.

Samples of aqueous sediments and surface water were collected from various bodies of water – streams and rivers, melioration ditches, canals, pools and ponds. The distance between watercourse sampling sites was about 250 m. Samples of sediments of 500 g weight were collected from water reservoir shores by means of a scoop.

Samples of surface water were collected from the same sites as sediment samples. Electrical conductivity (EC) and acidity (pH) of water were measured on site. Water samples of 30 ml were filtered in the field (by filters of 0.45 µm) and acidized with nitric acid.

Locations of all sampling sites were defined with GPS. Direct measurement with GPS equipment GS 20 Leica has accuracy of ±2–10 m. A GS 20 Leica was equipped with external antenna and system which can register not only coordinates but also additional

information (pH and EC of water samples, data on land development and land use as well as type of soil and aqueous sediment). Coordinates of soil sampling sites were put into read-only memory of GPS equipment, before going out in the field and the sites were next found in the field. For safety reasons all the field data was noted on sampling cards (Fig. 2).

LABORATORY WORKS

Sample preparation. All solid samples were air-dried. Soil samples were sieved to <2 mm using nylon screening (ISO 11464). Each topsoil sample was then split into three portions; one was archived, the second submitted for grain-size analysis and the third was pulverized in agate planetary mill to a grain size <0.06 mm submitted to chemical analysis. Each subsoil sample was split into two portions; one was archived and the other was pulverized in agate planetary mill to a grain size <0.06 mm and submitted to chemical analysis (Fig. 1).

Aqueous sediment samples were sieved to a grain size <0.2 mm. Each sample was then split into two portions; one was archived and other was used for chemical analysis.

Chemical analyses were done at the laboratory of the Polish Geological Institute, Warsaw.

Soil pH (water extraction) was measured with pH-meter. The total organic carbon content of topsoil samples was determined using a Coulomat analyser. The content of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in soil and aqueous sediment samples was determined after a hot *aqua regia* digestion by inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. The mercury content was measured using a cold vapour-atomic absorption (CV-AAS) method.

The determination of Al, B, Ca, Fe, K, Li, Mg, Na, P, SiO₂, Ti and Zn content in surface water samples was done by ICP-AES while the content of Ag, As, Ba, Cd, Cl, Co, Cu, Mn, Ni, Pb, Rb, Sb, SO₄, Sr, Tl and U was determined by inductively coupled plasma-mass spectrometry method (ICP-MS).

Analytical methods applied along with detection limits of measured elements are shown in Table 1.

The quality control of the analysis was performed by:

- analysis of duplicate samples (5% of total samples),
- analysis of reference materials with certified content of elements studied (2% of total samples),
- analysis of laboratory control samples confirming correct instrument calibration (5% of total samples),
- blank samples (5% of total samples).

The reagent blank samples and the preparation blank samples were used. Purity of acids, water and vessels was controlled with the reagent blank samples. The preparation blank samples (*sea sand extra pure Merck*) were used to monitor for possible contamination during the sample preparation procedure.

For the solid samples, analytical precision is about ±10–15%, based on duplicate samples. For the surface water samples, analytical precision is about ±10–20%, depending on the element's concentration.

Grain size analyses of topsoil. Grain-size distribution of topsoil samples measured by a laser particle size analyzer (Analysette 2) is expressed as fractions: 1.0–0.1 mm (sand), 0.1–0.02 mm (silt) and <0.02 mm (clay).

DATABASES AND GEOCHEMICAL MAPS PRODUCTION

Base topographic map. The 1:25 000-scale topographic base map was constructed using selected elements of the Vector Map Level 1 (VMap Level 1) 1:50 000. Topographic map contains vector-information layers: relief, hydrography (with division into rivers, streams, canals, ditches, lakes, pools, ponds), road communication net (with division into classes of roads), railway net, land development (with division into compact development, suburban development, industrial development, non-built areas), forests, industrial objects, mine excavations and mine dumps.

Geological map was constructed on the base Detailed geological map of Poland Jaworzno Sheet (Kurek *et al.*, 1999) 1:50 000. Particular vector layers of geological map were combined with topographic base producing a geological map at the scale of 1:25 000 (Plate 1).

Database management. The databases and material archives comprise: archives sample materials (topsoil, subsoil and aqueous sediments) stored at the Polish Geological Survey, field observation sheets, work maps, databases for field observations, analytical data files and GIS layers. Separate databases were prepared for: topsoil, subsoil, aqueous sediments and surface water.

Soil databases contain: number of samples, sampling coordinates, a site description (land development, land use, district, commune, and town), soil texture, date of collection, sampler name and analytical data.

Aqueous sediment and surface water databases contain: number of samples, sampling coordinates, a site description (land development, land use, district, commune, and town), type of water body (river, stream, canal, ditch, lake, pond) type of sediment (sand, mud, clay, peat) date of collection, sampler name and analytical data. For surface water database additional data were included – field measurements of pH and EC.

Statistical calculations. Statistical parameters were calculated (average, median, minimum and maximum values) both for the whole sets and subsets of soil, sediments and surface water (Tables 2–6). Subsets for statistical calculations were distinguished according to different media criteria, e.g. concentrations of elements in soils under cultivation, forest soils, urban soils and elements content in aqueous sediments and water of particular bodies of water. In the case of some elements (e.g. Ag, As, Cd, Hg) with the content lower than the value of detection limit for the applied analytical method, all values were converted to half of the detection limit value before making statistical calculations and map production.

Geochemical maps production. The following maps were made for the Myślachowice Sheet: geological map, land development and land use, the content of organic carbon and grain size of topsoil (1.0–0.1 mm, 0.1–0.02 mm and <0.02 mm); acidity of topsoil and subsoil; acidity and electrical conductivity of surface water; the content 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 aqueous sediments; the content 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 and Zn in surface water.

The distribution of elements is presented with a combination of proportional dot maps (for element distribution in sediments and surface water) and colour surface maps (for element distribution in soils). Dot maps revealing the actual sampling density were produced individually for Myślachowice Sheet. Colour surface maps were constructed for several neighbouring sheets to avoid disagreement of element distribution at the sheet borders. The data was interpolated to generate a regular grid using Inverse Distance to a Power method. A multi-grade colour scale was selected to present the elements distribution. The 1:25 000-scale map sheet of interest was then cut out from several neighbouring sheets after interpolation. The colour surface maps were produced using arbitrarily chosen colour classes (most often using geometric progression).

In the case of soil pH accepted level values according to the division used in soil science (soils very acidic, acidic, neutral and alkaline).

For publication reasons, geochemical maps were made by presenting the following pairs in one plate: topsoils and aqueous sediments as well as subsoils and surface waters. This method of presentation gives a direct comparison of geo-chemical images of various media (Plates 7–62).

RESULTS

SOILS

Grain size. Diversity of grain size of topsoils at map sheet area is related to the lithology of the parent rocks. Sandy soils containing >90% of sand fraction (1.0–0.1 mm) are dominant in the north-western part of the map area and in Łużnik Stream valley (Plate 4). In the eastern part of the map sandy soils occupy tiny isolated areas. They usually are forest soils. Their parent rocks are Pleistocene sands and gravel (Plate 1). These soils are characterized by small amount (<5%) of silt (0.1–0.02 mm) and clay fractions (<0.02 mm).

In soils of the southern and eastern part of the map sheet area, developed on pre-Quaternary deposits, the content of sand fraction ranges between 50% and 90% (Plate 4). Considerable high contents were observed for silt (10–30%) and clay fractions (10–35%). Maximum values of silt fraction (up to 48%) was noted in soils developed from loesses as well as from Permian and Triassic rocks at the south-eastern edge of the map (Plate 5). Clay fraction is high too in soils developed from loesses, Permian and Triassic rocks and from floodplain sediments of Kozi Bród Stream (Plate 6).

Acidity. In topsoil percentage of samples of acidic, neutral and alkaline reactions is 62%, 28% and 10% respectively. Acidic reaction is mainly observed for forest and wasteland soils. Soils of neutral and alkaline reaction, developed on Jurassic carbonate rocks, occur in the southern part of the map. Alkaline soils (pH 8.0–9.4) occur in the area of former Górká refractory factory in Trzebinia (Plate 7). Such a high pH is probably related to dissemination of dusts during long-term activity of Górká factory, using Jurassic limestones and marls for production of refractory materials and cement.

In subsoil clear relationship of acidity and chemical composition of bedrock was observed (Plate 8). The alkaline subsoils (covering 18% of sheet area) occur in the southern part of the map, where the basement is built up of Jurassic limestones and marls. At the depth 0.8–1.0 m percentage of neutral soils is 34% and acidic soils 48%.

Geochemistry. Particular types of soils originated from geological structures differ in terms of lithology and age (Plate 1). *Rendzinas* developed from Triassic and Jurassic limestones, whereas *Cambisols* and *Luvissols* developed from Quaternary sands. Soil-forming processes in terms of physic-chemical conditions of the environment changed chemical composition of soils in relation to parent rocks. However, more often basic geochemical features of parent rocks are well observed. Distribution of elements, which originated from the parent rocks, helps to focus on differentiation of geochemical background and distinguish local elements' anomalies.

Soils developed from Pleistocene sandy glaciofluvial deposits, occurring in the north-western part of the map area, contain low values of many elements. It involves both topsoil and subsoil. Low contents of elements are related to poor chemical composition of sandy bedrocks and acid reaction, which influences leaching of elements.

In the southern and eastern part of the map sheet area soils characterize with much higher contents of almost all elements in comparison to the north-western area. It is related to chemical composition of the bedrock (occurrence of Triassic rocks hosting Zn–Pb ores).

Average content of calcium, magnesium, cadmium, lead and zinc (expressed as median) is higher in topsoil (Tables 2 and 3) in relation to subsoil, but on the other hand – distribution maps of these elements in topsoil and subsoil are very similar.

The most distinct anomalies of calcium (Plates 19 and 20), cadmium (Plates 21 and 22), magnesium (Plates 36 and 37), lead (Plates 46 and 47) and zinc (Plates 61 and 62) occur in soils developed from Triassic ore-bearing dolomites (Plate 1). Enrichment in calcium was observed for soils developed from Jurassic rocks as well as man-made grounds, in areas of mine waste dumps of abandoned Siersza hard coal mine and furnace waste dump of Siersza power plant.

Historical exploitation of Zn–Pb ores in numerous open-pits brought dissemination of waste around pits. Anomalies of cadmium, lead and zinc around historical open-pits are as clear as in the area of current Zn–Pb ores exploitation – shafts of the Trzebionka Zn–Pb ore mine.

In some areas (for example in the vicinity of Balin and Luszowice) mining wastes of old open-pits were used during construction of the new highway and housing estates (Szuwarzyńska *et al.*, 2001), which caused enlargement of pollution area. Additional source of the Pb–Cd–Zn anomaly might be the historical smelting of lead (Szuwarzyńska *et al.*, 2001). Anomalies of cadmium, lead and zinc in the area of Trzebionka Zn–Pb ore mine shafts are related to their activity. Anomalies of cadmium, lead, and zinc in Krze village are related to the anthropogenic sources. They occur in the area where a zinc smelter and its extent waste dump existed in the 19th century (Szuwarzyński, Kryza, 1994).

In the area of the anomaly in topsoil cadmium content exceeds 8 mg/kg (Plate 21), lead 250 mg/kg (Plate 46), and zinc 1000 mg/kg (Plate 61). In subsoil anomalies are less extent but more intensive.

Reduction of areas of anomalous concentrations of cadmium, lead and zinc in the subsoil in comparison to the topsoil (Table 7) is very well observed at the whole map area.

Soils enriched in arsenic were found in the area of Triassic rocks outcrops (which is related to its presence in Zn–Pb ores) and also at the Zn–Pb ores historical mine waste dumps. Arsenic-rich soils occur in industrial areas of abandoned Siersza hard coal mine (Plates 13 and 14), which is the result of its high content in hard coal (Paulo, Strzelska-Smakowska, 2000).

Distribution of aluminium, barium, cobalt, chromium, iron, manganese, nickel, strontium, titanium and vanadium points out their relationship with chemical composition of the bedrock. Enrichment in these elements was noted in topsoil and subsoil, developed on Triassic and Permian rocks.

The most noticeable anthropogenic anomaly of aluminium occurs in the vicinity of Górka marl open-pit (Plates 11 and 12). The open-pit stores wastes containing aluminium hydroxide and dangerous wastes from the refractory factory. Maximum aluminium concentration in topsoil is 9.78% and in subsoil reaches 10.16%. In comparison – maximum aluminium content in topsoil at neighbouring Sławków Sheet is 1.5% only (Lis, Pasieczna, 1999).

Barium value is low in soils developed from Triassic rocks. Its content is higher in soils developed from Permian rocks as well as in anthropogenic soils around Siersza hard coal mine waste dumps and Siersza power plant furnace waste dump. The source of soils enrichment in barium is hard coal combustion (Różkowska, Ptak, 1995) and lithology of parent rocks (arkosic sandstones and volcanic rocks).

Soils enrichment in cobalt (Plates 24 and 25) and chromium (Plates 26 and 27) were noted in the areas of Triassic rocks outcrops. Slightly higher content of chromium and cobalt originates also from anthropogenic activity – soils enriched in the elements were found around Siersza power plant waste dump and Górka refractory company.

Distribution of iron, manganese, nickel and strontium is similar to that of calcium and manganese (both in topsoil and subsoil). Soils enriched in the elements were found mainly in the areas of Triassic and Permian rocks outcropping, whereas additional enrichment in strontium was also observed in soils developed from Jurassic carbonate rocks (Plates 53 and 54).

Titanium (Plate 55) and vanadium (Plate 59) content is generally very low in topsoils (an exception is the southern part of the map sheet enriched in the elements). In subsoils slightly higher values of those elements were observed around Siersza power plant waste dump.

Point anomalies of silver in topsoil (originating from anthropogenic activity) were noted in Luszowice, at Trzebionka Zn–Pb ore mine area, in the neighbourhood of former Górka refractory factory and Siersza power plant (Plates 9 and 10).

The copper topsoil distribution map shows enrichment in this element in the southern part of the area (Plate 28). It may point out that copper sources are mainly anthropogenic – emission of dusts from Siersza power plant and its waste dump, shafts of the Trzebionka Zn–Pb ore mine, hard coal waste dumps and dissemination of dusts from hard coal combustion in individual furnaces. In subsoil areas of enrichment in copper are reduced (Plate 29).

Clearly noticeable anomalies of mercury (>0.10 mg/kg) were found in topsoil in the southern and eastern part of the map area (Plate 32). In subsoil distribution map shows a somewhat different pattern – enrichment in mercury occurs only around Siersza power plant and its furnace waste dump as well as in industrial area of Krze village.

In topsoil and subsoil a very clear difference in sulphur content is observed 0.013% and $<0.005\%$ respectively. In topsoil sulphur anomalies were found in industrial areas, especially in the vicinity of former waste pond of Siersza power plant. Area of soils enriched in sulphur is reduced at the depth 0.8–1.0 m (Plates 49 and 50).

Phosphorus content is partly inherited from parent rocks but influx by fertilizers cannot be excluded. Low phosphorus values occur in forest soils in the north-western part of the map (Plates 44 and 45). The median content of phosphorus in topsoil is higher (0.013%) than in subsoil (0.006%), similarly as in the case of sulphur.

Industrial activity, both modern and historical, plays significant role in contamination of topsoil by metals. It is well documented by comparison of area sizes occupied by soils of various content of cadmium, zinc, and lead in the subsoil in relation to the topsoil (Table 7). High concentrations of those metals in the subsoil were only found within close existence of Zn–Pb ore-bearing rocks or at sites of their intense mining activity.

Content of many elements in soils depends on their use. The low contents of elements were found in forest soils and higher ones in cultivated soils, meadows, and areas of urban development (Tables 2 and 3). Contents of arsenic, cadmium, copper, mercury, lead and zinc in areas with urban development, street lawns and urban allotments are high. Maximum concentrations were noted in industrial and wasteland areas.

The heavy metal contamination of soils is a problem for the local authorities and should be discussed with respect to the land usage. To fit the geochemical data to local authorities needs, topsoils of Myślachowice Sheet were classified, applying current guideline values (Table 8) 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 effects on the ecosystem or the human health. Guideline values are applied for three-level scale: A (protected areas), B (agricultural, forest and residential areas) and C (industrial areas).

The rule of the classification is that the sample is classified to a particular soil use group if the content of at least one element reaches or exceeds the permissible limit values of this group. Using this classification method, 30.71% of the topsoil samples were classified into group A, 24.55% into group B, and 44.74% into group C (Table 8). Soils of C group occur mainly in the southern part of the map area, at the outcrops of ore-bearing dolomites and around industrial objects. The main pollutants are zinc, cadmium and lead (Table 7).

AQUEOUS SEDIMENTS

Aqueous sediments at Myślachowice Sheet area are streams, canals, drainage ditches and small ponds sediments. The main feature of geochemistry of analyzed aqueous sediments is domination of anthropogenic factors over natural ones in terms of concentration of elements, especially metals and sulphur.

Kozi Bród Stream. Most of the sheet area is located within the catchment of Kozi Bród Stream. Liquid industrial and rain sewage, cooling waters of Siersza power plant as well as communal sewage from Trzebinia town are discharged into Kozi Bród Stream. Its right tributary – Jaworzniak Stream supplies water from former settling ponds of Siersza power plant.

Elements, mainly of geogenic origin, occurring in Kozi Bród Stream sediments are: aluminium, arsenic, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, sulphur, titanium, and vanadium. Their content fluctuates slightly at the whole length of the stream. Low (natural) contents of the elements can be observed from east border of the map sheet to the storage reservoir Zalew Osowiec. Enrichment in many elements occurs below the storage reservoir as a result of the sewage discharge from Siersza power plant. High contents of calcium (Plate 19), cobalt (Plate 24), chromium (Plate 26), iron (Plate 30), magnesium (Plate 36), manganese (Plate 38), nickel (Plate 42), sulphur (Plate 49), and strontium (Plate 53) were noted. However, sediments are mostly polluted with copper (Plate 28) and mercury (Plate 32). Above the discharge site of sewage from Siersza power plant copper content ranges from <1 to 9 mg/kg, and below the discharge site the concentrations reach more than several hundred mg/kg (max. 703 mg/kg). Mercury content in the upstream of Kozi Bród Stream does not exceed 0.05 mg/kg and ranges within 0.13–2.36 mg/kg below the discharge site of sewage from Siersza power plant.

Sediments of unnamed watercourse (a tributary of Kozi Bród Stream) flowing from Trzebinia town are enriched in aluminium (Plate 11), chromium (Plate 26) and magnesium (Plate 36). Aluminium content usually ranges from 0.7 to 1.5%, whereas chromium from 33 to 66 mg/kg. The main source of the elements is the waste pond of Górka refractory factory. Refluxes from the mine dump and settlement pond of Siersza hard coal mine contaminate sediments of the watercourse with cobalt (up to 139 mg/kg), manganese (up to 16 mg/kg), nickel (up to 124 mg/kg) and vanadium (up to 43 mg/kg). In the area of Trzebinia-Siersza railway station sediments are also polluted with silver (Plate 9), arsenic (Plate 13), cadmium (Plate 21), chromium (Plate 26), copper (Plate 28), lead (Plate 46), strontium (Plate 53) and zinc (Plate 61). Pollution with mercury (originated possibly from communal sewage) reaches 2.75 mg/kg, and below the watercourse mouths – in sediments of Kozi Bród Stream reaches up to 14.60 mg/kg.

Another tributary of Kozi Bród Stream is the Jaworzniak Stream, which drains in its upstream the old furnace waste dump of Siersza power plant as well as shafts of the former Siersza hard coal mine in the downstream. Jaworzniak Stream receives also water from Szczakowa open-pit sand mine. Sediments of Jaworzniak Stream are enriched in calcium (Plate 19), cobalt (Plate 24), manganese (Plate 38), nickel (Plate 42), strontium (Plate 53) and vanadium (Plate 59). Particularly high concentrations of manganese and strontium in Jaworzniak Stream sediments were noted. Average content of manganese (median) is 2309 mg/

kg, while average of the whole sheet map area is 235 mg/kg (Table 4). Average content of strontium (86 mg/kg) is four times as much as the average content of the map sheet area (21 mg/kg).

Łużnik Stream. Sediments of Łużnik Stream, which drains Quaternary glaciofluvial deposits in the south-western part of the map area, characterize with low contents of the elements studied (Table 4). They are only enriched in strontium (Plate 53) originating from Triassic carbonates.

Żabnik Stream. The Żabnik Stream drains area covered with Pleistocene sands of alluvial fans and its valley is filled with swampy and silt-muddy soils. As a result Żabnik Stream valley is the area of fresh water and peat flora under protection. Some sediments of Żabnik Stream are slightly enriched in aluminium, arsenic, cadmium, copper, mercury, lead, sulfur, strontium, vanadium and zinc. Possible source of the enrichment, seems to be, the spring area of the stream where anomalies of those elements occur in the soils. Anomalies could originate from draining soils polluted by water from the furnace waste dump and waters from Siersza hard coal mine. In Żabnik Stream sediments arsenic content reaches 25–48 mg/kg whereas that of cadmium often exceeds 50 mg/kg (max. 260 mg/kg). Lead (100–300 mg/kg) also occurs in the stream sediments studied. Currently the stream flows into a man-made canal built for the Szczakowa open-pit sand mine dewatering.

Unnamed little watercourses. Contents of elements studied are highly diversified in sediments of particular unnamed little watercourses, draining northern and southern parts of the map sheet area.

Watercourse sediments in vicinity of Płocki (quarter of Trzebinia town) characterize with high content of aluminium (2%) silver (up to 5 mg/kg), cadmium (up to 48 mg/kg), copper (up to 94 mg/kg), chromium (up to 57 mg/kg), mercury (up to 0,65 mg/kg), lead (up to 5000 mg/kg), strontium (up to 130 mg/kg) and zinc (up to 6620 mg/kg). Pollution of the sediments with metals originates from natural source (erosion of Zn–Pb ore bearing Triassic deposits) and anthropogenic factors (runoffs of mine waste dumps and industrial areas).

Sediments of watercourses draining post-exploitation sand open-pit in the north-western part of the map sheet area are enriched in some elements. Locally, aluminium content in sediments reaches 1.5–2.0%. Slightly higher contents of cobalt, copper, chromium, iron, manganese, nickel, titanium and vanadium (probably from anthropogenic sources) were noted too.

SURFACE WATER

Kozi Bród Stream. Water of Kozi Bród Stream and its tributaries characterizes with acidity from 7.7 to 8.3 (Plate 7). Contents of silver, aluminium, arsenic, cobalt, iron, manganese, silica, strontium and titanium are similar at the whole length of the Stream.

Electrical conductivity is definitely different in the stream upwards – above the site of water discharge from Siersza power plant (0.30–0.40 mS/cm) – and downwards (1.00–1.30 mS/cm). It should be mentioned that EC value above 1 mS/cm points out high pollution of water (Witczak, Adamczyk, 1994). High increase of many elements content (boron, chlorine, lithium, magnesium, molybdenum, sodium, thallium and sulphates) was observed, similarly to the sharp EC change, in stream water below the discharge site of sewage from Siersza power plant. High contents of the elements are undoubtedly related to discharge of post-cooling water from Siersza power plant, which uses water for technological processes from abandoned Siersza hard coal mine. Boron content in Kozi Bród Stream water does not exceed 50 $\mu\text{g}/\text{dm}^3$ in the upstream (Plate 15), and ranges from 500 to 2500 $\mu\text{g}/\text{dm}^3$ below the sewage discharge from Siersza power plant. Chlorine content in both mentioned parts of stream is 13–17 mg/dm^3 and $>40 \text{ mg}/\text{dm}^3$ (Plate 23), copper $<0.5 \mu\text{g}/\text{dm}^3$ and 3–37.5 $\mu\text{g}/\text{dm}^3$ (Plate 29), potassium $<2 \text{ mg}/\text{dm}^3$ and 7–8 mg/dm^3 (Plate 34), lithium $<2 \mu\text{g}/\text{dm}^3$ and 30–40 $\mu\text{g}/\text{dm}^3$

(Plate 35), magnesium 12–13 mg/dm³ and 80–90 mg/dm³ (Plate 37), molybdenum 0.1–0.2 µg/dm³ and 7–9 µg/dm³ (Plate 40), sodium 5 mg/dm³ and 40–50 mg/dm³ (Plate 41), rubidium <2.5 µg/dm³ and 5–7 µg/dm³ (Plate 48), sulphates 40–50 mg/dm³ and 300–500 mg/dm³ (Plate 50) as well as thallium <0.05 µg/dm³ and 0.30–0.48 µg/dm³ (Plate 57) respectively.

Another distribution pattern can be observed for barium (Plate 17), cadmium (Plate 22), uranium (Plate 58) and zinc contents (Plate 62). Enhanced values of the elements occur in the upper part of the stream. At the site of sewage discharge from Siersza power plant, ions of elements migrating from the spring area (built up by Triassic Zn–Pb ore-bearing rocks and old open-pits) become precipitated (possibly reacting with sulphate or chloride ions).

Thallium content is <0.05 µg/dm³ above the sewage discharge of Siersza power plant and reaches 0.30–0.58 µg/dm³ (Plate 57) below this site. Such high concentration of toxic thallium is very dangerous for living organisms. The probable source of the element is runoff from soils developed from Zn–Pb ore-bearing dolomites in the spring area of the stream. In the nearby area thallium content in soils was reported with the range of 0.43–35.12 mg/kg (Lis et al., 2003), and in surface water from 0.16 to 3.24 µg/dm³ (Paulo et al., 2002), whereas the geochemical background in surface water in Poland does not exceed 0.006 µg/dm³ (Salminen, ed., 2005).

Water of unnamed left-bank tributary of Kozi Bród Stream, carrying communal sewage of Trzebinia town, is enriched in boron, chlorine, iron, potassium, lithium, magnesium, manganese, sodium, phosphorus and rubidium. High concentration of phosphorus, reaching 5–8 mg/dm³ was noted in water of this watercourse, whereas the geochemical background does not exceed 0.05 mg/dm³ at the whole map sheet area. Pollution of unnamed left-bank tributary of Kozi Bród Stream by phosphorus and other elements originates from disposing communal sewage of Trzebinia town, Górka refractory factory, railway station and drainage of the hard coal waste dumps.

Jaworzniak Stream. Equalized pH values (8.0) and high EC in the range of 1.05–1.33 mS/cm (Plate 7) were found in water of Jaworzniak Stream. High EC values are the evidence of high mineralization of water related to runoff of furnace waste dump area and a long-term discharging mine waters from hard coal mine. The sources of contamination are also related to water enrichment in boron (Plate 15), calcium (Plate 20), copper (Plate 29), potassium (Plate 34), lithium (Plate 35), magnesium (Plate 37), molybdenum (Plate 40), sodium (Plate 41), rubidium (Plate 48), antimony (Plate 51), sulphates (Plate 50), strontium (Plate 54), thallium (Plate 57), and uranium (Plate 58). The elements can be leached from wastes by infiltrating rain waters. Laboratory studies on wastes leaching from Łagisza and Łaziska power plants (Grabowska, Sowa, 2003) showed that studied ashes and their leachates do not fulfill safe storage conditions of the surface water and groundwater environments due to high mineralization, reaction and concentration of sulphate ions.

Łużnik Stream. The Łużnik Stream water is slightly alkaline (pH 8.2) and slightly mineralized (EC ranges from 0.30 to 0.50 mS/cm). The water contains low amounts of almost all elements studied and is enriched only in barium (140–160 µg/dm³), iron (up to 2 mg/dm³), manganese (up to 363 µg/dm³), strontium (up to 1334 µg/dm³), and uranium (up to 1.06 µg/dm³).

Żabnik Stream. The Żabnik Stream water is little mineralized and has equal reaction (pH 8.2). The water is slightly enriched in aluminium, cadmium, zinc, boron and manganese as well as in potassium (up to 37 mg/dm³) and lithium (up to 512 µg/dm³) in the spring area.

Unnamed little watercourses. Water of little watercourses has reaction values at 8.1–8.4 and low electrical conductivity (Plate 8).

Water of the watercourse flowing from the former Szczakowa open-pit sand mine (in the north-western part of the map sheet) is enriched in some elements. Concentration of

boron exceeds 400 $\mu\text{g}/\text{dm}^3$ whereas potassium 1–2 mg/dm^3 and lithium 3–6 $\mu\text{g}/\text{dm}^3$. Enrichment in the elements may be related to ascending inflow of saline waters from the Carboniferous deposits. Higher content of molybdenum (2–4 $\mu\text{g}/\text{dm}^3$) was also noted. The source of molybdenum similarly to strontium (280–370 $\mu\text{g}/\text{dm}^3$) and uranium (0.80–1.20 $\mu\text{g}/\text{dm}^3$) can be Carboniferous deposits.

CONCLUSIONS

1. Detailed environmental geochemical mapping at the scale 1:25 000 at Myślachowice Sheet indicates significant pollution of topsoil, subsoil, aqueous sediments and surface water with heavy metals and other chemical elements. The research distinguished geochemical multi-element anomalies, caused by mineralization and lithology as well as anthropogenic input of heavy metals from the zinc-lead ores and hard coal mining.

2. Natural, high levels of calcium, magnesium, iron and sulphur derived from parent rocks result in elevated concentrations of these elements in soils and sediments.

3. Zinc-lead ores and mineral occurrences are the natural (geological) sources of environment pollution with arsenic, cadmium, zinc, lead and mercury within areas of outcrops of Triassic carbonate deposits hosting ores. Within the mining districts, the concentrations of these elements are enhanced due to mining and mineral processing activities.

4. The surface water geochemistry clearly reflects pollution from various industrial activities. Industrial sewage, discharged from zinc-lead mine and processing plant, is the major source of pollutants of surface water. Increased conductivity and enrichment in cadmium, lead, zinc, thallium, boron, potassium, lithium, sulphates and sodium is related to hard coal and zinc-lead ores mining and disposal of saline mine waters into watercourses. Wastewater discharge from other industrial plants determines cobalt, copper, potassium, lithium, manganese, magnesium, sodium, phosphorus, rubidium, silica, and strontium content in water.

5. The results show an excellent correlation between topsoil and subsoil geochemistry as well as between soil geochemistry and chemical composition of underlying geological formations.

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