INTRODUCTION

The research performed to determine the conditions, principles and methodology for the 1:25 000 scale detailed geochemical mapping of the Silesia-Cracow region started with the pilot Sławków Map Sheet M-34-63-B-b. The map area (approximately 82 km^2) covers the eastern part of the Dąbrowa Górnicza town, and parts of the Sławków, Bukowno, Bolesław and Klucze communes. The pilot project was ordered by the Ministry of the Environment and financed by the National Fund for Environmental Protection and Water Management.

The issue of the pilot sheet (Lis, Pasieczna, 1999) is out of print, which indicates high interest in cartographic form of geochemical data presentation of this area. Geochemical maps were developed on the topographic base map outdated now, which do not ensure the continuity of adjacent sheets. All the sheets of "The Detailed Geochemical Map of Silesia-Cracow region" were elaborated according to the coordinate system 1992 (VMap L2). The above facts were reasons to develop the second edition of the atlas and its presentation on the Web.

Silesia-Cracow region is unique in the environmental geochemical mapping of Poland, being a prominent regional anomaly. The anomaly of Pb–Zn–Cd, strongly marked in soils, aqueous sediments and surface water (Lis, Pasieczna 1995a, b), has been generated by both natural and anthropogenic factors. The main natural factor is the occurrence of ore-bearing dolomite outcrops and associated zinc-lead ore deposits. The natural factors giving rise to geochemical anomalies are imposed by factors associated with ore extraction and processing as well as metals smelting.

The Sławków Sheet area is located in the Silesian-Cracow Upland within the Biała Przemsza and Sztoła rivers catchments.

It is an industrial region with a well-developed network of roads and railway lines and two small towns – Sławków and Bukowno. When selecting the map sheet as a pilot one, the characteristics of the geological structure; land use; Zn–Pb ore mining, processing and smelting; urban and industrial infrastructure as well as landscape values were taken into account. The land use is variable within the sheet area: its northern and southern parts are covered with forests (about 40%) whereas the central part (about 18%) by agricultural land of low quality soils (Preidl *et al.*, 1995). The rest of the sheet is covered by urban and industrial areas, roads and railways, water reservoirs and barren land.

In the vicinity of Bolesław, Bukowno and Sławków, the soils show the maximum concentrations of cadmium, lead and zinc, related to the outcrops of ore-bearing dolomites and both contemporary and historical exploitation, processing and smelting of Zn–Pb ores, that have lasted from the 12th century (Grzechnik, 1978). The Bolesław and Bukowno towns host one of the country's largest mining and metallurgy plant Bolesław Mining and Metallurgy Company (Zakłady Górniczo-Hutnicze ZGH Bolesław) exploiting and processing Pb–Zn ores. The area covered by mining waste dumps and settling ponds is approximately 2000 ha.

Some parts of the sheet area are also used for recreation because of their scenic landscape values. Forests of the north-eastern part of the map sheet are the protected landscape area of the Eagles' Nests Landscape Park (Park Krajobrazowy Orlich Gniazd). Near the Boleslaw mine dump, there is a site of ecological interest, established to protect the most valuable fragment of calamine grasslands. The calamine flora is composed of grasslands developing spontaneously on post-mining waste or soil, which is usually stony, slightly alkaline, nitrogen-poor, contaminated with zinc, lead and cadmium (Kapusta *et al.*, 2010).

The results of geochemical research, presented in a cartographic form with a comprehensive explanatory text and data tables, show the current conditions of soils, aqueous sediments and surface water in relation to the natural regional background and the regulation guidelines. The information provided in this publication can be useful in preparing physiogeographic reports, 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 within the framework of the state monitoring system.

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

A number of specialists participated in the preparation of this report:

- **J. Lis, A. Pasieczna** – concept and project proposal, supervision and coordination of research; databases; statistical calculations; construction of geochemical maps; characteristics of the map area, geology and mineral deposits, human impacts, interpretation of results;
- **L. Kaleta, E. Kotlarski, M. Toczyski, J. Szyborska** – sample collection;

- **P. Pasławski, K. Jakimowicz-Hnatyszak** – leadership and coordination of analytical works;
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- **B. Budzicka, I. Witowska** – chemical preparation of samples for analyses;
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- **W. Wolski, Z. Frankowski** – grain size analyses;
- **J. Lis** – geological map construction.

CHARACTERISTICS OF THE MAP AREA

Geographical and administrative setting. The map sheet area is located at the borderland of the Śląskie and Małopolskie Voivodeships. The Śląskie Voivodeship includes the eastern part of the Dąbrowa Górnicza town and the eastern part of the Sławków commune (Będzin poviat). Most of the study area belongs to the Bukowno, Bolesław and Klucze communes (Olkusz poviat) included in the Małopolskie Voivodeship.

According to the physiogeographic subdivision of Poland (Kondracki, 2000), the Sławków Sheet area is situated within the Silesian-Cracow Upland. Lower-order geographical units include the Garb Tarnogórski Ridge that occupies most of the map area and the Katowice Upland extending in its south-western part.

Relief and geomorphology. Garb Tarnogórski Ridge is composed of Middle Triassic dolomites and limestones rising to the 340–370 m a.s.l. and sloping southwards as a tectonic-denudation escarpment towards the Katowice Upland. The whole map sheet area is a part of the Vistula River catchment. The western part of the map sheet area is dissected by the Biała Przemsza River valley, whereas the southern part is drained by the Sztoła River.

The region is an industrial area of anthropogenically transformed landscape. Zn–Pb ore mining and zinc smelting industries are located in its eastern and central part. This area hosts the facilities of the Pomorzany mine extracting zinc and lead ores, and the abandoned Bolesław mine that for many years specialized in opencast mining of calamines. Mining and ores processing resulted in geomechanical transformations of ground near the Bolesław town.

These are mine heaps and landfills, terrain deformations due to underground excavations, post flotation ponds and other industrial objects. In the vicinity of the zinc smelter at Bukowno, included in the ZGH Bolesław Mining and Metallurgy Company, there is an above-ground post flotation tailings dump covering an area of approximately 130 ha (Cabała, 2009).

The Szczakowa open-pit sand mine, located in the southern part of the map area, extracted extremely big amounts of filling sands. Such a great production was forced by the demand from the coal mining sector in the Upper Silesian Industrial Region. Now the extraction is abandoned and the reclamation of the site was performed through afforestation, restoring it to natural values.

Land use. Undeveloped areas and areas of village development cover most of the sheet (Plate 2). Urban and suburban development of Sławków, Bukowno and Bolesław towns occupies about 5% of the map sheet. Industrial development, accounting for approximately 4% of the area, is represented mainly by the facilities of the ZGH Bolesław company. Land use is variable. More than 40% of the sheet area is covered by forests, 20% is covered by meadows and cultivated fields (Plate 3). The forests are moderately distorted, despite the close proximity of industrial plants arduous for the environment. They are dominated by pine, smaller areas are occupied by mixed pine-oak and beech forests. The remaining area is used as barren land, water reservoirs, roads and railways .

Economy. Extraction of Zn–Pb ores and zinc metallurgy are the most important sectors of the region's economy. The occurrence of shallow ore deposits enabled the development of mining in the early 12th century. Historical exploitation of ores brought about a number of problems due to substantial inflow of water into the mine workings. Until the 16th century the exploitation was carried out above the water level in opencast excavations. In the second half of the 17th century, a permanent dewatering of deposits was used by making a system of adits, and the ore was mined from beds lying below the water table (Grzechnik, 1978). The adits had two functions: ventilation and drainage. The following adits operated: Czajowska (Leśna), Ostowicka (Centauryjska), Dąbrówka and Pilecka i.e. Staroolkuska in the Bolesław mines as well as Starczynowska and Czarkowska near Starczynów (Kosiński, 1882; Albrecht, 1901; Śpiewak, 1955; Molenda, 1960a,b; Pazdur, Pietraszek, 1961).

By the end of the 18th century, mainly galena was mined for lead and silver production. In the 19th and 20th centuries, Zn–Pb ores became increasingly important. Shallow seated ore deposits were extracted in many places between Olkusz and

Strzemieszyce (including Sławków). There was also an increase in zinc production due to the development of the method of zinc oxide production from calamines and sulphide ores. The Dąbrówka mine operated near Hutki, and the Jerzy mine in Ujków (Kosiński, 1882). The Ulisses mine, located in Krążek (1818–1953) and the Bolesław mine (1822–1998) extracted mainly sulphide ore. Ore was also mined near Sławków (Degenhardt, 1870). The first use of pumps in the mine dewatering system took place in 1813 (Adamczyk, 1990) and contributed to the rapid development of mining and simultaneous drainage of the rock mass.

The Bolesław and Ulisses mines conducted underground extraction supported by opencast mining. In 1931, the mines were flooded due to low profitability. The collapse of mining continued until 1940, when the mines were dried up. After the merger of the mines under the name of Bolesław, production has been very intense since 1945. Until the 1960s, calamine ores were also exploited from opencast workings in Krążek, and until the 1990s from the Krzykawa ore deposit.

Currently, ZGH Bolesław is the company of the greatest economic importance in the region. This is a modern extracting and processing complex, which is principally engaged in mining of Zn–Pb ores in the Olkusz-Pomorzany mine. It produces electrolytic high quality zinc (99.99%), lead-zinc concentrates, alloys and sulphuric acid (Zakłady..., 2010). Ore extraction is carried out using the most modern technology, mainly automatic. After crushing, the ore is subjected to the flotation process, and the obtained concentrates (blende, galena and zinc-lead concentrates) go to a zinc smelter for further processing.

Metal works, machinery and small food production plants and a brickyard are located in Sławków.

The Boleslaw rural commune has a well-developed road network supporting the development of tourism, which is an alternative source of income for farmers.

GEOLOGY AND MINERAL DEPOSITS

The map area belongs to the Silesian-Cracow Monocline (Gałkiewicz, 1977). Its bedrock is composed of the Caledonian-Variscan orogen rocks, from Cambrian to Upper Carboniferous formations. They are formed into asymmetrical anticlines and synclines transected by numerous faults (Bukowy, 1978). During the last stage of the Variscan tectonic cycle, the NW–SE trending Sławków–Pomorzany Graben was formed and filled with

Permian and Triassic sediments (Bukowy, 1974; Kurek *et al.*, 1994). Volcanic activity related to the Variscan tectonic cycle (Filipowice Tuffs) is observed along the graben in the area located south of the map sheet boundary. Permian and Triassic deposits composing the Alpine structural stage are outcropped at the sub-Quaternary surface. Alpine tectonic movements rejuvenated the Variscan tectonic pattern and resulted in cutting of the Triassic dolomite-limestone plate by a number of faults. As the result of these processes grabens and horsts were formed.

Permian deposits outcrop only in small patches (Plate 1). In the Kanał Sztolnia Canal valley these are conglomerates composed of fragments of Carboniferous and Devonian rocks bonded with sand-clay-carbonate cement (Kurek *et al.*, 1994). Near Przymiarki–Bukowno Wieś and south of Sławków, varicoloured claystones and mudstones (Sławków clays) occur. They are built mainly of the silt fraction represented by illite and kaolinite (Kaczmarek *et al.*, 1995).

In the centre of the map sheet and in its north-western part (west of the Biała Przemsza River valley) **Triassic** rocks form a broad belt of outcrops.

The Lower Triassic is represented by Buntsandstein and Roethian deposits outcropped in Sławków only. Buntsandstein deposits are known from numerous boreholes. These are gravels, conglomerates, sands, sandstones, claystones and siltstones usually filling erosion channels. The Roethian is represented by cavernous dolomites and marls with infrequent faunal remains (Kurek *et al.*, 1994, 1999).

Middle Triassic (Muschelkalk) deposits form outcrops in the central part of the map sheet. The most important part of these rocks are ore-bearing dolomites, due to the zinc and lead mineralisation. The dolomites are not a stratigraphic horizon, but they are secondary rocks, often preserving original rock structure (Śliwiński, 1978; Górecka 1993, Sass-Gustkiewicz, 1995; Cabała, Konstantynowicz, 1999). The dolomites are commonly finely crystalline, porous, often fractured, sometimes brecciated. Pores and caverns are filled with lead and zinc sulphides, pyrite, calcite, limonite or barite. The accumulation of ores is of economic importance in many areas. The ore-bearing dolomites are underlain by limestones, marls and conglomeratic limestones. Their outcrops occur south of Bukowno and between Skotnica, Podlipie and Sławków. Between the ZGH Bolesław company area and the Bolesław settlement, near Dąbrówka, Nowa Krzykawa and north of Sławków, there are outcrops of diplopora dolomites, containing numerous fragments of poorly preserved fauna. The youngest Middle Triassic deposits are represented by locally preserved dolomites, marls and shales.

The Upper Triassic is composed of claystones, siltstones and limestones that uncomfortably overlie various Middle Triassic members. They outcrop near Laski-Kolonia and Ujków Nowy.

The **Quaternary** is built mostly of Pleistocene glaciofluvial sands and gravels in the north of the map area and by glaciofluvial sands of alluvial fans in the south. These deposits locally contain gravel or mud layers. Petrographic composition of the sand fraction is dominated by quartz.

A belt of loess, 2 to 20 m in thickness and represented by silts and silty-sandy clays, stretches between the Biała Stream and Biała Przemsza River valleys (Kurek *et al.*, 1994). Deluvial sandy loess covers the valleys of their tributaries.

In the central part of the map sheet, there are numerous rock debris composed of the Triassic rocks crumbs.

Aeolian sands occur south-east of Bukowno. Some of them form distinct belts of sand dunes in the southern and northern part of the map area.

The Holocene deposits, most frequently observed between Bukowno and Sławków, include deluvial sands and clays containing crumbs of local rocks. River valleys are filled with sands, gravels and muds forming alluvial terraces. Peats occur locally in stream valleys.

Mineral deposits. Zinc–lead ore deposits, associated with the post-Variscan platform cover, occur in ore-bearing dolomites of all the Triassic stratigraphic units (Serafin-Radlicz, 1972; Przeniosło, 1974; Gruszczyk, Wielgomas, 1987). In the Sławków Sheet area, these are Lower Muschelkalk dolomites cut by faults that resulted in the preservation of sulphide ore in the grabens and its alteration into calamines in the horsts. In the Bolesław area, the thickness of ore-bearing rocks averages from 20 to 25 m (Gruszczyk, Wielgomas, 1987), and the horizontal size of orebodies does not exceed 200 m (Kurek *et al.*, 1994). The ore bodies are represented by layers, beds, lenses, nests and brecciated fillings of karst forms (Przeniosło, 1995; Górecka 1996; Sass-Gustkiewicz, 1996).

The main primary ore minerals are sphalerite, galena (and their cryptocrystalline varieties: brunckite and boleslavite), pyrite and marcasite. Lead-arsenic sulphosalts, including jordanite and gratonite (Harańczyk, 1960, 1962; Ziętek-Kruszewska, 1978; Górecka, 1996, Viets *et al.*, 1996; Cabała, 2009) are subordinate. Zinc sulphide contains cadmium, silver, cobalt, copper, thallium and germanium, whereas galena is generally silver-bearing mineral (Harańczyk, 1962; Ekiert, 1971). As characteristic admixtures of galena from the Ulisses mine, Kuźniar (1930) mentioned arsenic and antimony compounds. Cadmium content in sphalerites of the Silesian-Cracow deposits reaches 5000–10 000 mg/kg (Viets *et al.*, 1996; Cabała, 2009). Thallium and arsenic accumulate mainly in iron sulphides (up to 1000 mg/kg of thallium and about 500 mg/kg of arsenic). Silver occurs in the crystal lattice of all the sulphides, but it is most commonly associated with galena (up to 180 mg/kg). The ore minerals are accompanied by calcite and barite. The average zinc and lead contents in the Bolesław deposit were 3.3% and 0.7%, respectively.

Oxidized ores (calamines) occur in the area extending from Krążek in the west to Ujków Stary and Starczynów in the east. Their main components are carbonate minerals of zinc (smithsonite, monheimite) and lead (cerussite). They are accompanied by limonite, occasionally by sulphate minerals (jarosite, melanterite), hydrozincite and calcite (Żabiński, 1960; Cabała, 2009). Many other minerals have been noted as rarities.

Raw rock materials. The most common raw rock are large amounts of Pleistocene glaciofluvial **sands** of an ancient valley and alluvial fans. These are medium- and fine-grained sands containing 93 to 95% of the 0.1–2.0 mm fraction. The southern part of the map sheet, covers only part of the Szczakowa deposit sands, used mainly as filling and sometimes building materials (Preidl *et al.*, 1995). Triassic **carbonates** are used for local constructing and road maintenance, whereas **clays** (Sławków clays) mined in open pits are the raw material for the production of building ceramics.

HUMAN IMPACT

In the north-east of the map sheet there is a part of the Zn–Pb ore mining area of the Bolesław-Pomorzany mine. Environmental pollution in the vicinity of Bukowno, Bolesław and Sławków is caused by the outcrops of rocks containing mineralized zones (natural anomalies), as well as Zn–Pb ore mining, processing and smelting, and by discharge of industrial and municipal sewage (anthropogenic anomalies).

Extraction and processing of Zn–Pb ore resulted in geomechanical transformations of the environment, mainly in the Bolesław mining area. These are mine heaps and landfills, terrain deformations caused by underground excavations, post-flotation tailings ponds and other industrial objects. The area covered by the alterations occupies about 450 hectares (Czubak *et al.*, 1975).

The most harmful to the environment is the ZGH Bolesław company – including Olkusz-Pomorzany Zn–Pb ore mine as well as the metallurgical ore treatment plant located in Bukowno. The company produces sphalerite concentrate using the flotation method. The production waste includes dolomite, calcite, barite and sulphides, as well as oxygenous minerals of zinc, lead and iron, which are brought to the post-flotation ponds. Tailings ponds, covering an area of approximately 109.5 ha, are located above-ground at the border of the Bolesław and Olkusz mining areas (Górecka *et al.*, 1994; Program ..., 2005). The zinc oxide production plant processes sulphide and oxide ores, ore pulp and calamine tailings from mine heaps (Przeniosło, 1995). These processes cause significant pollution of the environment, as evidenced by extensive lead and zinc anomalies documented in soils and aqueous sediments (Lis, Pasieczna 1995b).

Atmospheric air. Atmospheric air is polluted by emissions from industrial sources, dusts from post-flotation tailings dumps, road transportation, communal economy and individual furnaces.

A monitoring station measuring concentrations of sulphur dioxide, nitrogen oxides and dust is located in Olkusz town. Observations of this station show that the concentrations of the main gas and dust pollutants are among the largest in the Małopolska region. Most of the air pollution comes from the ZGH Bolesław company, which emits sulphur dioxide, sulphuric acid, nitrogen dioxide, carbon monoxide, metallic dusts (with lead, zinc, cadmium, manganese and iron). Metallic dusts are also emitted from the post-flotation tailings dump. The zinc and lead concentrations in the post-flotation wastes are within the limits of 0.64–3.94% and 0.22–0.68%, respectively. Metallic dusts (mainly containing <0.04 mm fraction) are disseminated by the wind.

The Dąbrówka heating plant introduces into the atmospheric air PM 10 dust, furnace black, sulphur dioxide, nitrogen dioxide, carbon monoxide, and benzo-a-pyrene (Program..., 2005). Dust and gas pollutants are also introduced into the air by some small plants located in Bolesław. The main industrial sources of air pollution in Sławków are emissions from the metal works (Zakłady Wyrobów Metalowych), a local heating plant, a brickyard and emissions from fuel combustion for heating (Program..., 2004a).

Emissions from car engines (hydrocarbons, nitrogen dioxide, carbon monoxide and metal compounds) along transportation routes and contamination by dust and gases carried by winds from the western part of the Upper Silesia agglomeration, are also significant sources of air pollution. Point sources of pollution include emissions from furnaces of individual houses, emitting mainly dust.

Surface water and groundwater. The long-lasting Zn–Pb ore mining and metals smelting have caused transformation in the hydrographic network and the water quality deterioration. Drainage of the exploited deposits led to the formation of depression cones and changes in the surface water and groundwater recharge. The water quality is also affected by the disordered water and sewage management. The sewage system is currently being developed.

Underground extraction of Zn–Pb ore requires pumping of highly mineralised mine water to the watercourses that causes pollution of surface water and aqueous sediments with heavy metals and suspended matter. The Olkusz mine discharges mining water into the Kanał Sztolnia Canal. Wastewater from the Pomorzany mine objects is discharged into the Dąbrówka Canal, while that from the Bolesław mine – into the Biała Przemsza River via the Warwas Stream (Wójcik *et al.*, 1990). These watercourses receive also wastewater from mechanical and metallurgical Zn–Pb ore processing (after sedimentation in post-flotation ponds or mechanical-biological treatment).

Changes in the hydrological system result from a deep drainage of Triassic formations by mines and large water intakes, which caused the formation of a depression cone covering an area of several hundred square kilometres (Program..., 2005). As a result of mining activity, the Biała Stream has dried up over a distance of about 8.5 km. This situation will likely change after the completion of mining activities by the ZGH Bolesław company. It is possible to fill in the depression cone with water, to restore the natural river network and to rebirth disappeared springs. However, the predicted transformations may in turn lead to the local flooding.

The significant influence on the groundwater quality is exerted by pollution sources occurring on the ground surface. The largest ones are dumps of post-flotation tailings and old reclaimed landfills. The hazard posed by migration of pollutants from the surface into the groundwater takes place due to lack of an appropriate insulating layer.

Contaminated groundwater occurs in the area of a former opencast calamine mine near Ujków. A municipal landfill for local wastes from the Bolesław and Bukowno municipalities has been located in the abandoned calamine pit. The outcrop has been reclaimed by the ZGH Bolesław company using post-flotation tailing and afforestation. Results of groundwater chemical analyses from piezometers located in this area show exceeded permissible limits of drinking water for sulphates, manganese, iron, chloride, sodium, zinc, cadmium, lead, selenium and ammonium and the number of coli bacteria (Program..., 2005). Infiltration of contaminants from post-flotation tailings, acid liquid sewage and domestic sewage at the Starczynów is an additional cause of poor water quality.

The sulphates pollution is related to the influence of post-flotation tailings storage in ponds, where oxidation of sulphide minerals takes place. Leachates from the tailings ponds contain from 1100 to 1800 mg/dm^3 of sulphates and are enriched with zinc, lead, cadmium, copper, arsenic and nickel. The leachates from the tailings ponds infiltrate mainly into excavations of the Olkusz and Pomorzany mines and then migrate into the aquifers.

Saline mine water and sewage from water treatment plants and industrial facilities situated outside the eastern border of the map sheet area are discharged to the Biała Przemsza River through the Biała Stream, Dąbrówka Canal, Kanał Sztolnia Canal and Sztoła Stream.

The Biała Stream receives mine water from the Pomorzany Zn–Pb ore mine and sewage from the Olkusz municipal treatment plant through the Dąbrówka artificial open canal. The ZGH Bolesław company (Dąbrówka and Mieszko shafts) discharges mine water, and water from post-flotation tailings ponds into the Biała Stream by the Kanał Dąbrówka Canal. The water of the Dąbrówka Canal is among the most polluted (substandard water) due to the zinc and lead concentration exceeding several times the permissible values of pollution for surface water.

The waters from the mining facilities (Stefan, Bronisław and Chrobry mine shafts) are discharged into the Baba Stream through the Kanał Sztolnia Canal, whereas this from the sewage treatment plant is released to the Biała Przemsza River by the Kanał Zachodni Canal and Warwas Stream. Neutralized acid wastewater, industrial wastewater, unused mine water and domestic sewage are subjected to mechanical and chemical treatment. The purification process is carried out through sediment precipitation to reduce concentration of heavy metals (Zn, Pb, Cd) as much as possible.

Water monitoring of the Biała Przemsza River indicates an improvement of its quality with respect to BOD5, suspended solids, total phosphorus and phosphates. In the bacteriological classification, it is mainly substandard water (Program..., 2004b).

Soils. Degradation of soils is the result of Zn–Pb ore mining and smelting activity, emissions from the transportation, dust and leachates from post-flotation ponds, industrial wastewater discharges and fallout of metallurgical dust. High metal concentrations, related to the natural geochemical background in areas of outcrops of Zn–Pb ore-bearing rocks, are observed in some places (Sass-Gustkiewicz *et al.*, 2001; Trafas *et al*., 2006).

Soils of built-up areas are contaminated by salts (sodium, calcium and magnesium chlorides) due to the snow removal from streets. Alkalinisation of soils is related to admixtures of calcareous debris and dust fall containing calcium and magnesium compounds. In valleys, soils are polluted due to rivers floods, especially those with contaminated water.

Both natural and anthropogenic factors result in soil fertility decline. They cause a decrease in the quality and quantity of humus, changes in soils acidity and texture, and leaching of alkaline cations. In many places, the soils are mechanically and chemically altered. Mechanical damage of soil is related to removal of the soil cover during opencast mining of calamines and sand as well as to the construction activities (building works, drilling installation, pipeline**)**. In the vicinity of the Olkusz-Pomorzany mine, the soil cover was destroyed over the area of about 600 ha (Trafas *et al*., 1990). Other mechanical transformations are the result of sealing; surface hardening and compaction; mixing of soil with the debris, cement, glass and metals; drying (by heating networks, covering the surface with asphalt and paving stones) and the displacement of ground layers during earthworks building of foundation trenches and embankments etc. The specific forms of soil degradation include disturbance of the natural hydrogeological conditions in mining subsidence troughs and tailings ponds as a result of mining activities.

In 1981–1982, the following concentrations were noted in the topsoil of the Olkusz area: up to 30 000 mg/kg of zinc, up to 6 000 mg/kg of lead and up to 150 mg/kg of cadmium (Trafas *et al.,* 1990). In the vicinity of Bukowno the agricultural soils showed the contents of 46–1520 mg/kg of lead, 1–42 mg/kg of cadmium and 90–920 mg/kg of zinc (Kucharski, Marchwińska, 1990). The contents of these elements around the Sławków were as follow: 37–352 mg/kg of lead, 2–16 mg/kg of cadmium and 148–2960 mg/kg of zinc. Near the zinc smelter in Bukowno, the soils contain up to 392 mg/kg of lead, 12 mg/kg of cadmium and

1473 mg/kg of zinc (Verner *et al.*, 1996). The soils from the area of former calamine open-pit mine in Bolesław are among the most polluted by these metals. Fine-grained fractions of the soils contain up to 83 000 mg/kg of zinc and 26 400 mg/kg of lead (Cabała, Teper, 2007).

In some areas, topsoil is more contaminated, and the anomalies disappear with depth (Lis, Pasieczna, 1997) indicating that the pollution comes mainly from dust emitted by industrial plants. It does not refer to the areas of outcrops of Zn–Pb ore-bearing rocks and the places of long-lasting activity of metallurgy plants.

MATERIALS AND METHODS

The 1996–1998 researches included studying published and archived materials, selecting sampling sites in topographic maps at a 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 map, statistical calculations, constructing geochemical maps and a geological map, and finally interpretation of the results. The sequence of investigations is shown in Figure 1.

FIELD WORKS

Soil sampling was conducted in 1996, and the samples of aqueous sediments and surface water were collected in 1997.

Soil samples were collected on a regular grid of 250x250 m (16 samples per 1 km^2). The total number of soil sampling sites was 1393 sites (Plate 2).

At every site, two samples were collected from two depths: 0.0–0.2 (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, tailings ponds, pools and ponds. The distance between the watercourse sampling sites was about 250 m. 500 g sediment samples (of possibly the finest fraction) were taken from water reservoir shores using a scoop. They were subsequently placed in linen bags labelled with numbers. The bags were then put in a special plastic-sieve container to allow for water drainage and preventing them from contact one with another.

Surface water samples were collected at the same sites as aqueous sediment samples. 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. The sampling method followed that presented by Witczak and Adamczyk (1994) for spring sampling.

All the sampling sites were indicated in topographic maps at a scale of 1:10 000 and numbered. All the field data were noted on special sampling cards (Fig. 2).

Locations of sampling sites were determined with GPS. The measurements were made with a March I GPS (Cornallis Microtechnology), equipped with a computer which can record not only coordinates but also additional information (data on land development and land use, type of soil and aqueous sediment). The direct measurement of this device is recorded with an accuracy of ± 100 m. Then the coordinates data were corrected using a ProXL Trimble Pathfinder device running as corrective base at the point of known coordinates. Accordingly, the location of the points was determined with an accuracy of 1–3 metres (Doktór *et al.*, 1996).

LABORATORY WORKS

Sample preparation. The soil samples were air-dried and sieved through a 2 mm nylon sieve. Each topsoil sample (0.0–0.2 m) was split into three portions: one of them was submitted for chemical analysis, the second one was analysed for the 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 in the Polish Geological Institute-National Research Institute in Warsaw.

Chemical analyses were carried out in 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 soil and aqueous sediment samples were determined by the ICP-AES method. Mercury content was measured using the CV-AAS method. Acidity of soil was measured using a pH meter (Norma..., 1975). Organic carbon content in topsoils was determined by the coulometric method.

Determinations of Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, SiO_2, SO_4, Sr, Ti, V and Zn in surface water were performed by the ICP-AES method. Lead was analysed by the GF-AAS method.

The applied analytical methods and the detection limits of measured elements are shown in Table 1.

Quality control of the determinations was performed through analysis of duplicate samples (about 10 percent of all samples) and analysis of reference materials with a certified content of the elements studied: LOAM 7004, SRM 2709 (NIST) and SRM 2711(NIST) for soils, and SRM 2704 (NIST) and PACS for aqueous sediments.

Grain size analyses of topsoils were carried out in the Polish Geological Institute-National Research Institute in Warsaw, using the laser and sieve methods. Air dried samples were sieved through a 2 mm and 1 mm sieve set. In the case that the material was agglutinated, the sample was grounded in a porcelain mortar before splitting and sieving.

The fractions of >2 mm, 2–1 mm and <1 mm were weighed. The <1 mm fraction was quartered in order to obtain analytical samples in weight ca 100 g for laser analysis. The proportions of the fractions were calculated to percentage shares in relation to the total weight of samples.

DATABASES AND GEOCHEMICAL MAPS 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 a scale of 1:50 000, Jaworzno Map Sheet M-34-63-B (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 base of Detailed geological map of Poland Jaworzno Sheet 1:50 000 (Kurek *et al*.,1999). Particular vector layers of the geological map were combined with topographic base map producing a geological map at a scale of 1:25 000 (Plate 1).

Database management. Separate databases were prepared for: topsoil (0.0–0.2 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 sediments 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 for geochemical maps construction and to create subsets for statistical calculations according to different 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. Statistical calculations were made for both whole datasets and subsets created for soils, aqueous sediments and surface water. In case of some elements with the content lower than the detection limit value for the given analytical method, half of the detection limit value was taken. The arithmetic and geometric means, median, minimum and maximum values were calculated. These data specified for individual elements are shown in Tables 2–5 and presented in the geochemical maps.

Maps construction. The following maps were produced for the Sławków Sheet (Plates 2–57): land development, land use, content 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, contents of Al, As, B, Ba, Ca, Cd, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, SiO_2, SO_4, Sr, and Zn in surface water, topsoil classification indicating appropriate soil use.

Land development, land use and topsoil classification indicating appropriate soil use are presented as point maps (Plates 2, 3 and 57).

To show the distribution of the grain size classes (Plates 4–6) and the contents of elements in soils, contour maps were constructed because of their clarity and legibility. The contour maps were produced using the Surfer software and the *Inverse Distance to a Power* method. The classes of contents of elements were created 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 Sławków Sheet and the datasets of 1:25 000 scale neighbouring sheets. Thus disagreements at the sheet borders were avoided. After interpolation the Sławków Sheet was extracted from mono-element maps and combined with the topographic base map.

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

While constructing the map of soil classification (Plate 57), indicating appropriate soil use, the results of geochemical analyses were referred to the permissible levels of metals, defined by 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 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 sediments map, and the subsoil map is shown with the surface water map. This method of presentation provides the possibility of direct comparison of geochemical images of various media. Taking into account the comfort of potential users, the maps (with a bar scale shown) have been printed out in a slightly smaller format (A3). This operation did not cause omitting any important details of the maps. The whole report or its individual plotter printed maps are available for those who are interested in 1:25 000 scale maps.

RESULTS

SOILS

The soils parent rocks are represented by Permian, Triassic and Quaternary deposits. Accumulation of chemical elements in the soils is a result of geological (outcrops of rock formations, geochemical barriers) and anthropogenic (mining water and sewage discharge, leachates from post-mining waste dumps and tailings ponds, coal combustion, and zinc smelting) processes.

The most common soil type are *Podzols* formed on sands (Program..., 2005). These are the acidic soils developed with the influence of coniferous forests vegetation. *Rendzinas* developed on limestones and dolomites. *Cambizols* occur rarely. Initial *Rendzinas* are characteristic in areas of former calamine exploitation. River valleys are covered with alluvial soils (muds), and *Histozols* are observed locally in the valleys and in topographic lows.

Grain size. Comparison of the results of the grain size studies obtained by the sieve-sedimentation analysis (according to the International Classification of FAO and USDA), and the laser analysis shows significant differences in the content of individual fractions (Kasza, 1992; Issmer, 2000). Therefore, direct use of the results obtained using the laser method does not permit to classify soils according to the soil science criteria. The data, however, is very useful to interpretation of geochemical studies results.

The results of sieve analysis and laser measurement (recalculated to percentage shares) 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).

Almost all chemical and physical properties of soils are either directly or indirectly related to their mechanical composition. Determination of grain size 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. Soils rich in the clay (<0.02 mm) and silt (0.1–0.02 mm) fractions are commonly characterized 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 into account 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).

Grain size variability of the soils in the Sławków Sheet area is related to parent rocks lithology. Sandy soils containing >75% of the 1.0–0.1 mm fraction developed on Pleistocene sands and gravels in the southern and north-eastern part of the map area. The soils that developed on glaciofluvial sands of alluvial fans contain 20–30% of coarse grained sand 1.0–0.5 mm, while soils formed on glaciofluvial sands and gravels contain 10–20% of this fraction. The proportions of medium grained sand (0.5–0.25 mm) and fine grained sand (0.25–0.1 mm) are similar in both groups of soils. All soils formed on Pleistocene deposits are characterized by a low content (<5%) of the silt (0.1–0.02 mm) and clay (<0.02 mm) fractions.

A specific grain size composition occur in the soils developed from Upper Pleistocene loess in the area between Bolesław town and the Biała Przemsza River valley. They contain over 15% of the gravel fraction (>1.0 mm). The amount of the sand fraction rarely exceeds 10%, and the dominant are silt and clay fractions.

Soils of the central part of the map sheet, developed on Permian and Triassic rocks, are a mixture of different sand fractions and contain <5% of the silt and clay fractions. A significant proportion of the gravel fractions (fragments of basement rocks) is their characteristic feature.

Acidity. Acidic soils predominate both in the topsoils and subsoils, which is related to the lithology of the parent rocks and the soils use. Acidic forest soils (pH <6.3) that developed on glaciofluvial sand-gravel and loess deposits cover approximately half of the map area. Locally, in forests patches of very acidic soils (pH <5) were observed. Such low acidity causes leaching of nutrients and can lead to the release of toxic aluminium ions.

The occurrence of neutral and locally alkaline soils is limited to small areas around Bolesław town and the ZGH Bolesław company (including post-flotation ponds) and those north of Sławków (Zn–Pb ore-bearing dolomite outcrops). The proportion of neutral and alkaline soils clearly increases with depth.

Geochemistry. Chemical elements in soils originate mainly from parent rocks altered due to soil forming processes. As a result of physicochemical conditions of the environment, soil forming processes lead to chemical changes of soils in relation to the chemistry of their parent rocks; however geochemical features of the parent rocks are usually decipherable. Distribution patterns of elements inherited from parent rocks enable determination of geochemical background variability and identification of local anomalies.

The soils developed from Pleistocene loess are rich in aluminium, cobalt, chromium, iron, titanium and vanadium, which is more noticeable at a depth of 0.8–1.0 m. Especially characteristic is the distribution of titanium, whose pattern well coincides with the loess outcrops.

The typical chemical elements of the soils developed on Triassic and Permian outcrops are calcium, magnesium, aluminium, iron, cobalt, chromium, nickel, strontium and vanadium. Enrichment in these elements in soil is much more pronounced at a depth of 0.8–1.0 m. The most characteristic association, related to Triassic carbonates, is represented by calcium, magnesium, manganese and strontium. Soils containing the highest concentrations of these elements occur in the centre of the map sheet.

High concentrations of calcium (>8%), magnesium (>4%), iron (>8%) and strontium (>80 mg/kg) are observed in the soils near post-flotation tailings ponds of the ZGH Bolesław company.

Cadmium, zinc, lead, silver, arsenic, copper, mercury and sulphur are the elements related to both Zn–Pb ore-bearing dolomite outcrops and mining-metallurgical activity. Unlike the previous group of elements, these are concentrated mainly in the topsoil, due to contemporary and historical exploitation and processing of Zn–Pb ores. In the subsoil, the area occupied by anomalous concentrations of cadmium, lead and zinc is reduced (Table 6). The largest concentrations of metals in subsoil were found in areas of historical open pit extraction of ore-bearing rocks (Bolesław-Ujków), near the Bukowno zinc smelter and in the vicinity of its post-flotation tailings ponds. In the latter case, there is a very strong contamination likely occurring to a significant depth.

Within the topsoil, anomalies of silver (>2 mg/kg), arsenic (>40 mg/kg), cadmium (>8 mg/kg), copper (>40 mg/kg), mercury (>0.20 mg/kg), lead (>500 mg/kg) and zinc (>1000 mg/kg) occur in the industrial zone of ZGH Bolesław company. These anomalies are of mixed anthropogenic-geogenic nature and most of them were also noted in deeper parts of the soil profile. The most intense anomalies of many elements were observed around the post-flotation tailings pond of the ZGH Bolesław company, the eastern part of which is located in the Olkusz Map Sheet area. In both the topsoil and subsoil there are high concentrations of calcium (up to 23.12% and 17.79%), magnesium (up to 8.34% and 19.83%), iron (up to 26.30% and 16.18%) and sulphur (up to 10.83% and 13.34%), respectively. The maximum concentrations in topsoil were as fallows: 41 mg/kg of silver, 1750 mg/kg of arsenic, 2107 mg/kg of cadmium, 3429 mg/kg of copper, 1.52 mg/kg of mercury, 59 887 mg/kg of lead and 162 143 mg/kg of zinc.

The soils of the sheet area are not rich in organic carbon (TOC). The low amount of carbon (<3%) was noted in the soils developed on Quaternary sandy deposits. The soils developed on loess and alluvial sediments of river valleys contain 3–6% of TOC, locally exceeding 12%, and reaching a maximum of 37.91% (Table 2).

Sulphur content rarely exceeds 0.16%. The only anomaly with the content over 0.64% was noted at the premises of ZGH Boleslaw company and its post-flotation tailings ponds.

The topsoils are remarkably enriched in phosphorus in relation to the subsoils. The average phosphorus content (0.020%) in topsoil is more than doubled as compared with the subsoil (0.009%). The phosphorus distribution indicates that its origin is mainly anthropogenic. The area of increased phosphorus content (>0.030%) is significantly larger in topsoil than in subsoil. Phosphorus comes from both fertilizers (once used in agricultural areas, which are now mostly uncultivated land) and municipal sewage discharges.

The areas of the soils contaminated to a different extent by cadmium, lead and zinc are presented in Table 6. Over most of the map sheet (65%), the topsoils contain <5 mg/kg of cadmium. The lead concentration of ≤100 mg/kg was found in 43% of soils, and the zinc concentration of ≤200 mg/kg in 37.1% of soils. Topsoils heavily contaminated with cadmium (>5 mg/kg), lead (>500 mg/kg) and zinc (>700 mg/kg) occupy 35%, 12.60% and 33.80% of the sheet area, respectively. At a depth of 0.8–1.0 m, the areas of the anomalies are markedly reduced.

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 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 the 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 the contents of metals, 21.39% of the soils were included into group A, 24.69% into group B, and 53.92% into group C (Table 7). The only soils meeting requirements of multi-purpose use are those categorized into classes A and B. Class C soils occur in the central part of the map area, mainly in the industrial zone of ZGH Bolesław company and in the regions of historical opencast extraction of calamines.

The classification (Plate 57) indicates recommended land use according to guidelines provided in Rozporządzenie... (2002). Much of the soils are currently improperly used and require 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.

AQUEOUS SEDIMENTS

Chemical composition of aqueous sediments perfectly reflects the environmental contamination because they retain most of mobilized heavy metals and other elements (due to both natural and anthropogenic processes). Toxic effects of polluted sediments on aqueous ecosystems have been widely documented for many years (Calmano, Förstner, 1995; Wolska *et al*., 1999; Burton, Landrum, 2003).

The sediments of the map area were sampled from rivers, canals and streams, and, in a smaller degree, from stagnant water reservoirs. The main feature of their geochemistry is the dominance of anthropogenic over natural factors in the concentration of most of chemical elements, especially metals and sulphur.

The tributaries of the Biała Przemsza River: Sztoła River, Dąbrówka Stream and Kanał Sztolnia Canal are sewage canals receiving industrial and municipal liquid wastes and mine water from the areas of Olkusz, Bukowno and Bolesław towns, and ZGH Bolesław company. The sediments of these watercourses differ a lot.

Kanał Sztolnia Canal. The sediments of the Kanał Sztolnia Canal, transporting industrial water from the smelting section of the ZGH Bolesław company, are polluted by enormous amounts of zinc (average 54 853 mg/kg) sporadically exceeding 400 000 mg/kg (Wójcik *et al.*, 1990). An extremely high zinc concentration (>200 000 mg/kg) was also noted in sediments of a small pond near Krążek. X-ray diffraction analysis of these sediments revealed that they are almost pure hydrozinkite. The occurrence of hydrozinkite in a weathering zone of Zn–Pb ore is common in this region. Cadmium (average 250.7 mg/kg), mercury (average 0.3 mg/kg) and nickel (average 35 mg/kg) concentrations are observed over the entire course of the canal. Sediments of the upstream section of the canal are enriched in silver (>4 mg/kg), arsenic (>500 mg/kg) and copper (>250 mg/kg). The metals may be sourced from eroded outcrops and mine dumps after historical calamine extraction in the area between Bolesław and Bukowno.

Kanał Dąbrówka Canal and Biała Stream. The concentrations of most elements, particularly metals and sulphur in sediments of the drainage basins is caused by anthropogenic factors. The most polluted are sediments of the upper section of the Dąbrówka Stream. Mine water from the Olkusz-Pomorzany mine (from the Dąbrówka and Mieszko mine shafts), water from post-flotation tailings ponds of the ZHG Bolesław company and water from the sewage treatment plant near the Dąbrówka mine shaft are discharged through the Dąbrówka Stream to the Biała Stream (Program..., 2004c). The characteristic feature of the Dąbrówka Stream sediments is contamination by lead (up to 23 409 mg/kg; average 10 021 mg/kg), silver (up to 9 mg/kg; average 5 mg/kg), arsenic (up to 626 mg/kg; average 264 mg/kg), cadmium (up to 488.6 mg/kg; average 185.4 mg/kg) and zinc (up to 128 880 mg/kg; average 44 722 mg/kg). These sediments are also rich in calcium (up to 13.98%; average 9.26%), magnesium (up to 4.89%; average 2.65%), iron (up to 5.02%; average 3.20 %) and sulphur (up to 10.82 %; average 4.682%). The similar concentrations of mentioned elements were found in sediments of the Biała Stream, downstream of its confluence with the Dąbrówka Stream.

Sztoła River and Baba Stream. Beyond the eastern boundary of the map sheet, the Baba Stream receives mine water from an underground mine of Zn–Pb ore and industrial water from the heating plant (Przedsiębiorstwa Energetyki Cieplnej) in Olkusz (Program ..., 2004b). The water contains, among others: suspended matter, sulphates, chlorides, zinc, lead, cadmium and iron. Downstream of the industrial district of Olkusz town, over a distance of about 2.5 km, the Baba Stream sediments are enriched in silver (up to 10 mg/kg), cadmium (up to 94 mg/kg), cobalt (up to 39 mg/kg), chromium (up to 77 mg/kg), copper (up to 86 mg/kg), nickel (up to 96 mg/kg), lead (up to 1242 mg/kg) and titanium (up to 689 mg/kg).

The contaminants can be related to the sewage discharges from plants operating in this area: enamelling plant (Olkuska Fabryka Naczyń Emaliowanych Emalia S.A.), heating company (Przedsiębiorstwo Energetyki Cieplnej), ventilators manufacturer, metal processing plants, and repair, transportation and other services (Lis, Pasieczna, 2008).

A rapid increase in the concentrations of elements is observed in sediments of the Baba Stream, downstream of the confluence with the Kanał Południowy Canal transporting mine water from the Olkusz Zn–Pb ore mine (Stefan, Bronisław and Chrobry mine shafts). Huge concentrations of zinc (median 34 000 mg/kg; max. 322 600 mg/kg) and lead (median 8500 mg/kg; max. 14 791 mg/kg) have been recorded. The sediments are also enriched in many other elements: arsenic (up to 269 mg/kg), barium (up to 382 mg/kg), calcium (up to 17.03%), cadmium (up to 369 mg/kg), cobalt (up to 50 mg/kg), iron (up to 4.10%), magnesium (up to 5.57%), manganese (up to 2727 mg/kg), sulphur (up to 3.40%) and strontium (up to 155 mg/kg).

Within the limits of the Sławków Sheet area, the concentration of metals in sediments of the Sztoła River and Baba Stream remains very high. Worth noticing is the small variability in the elements content at the analysed sections of the watercourses, which indicates stable physicochemical conditions and the origin of the metals from a single point source. The influence of surface runoff as the source of pollution by metals seems to be insignificant.

Biała Przemsza River. Chemical composition of the river sediments is dependent on the sediments of its tributaries – Sztoła River and Biała Stream, heavily contaminated by metals. The average concentrations of individual elements in the Biała Przemsza River sediments (expressed by median values) are as follows: 2 mg/kg of silver, 151 mg/kg of arsenic, 106.4 mg/kg of cadmium, 3915 mg/kg of lead, 0.779% of sulphur and 15 293 mg/kg of zinc (Table 4).

Sediments of small watercourses. Sediments of the Sztolnia Ponikowska Stream contain much smaller amounts of metals in relation to the above discussed. Sediments of small unnamed streams draining the central part of the map area and sediments of stagnant water reservoirs are usually characterized by low contents of the elements, similarly to the sediments of the Kanał Główny Canal and ditches draining the Szczakowa sand mine area.

SURFACE WATER

The waters of individual watercourses differ in their chemical composition and concentrations of characteristic elements.

Estimation of the water pollution degree in the map area was carried out according to the surface water quality guidelines in Poland (Rozporządzenie,...1991) and taking into consideration only those elements whose concentrations exceed the limits for class I (very good quality water). Phosphorus was omitted due to insufficient detection limit of applied analytical method. Only water of the Kanał Główny Canal, draining working pits of the Szczakowa sand mine, falls within class I of water purity (for all the tested elements). The other watercourses are more or less contaminated.

Zinc is the element that contaminates the waters of the sheet area most. Due to the presence of zinc the waters have been classified as substandard: 100% of the Baba Stream water, 94.9% of the Biała Przemsza River water, 92.5% of the Sztoła River water, 90% of the Dąbrówka Stream water, 84.8% of the Kanał Sztolnia Canal water and 60.6% of the Biała Stream. Waters of small reservoirs of stagnant water, unnamed streams and the water of the Sztolnia Ponikowska Stream are less polluted by zinc.

Another element which heavily pollutes water is lead. Due to lead contamination, the waters of Dąbrówka Stream (90%), Biała Przemsza River (89.7%) and Biała Stream (48.5%) are classified as substandard waters. Due to the contents of sulphates, 90% of the Dąbrówka Stream water and 75.8% of the Kanał Sztolnia Canal water are considered substandard. Contamination by sulphates is also observed in 51.6% of small reservoirs of stagnant water.

Kanał Sztolnia Canal. The Kanał Sztolnia Canal water is strongly contaminated by metals. The zinc concentration is up to 9 294 µg/dm^3; median 5840 µg/dm^3, and the cadmium up to 135 µg/dm^3; median 65 µg/dm^3. It is also rich in calcium (up to 231 mg/dm^3; median 214 mg/dm^3), magnesium (up to 114.2 mg/dm^3; median 103 mg/dm^3), sulphates (up to 890 mg/dm^3; median 805 mg/dm^3) and lithium (up to 19 µg/dm^3; median 18 µg/dm^3). The lead concentration is relatively low (up to 34 µg/dm^3; median 1 µg/dm^3).

Kanał Dąbrówka Canal and Biała Stream. The characteristic elements in the streams water are barium, iron and lead. In the Dąbrówka Stream water the concentration of barium reaches 211 µg/dm^3 (median 203 µg/dm^3), iron 1.41 mg/dm^3 (median 1.27 mg/dm^3) and lead 141 µg/dm^3 (median 103 µg/dm^3). In the Biała Stream water, the values are as follows: 219 µg/dm^3 (median 177 µg/dm^3) of barium, 1.77 mg/dm^3 (median 0.70 mg/dm^3) of iron and 118 µg/dm^3 (median 50 µg/dm^3) of lead. Lead is also abundant in the water of Sztoła River – up to 50 µg/dm^3 (median 34 µg/dm^3) and in the Biała Przemsza River – up to 118 µg/dm^3 (median 78 µg/dm^3).

CONCLUSIONS

1. The contents of the analysed chemical elements indicates significant contamination of the topsoil (0.0–0.2 m), subsoil (0.8–1.0 m), aqueous sediments and surface water. Heavy metals (especially cadmium, lead and zinc) are concentrated mainly in the topsoil. At the depth of 0.8–1.0 m, a reduction in the area of anomalies and a simultaneous increase in their intensity is observed.

2. The results show an excellent correlation between topsoil and subsoil geochemistry (as well as between soil geochemistry and chemical composition of underlying parent rocks).

3. The natural (geological) sources of pollution are Triassic outcrops of Zn–Pb ore-bearing deposits.

4. The anthropogenic sources of environmental pollution are extraction, processing and smelting of Zn–Pb ores, and especially the impact of mining waste dumps, leachates from post-flotation tailings ponds and saline mine water discharges to surface water.

5. In the coming years, it is expected that the exploitation and processing of Zn–Pb ore will be finished, which will cause reduction in environmental pollution. However, tailings ponds will still be a hazard. The planned attempt to restore natural water conditions after the liquidation of Zn–Pb ore mines may cause local flooding and subsidence troughs above mining excavations.

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