# INTRODUCTION

Geochemical mapping of Poland carried out in 1990–1995 proved that the Silesian-Cracow region is among the country's most polluted areas (Lis, Pasieczna, 1995a). Long-lasting exploitation of mineral deposits in this region and increasing demand on them resulted in an influx of a large number of people and urban development, which gave rise to the growth of the Upper Silesian agglomeration – the largest and most densely populated in Poland.

The level of pollution in the region (particularly by heavy metals and other toxic elements and compounds), which is hazardous to fauna, flora and human health, is similar to that of other European regions where prolonged exploitation and processing of non-ferrous metal ores occurred: e.g. Plovdiv region, Bulgaria, (Atanassov, Angelova, 1995; Velitchkova *et al.*, 2003), Příbram in the Czech Republic (Rieuwerts, Farago, 1996), Smolnik region in Slovakia (Cicmanova, 1996), Plombiers – La Calamine region in Belgium (Swennen *et al.*, 1994, Cappuyns *et al.*, 2005), Derbyshire in central England (Cotter-Howells, Thornton 1991; Thornton, 1994), Harz in Germany (Gäbler, Schneider, 2000) and the German/Czech borderland (de Vos *et al.*, 2005).

The geochemical studies conducted in the Silesia-Cracow region (Lis, Pasieczna, 1995b, 1997, 1999) enabled the characteristics of the extent and intensity of the strongest geochemical anomalies of cadmium, lead and zinc, stretching from the Chrzanów and Olkusz in the east to Bytom and Tarnowskie Góry in the west. Detailed geochemical mapping 1:25 000 scale started in this area in 1996. It provides information useful for environmental management and making decisions by local authorities.

Geochemical mapping carried out in the Jaworzno Map Sheet M-34-63-B-c area at the scale 1:25 000 is a continuation of detailed cartographic survey ordered by the Ministry of the Environment and financed by the National Fund for Environmental Protection and Water Management.

The sheet is located in the Upper Silesia/Małopolska borderland regions, in the eastern part of the Silesian Voivodeship. The western part of the map area is occupied by the Jaworzno city where Zn–Pb ore mining activity dates back to the beginning of the 13th century. Hard coal has been mined in this region since the 18th century.

Intensification of coal mining took place in the first half of the 19th century and just after World War II. As a result of the coal mining industry restructuring in recent years, the Jaworzno and Jan Kanty coal mines were closed.

The north-western part of the map area is an industrial region (mining, power supply, glass and chemical industries) and is anthropogenically modified (Preidl *et al.*, 1995). The central and north-eastern parts of the sheet are mostly covered by forests.

The study area includes protected landscape areas of Dobra-Wilkoszyn and the Sasanki nature reserves which were established to the west of Ciężkowice. Original landscape landforms in areas of opencast mining of rock raw materials (in the Szczakowa and

Ciężkowice regions) have undergone substantial transformation, becoming habitats of specific and valuable flora.

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

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

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## CHARACTERISTICS OF THE MAP AREA

**Geographical and administrative setting**. Most of the map sheet is covered with the Jaworzno city area (situated in the Silesian Voivodeship). Small areas in the north-east (Bukowno commune) and south-east (Chrzanów commune) are included in the Małopolska Voivodeship.

According to the physiogeographic subdivision of Poland (Kondracki, 2000), the map sheet area is situated within the Pagóry Jaworznickie hills located within the Silesian Upland.

**Relief and geomorphology.** The Pagóry Jaworznickie hills are a belt of tectonic horsts composed of Triassic carbonate deposits (Plate 1). Two parallel NW–SE trending belts of hills attaining an elevation of 300–340 m above the sea level occur in the map sheet area. The south-western belt extends from the springs of the Byczynka Stream in the south, through the eastern districts of Jaworzno city, Galmany and Warpie to Góra Piaskowa mountain in the north. The north-eastern belt stretches from Ciężkowice in the south to the Kozi Bród Stream valley in the north. Between these hilly belts there is a Pleistocene denudation plain (Wilkoszyn Basin) filled with alluvial fan sediments. The basin is dissected by the Łużnik Stream (Preidl *et al.*, 1995). Along the western border of the plain, in the Łużnik Stream valley, there is an arched belt of sand dunes (reaching 10 m in height).

The north-eastern part of the map area is the Biskupi Bór erosion basin, which is the southern part of the Przemsza River erosion basin, (Program..., 2003). Its monotonous relief is diversified only with minor dunes attaining heights of 2–4 m and with deeply incised valleys of the Kozi Bród and Żabnik streams. The Biskupi Bór basin surface gently descends to the north, towards the Biała Przemsza River valley. Most of this area is covered by forest.

The centre of Jaworzno city and its suburbs (Cezarówka Dolna, Cezarówka Górna and Koźmin) are located within the Wilkoszyn Basin. The Jaworzno city developed by successive incorporating villages into its area, currently forming individual districts. Both the city centre and surrounding residential areas are partially urban-industrial or rural in character. The former villages have preserved their distinctiveness and variable degree of settlement dispersion. Individual parts of the built-up area are connected by a network of railways, roads, electrical supply lines, and pipelines.

Anthropogenic transformations of the natural environment are caused by long-lasting exploitation of mineral deposits: Zn–Pb ores, hard coal, carbonate rocks and sand. Until the mid-20th century, a Zn–Pb ore mine operated in the Galmany district of Jaworzno.

A huge open pit has been formed near Szczakowa as a result of filling sand extraction, which began in 1954. Until 2005, more than 650 million $m^3$ of sand were excavated. The depth of the pit down to the first exploitation level is 6–14 m, and its area is about 27 $km^2$. Most of the mine area is located on the adjacent north-east map sheets.

Among large concave anthropogenic landforms, the most characteristic are dolomite quarries in the Sodowa Góra hill (west of Dobra), and between Pieczyska and the Łużnik Stream valley. Many former small quarries are located in the hills composed of Triassic carbonates.

A specific element of the Jaworzno sheet landscape are tailings of galena-calamine mining activity, originating from the periods of manual opencast mining of Zn–Pb ores. Traces of the historical mining are marked in the form of both irregular depressions, up to several metres deep, and stockpiles.

Waste heaps of different origin, produced by the mining (Jaworzno), smelting (Szczakowa) and power supply industry (Stara Huta), are located in the map area.

Discontinuous deformations (attaining 5–10 m), caused by land subsidence due to coal mining, are observed in a large part of the Jaworzno city.

The whole map area belongs to the Vistula River catchment and is drained mainly by the Biała Przemsza River and its tributaries (Kozi Bród Stream, Kanał Główny Canal and Łużnik Stream). The Kanał Główny Canal and Kozi Bród Stream partially flow in engineered stone-walled or concrete-walled channels. The Łużnik Stream flows mostly in the natural riverbed. The Kanał Główny Canal and its dense system of drainage ditches drain the Szczakowa sand mine in the northern part of the map area. Springs of the Byczynka and Wąwolnica streams (tributaries of the Przemsza River) are located in the southern part of the map sheet.

Shallow sitting of impermeable deposits in the Łużnik Stream and Kozi Bród Stream catchments results in strong flooding of the central and north-eastern parts of the sheet area.

To the east of Szczakowa there is an artificial reservoir Sosina Lake that occupies an area of 43.8 ha and is 3 m deep. It was create in a former open pit sand mine and is currently used for recreational purposes.

**Land use.** The western and north-western part of the map (about 25%) is occupied by urban and industrial areas of Jaworzno and Szczakowa (Plate 2).

Barren land and woodland dominate in the land use, occupying 40% and 38% of the map sheet, respectively. Forests cover the central and north-eastern part of the area, and barren land occurs mainly in its western part (Plate 3). Farmland disseminated in various parts of the map sheet covers about 6%.

**Economy.** Many plants operated in Jaworzno city over the past one hundred years. The basic traditional industries for the regional economy are the mining, power supply, mineral and chemical industries.

At present the largest companies operating in the study area are as follows: ZG Sobieski hard coal mine (Zakład..., 2005), Jaworzno III power plant, Organika-Azot chemical plant, Szczakowa tannery, Szczakowa sand mine and PKP Cargo railway freight company in Szczakowa. The KWK Jan Kanty coal mine and the Szczakowa cement plant were closed in recent years. The Huta Szkła Szczakowa glassworks is in bankruptcy now. The Szczakowa dolomite plant is currently also in liquidation.

The beginning of the Jaworzno power supply industry is related to building small power plants operating since the late 19th century. Presently, the most important role is played by the Jaworzno III power plant. Due to ecological investments introduced in this plant (producing gypsum, which is a by-product of the technological process of combustion gas desulphurisation), the Knauf Jaworzno III and the ORTH-Gipse companies producing gypsum plasters and plates have been built in the area of Jaworzno III power plant.

The Organika-Azot chemical plant, founded in 1917, is one of the oldest chemical companies in Poland. It is a producer of plant protection products (herbicides, fungicides, insecticides and seed dressings). Initially, the plant produced nitric acid, potassium cyanide, potassium chloride, reeds and, and since the mid-1930s, copper sulphate, trichlorethylene, calcium cyanide and ferrocyanide (Proksa, 2008). After World War II, plant protection products (mainly DDT) were produced by the factory.

The Szczakowa cement plant, located in the Pieczyska, was founded in 1883 (Kłodzińska, 2005). It became one of the largest and most modern plants in Europe with the largest *rotary* cement *kiln* opened in 1930. After World War II, the cement plant activity gradually declined and it was finally closed in the 1970s. Obsolete equipment and technologies as well as high production costs caused the abandonment of its primary production and the eventual closure of the company at the end of the 20th century

The Szczakowa tannery has operated since 1919, producing shoe leather, clothing leather and glue.

The Huta Szkła Szczakowa glassworks, established in 1911, has produced different kind of glass (Proksa, 2008).

North of Jaworzno city centre (in the Niedzielska district), a zinc white factory operated in 1865–1976. It was closed because of obsolete technical equipment and its harmul impact on environment.

In addition to industrial production, the study area is also a region of intensely developing service activities conducted by firms involved in wholesale trade, retail and door-to-door service, as well as repair, transport, retail brokerage and catering services (Program…, 2003).

## GEOLOGY AND MINERAL DEPOSITS

Separate structurally complex tectonic blocks are clearly marked in the geology of the sheet area: the fold-horst structure of the Wilkoszyn Basin (in the central part of the map sheet), the Jaworzno block (in the west) and the northern part of the Cezarówka horst in the south (Plate 1). Rocks that compose these structures represent three structural stages: the early Palaeozoic (Carboniferous), Mesozoic (including complete Triassic profile) and Cenozoic (Kurek *et al.*, 1994, 1999).

**Carboniferous** rocks of the map area are known from numerous boreholes and mine workings. The Carboniferous strata dips towards the south west at small angle (10–15$^{o}$), forming anticlinal structures cut by faults. At the surface, only Upper Carboniferous deposits represented by the Westphalian Orzesze and Łaziska beds outcrop near Jaworzno. The Orzesze Beds (not exceeding 100 m in thickness) are composed of pelitic rocks: claystones and siltstones with siderites and hard coal seams (group 300). The Łaziska Beds (exceeding 350 m in thickness) are dominated by coarse-grained sandstones containing few coal seams (group 200).

The **Triassic** profile was examined in both boreholes and numerous exposures. The Lower Triassic (Buntsandstein) is composed of coarse-grained oligomictic continental sediments: gravels, conglomerates, sands and sandstones, less than 30 m thick, and 30-m thick Rhoetian marine deposits: dolomites, dolomitic marls and marly limestones. The Lower Triassic deposits are exposed at the surface near the Pagóry Jaworznickie hills (from the spring area of the Byczynka Stream in the south to Długoszyn in the north) and near Ciężkowice.

The Middle Triassic (Muschelkalk) attaining a thickness of 140 m is represented by marine carbonates that form extensive outcrops in the central and south-western part of the map sheet. The lower part of the section is built by limestones and marls of the Gogolin Beds overlain by a series of epigenetic Zn–Pb ore-bearing dolomites. This series includes the carbonate Górażdże Beds, Terebratula Beds and Karchowice Beds, and locally probably the top of the Gogolin Beds. The upper part of the Middle Triassic section consists of diplopora dolomites and dolomites, marls and shales of the Tarnowice Beds and Boruszowice Beds.

Upper Triassic deposits represented by claystone and siltstone facies with limestone interbeds are known only from boreholes.

The Neogene is represented by freshwater and brackish clays, silts, sands and gravels, not exceeding 10 m in thickness, outcropping locally in the area of Ciężkowice.

**Quaternary** sediments show a wide variety of lithological and genetic types. The oldest Pleistocene deposits of the South-Polish Glaciations are glaciofluvial clays and gravels. The younger glacial periods are represented by glaciofluvial sands and gravels, sands of the ancient Przemsza River valley and alluvial fans deposits, covering the central and north-eastern part of the map area. Thickness of the Pleistocene deposits ranges from several to 50 m. Aeolian sands, which form distinct natural draught of parabolic dunes, are quite numerous throughout the entire area. Holocene sediments (sands, muds, gravels and peats) cover the river valleys.

**Mineral deposits.** The first deep hard coal mine called Fryderyk August, later renamed to Piłsudski and Bierut, was founded in 1795. Other state and private mines were established in the following years (Ziemia.., 1969). Extraction was carried out in the Śródmieście, Szczakowa, Dąbrowa, Narodowa, Długoszyn and Byczyna districts of Jaworzno (Proksa, 2008). At first, the main technical problem was mine drainage. Due to large water inflow into the mines, the maximum production depth was only 80 m. Coal mining in this area was gradually developed; mine production and transport were mechanized and hydraulic filling was introduced. The Fryderyk August (Piłsudski-Bierut), Jacek Rudolf (Kościuszko-Sobieski) and Jan Kanty (Komuna Paryska) coal mines operated for the longest time.

The only mine presently active is the ZG Sobieski coal mine (Pawłaszek, Jarosz, 2001) separated from the already closed KWK Jaworzno coal mine. Much of the ZG Sobieski mining area is located in the south-western part of the map sheet. In 2005, it joined the structure of the Południowy Koncern Węglowy coal company (Południowy..., 2005). Its mining area is 56.6 $km^2$, and the resources are large enough to extract coal for the next several decades. The annual production capacity of the mine reaches 2.7 million tonnes of commercial coal. Mining operations are conducted at the levels of 207, 209 and 302 in the Piłsudski and Sobieski mining areas a few kilometres apart. They are connected by transport and ventilation systems. In the future, extraction will be carried out at the additional levels of 208, 214, 301 and 304/2.

The ZG Sobieski mine is among the mines affected by the largest mine water inflow into excavations in Europe, which is up to 50 $m^3$/min. Excess water that is not used for technological purposes, is discharged through a settling pond to the Przemsza River. The coal mine extracts the Łaziska and Orzesze beds (coal seam groups 200 and 300). The coal seams show considerable thickness variations, ranging from 0.6 to 3 m. These are medium-calorie coals (23 000 kJ/kg), containing 7% of ash and up to 2.5% of sulphur. They are subject to mechanical processing and then a fraction <30 mm is directed to the modern division of coal enrichment. Tailings are dumped in underground excavations. It is expected that an installation for deep injection of saline mine waters will be constructed soon (Południowy... 2005).

In the western part of the map sheet, there is part of a mining area of the closed KWK Jan Kanty coal mine, in which mining was abandoned for economic reasons.

**Zinc and lead ores.** Zn–Pb ore mining has a long tradition in the Długoszyn, Jaworzno and Ciężkowice area. At the beginning (in the 13th century), Zn–Pb ore mining took place in opencast mines and the extraction depth was constrained by the depth of water table (Molenda, 1960). By the end of the 18th century, mining was focused on galena. The ore was mined from shallow ore bodies and seams, which occur in areas of tectonic horsts and Triassic outcrops. The ore was extracted in open-cast mines, processing on-site and then smelted for lead and silver.

In the early 19th century, zinc ore mining became the dominant. At first, oxidized ore was mined (calamines), and later also sulphide ore containing Zn–Pb–Fe mineral paragenesis accompanied by Ag, Cd, Tl and As (Górecka, 1996; Szuwarzyński, 1996) was extracted. Already in the 13th century, a drainage adit was constructed in Długoszyn. From the 13th to 16th century, the Mistrze, Sobota and Wielkanoc mines operated in this area. New calamine mines were established in the early 19th century in Długoszyn, Byczyna, Jaworzno and Ciężkowice. Mining was very intense, as evidenced by the fact that the mines had 18, 7 and 7 shafts, respectively (Cabała, Sutkowska, 2006).

In 1922–1958, oxidized ore was mined mainly in the Galmany mine in Jaworzno. After World War II, the mine was used for training miners in Zn–Pb ore extraction and it was finally closed in 1974 (including filling the shaft.)

In the south-eastern part of the map area, there is a small part of a mining area of a large Zn–Pb ore mine – Zakłady Górnicze Trzebionka, active from 1962 to 2009. Currently, the mine is in liquidation due to depletion of resources, and the excavations are being flooded.

**Raw rock materials** of economic significance include Triassic dolomites and limestones and Quaternary sands. Three Triassic **dolomite** deposits (Gródek, Jaworzno-Ciężkowice and Byczyna) have been proven, intended for the metallurgy and road construction industries. The Gródek deposit was exploited until the end of the last century, while the others are still undeveloped.

In the north of Jaworzno city, there is the closed Sodowa Góra quarry of the Gogolin Beds **limestones** (Middle Triassic). Nearby, another deposit Sodowa Góra II has been proven, intended for the cement industry.

In the north-eastern part of the map sheet, there are parts of proven Quaternary **sand** deposits of Szczakowa – Field I and II. Medium- and fine-grained sands are mined from these deposits and used as construction and filling material. Post-mining excavations are gradually reclaimed. In the central area of the map sheet, the Ciężkowice aeolian sand deposit was preliminarily identified for the needs of the construction industry.

In addition to these proven reserves, there are many places of periodical mining of sands, limestones and dolomites for local use.

## HUMAN IMPACT

The Jaworzno Sheet is an area of well-developed past and present coal mining and power supply activities. Industry and the accompanying infrastructure (railways, power transmission lines, landfills and industrial buildings) caused significant degradation of the natural environment (Plan..., 2003; Preidl et al. 1995).

**Atmospheric air.** The air quality is affected mainly by emissions of dusts and gases from industrial plants, landfills, local heating stations and heating of individual houses. Additional air pollution originates from fuel combustion. It results in contamination along transportation routes due to emission of hydrocarbons, nitrogen dioxide, carbon monoxide and lead compounds.

Much of air pollution originates from the Jaworzno–Szczakowa industrial area (flue dust, sulphur dioxide, nitrogen oxides and heavy metals). The Jaworzno power plant is the major emitter of pollutants that produces more than five thousand tonnes of dust and nine thousand tonnes of gases a year. Gas emissions of the power industry contain significant amounts of carbon monoxide, sulphur and nitrogen oxides (Program..., 2003). Permissible concentration levels of sulphur dioxide are exceeded within the whole map sheet area.

The atmospheric air pollutants originate from fly ash and slag landfills of the Jaworzno power plant and waste dump of outdated pesticides produced by the Organika-Azot chemical plant. A separate group of pollution is emission from wastewater and municipal sewage treatment plants.

Point sources of air pollution are represented mainly by furnaces of individual houses, emitting dust whose concentration in the heating periods often exceeds acceptable levels.

An additional volume of air pollution (20% of dust and 30% of gaseous pollutants) is brought to the Jaworzno region by westerly winds from the Upper Silesian Industrial Region (Plan.., 2003).

**Surface water and groundwater.** Pollution of surface water and groundwater is caused by discharge of industrial sewage and waste dumps, most of which are inadequately secured. Significant impact on the quality of surface water is also exerted by discharge of municipal sewage. All monitoring points distributed across the map sheet show the presence of substandard water (Program…, 2003).

The highest level of surface water pollution is related to the drainage of the ZG Sobieski coal mine, discharging water enriched in chlorides, sulphates and heavy metals, in the amount of about 70 thousand $m^3$/day.

Drainage works in the Trzebionka Zn-Pb ore mine has recently caused the necessity of pumping out about 34 $m^3$/min of good quality water. As a result, a large cone of depression has developed. Mine water has been used by local population in nearby towns, settlements and industrial plants, including the mine's ore-processing plant.

Discharge of municipal sewage causes oxygen deficit in surface waters, bacteriological contamination and increasing contents of biogenic volatile organic compounds (Program..., 2003). Sewage from Jaworzno flows to a mechanical-biological treatment plant located in the Jeleń-Dąb district (beyond the southern boundary of the map sheet), then it is discharged into the Przemsza River (Oczyszczalnia..., 2008). Discharge of the treated sewage to the Przemsza River (downstream of the Jeleń Stream water-gauge) reduces the amount of oxygen in its water and increases the contents of manganese, ammonia, total suspended solids, iron, phosphates and sulphates.

The Kozi Bród Stream water has been found substandard based on physicochemical determinations and pollution by lead and zinc (Program..., 2003).

Two major groundwater basins were identified in the map area. They are vulnerable to pollution caused by air contamination and leachates from industrial and municipal waste dumps (Kleczkowski, 1990). In the north-east, there is the Biskupi Bór Quaternary groundwater basin representing an ancient valley basin. The basin is exposed and vulnerable to pollution so its water requires purification. The hazard is posed by large open-pit sand mines and discharges of polluted water into the river system. The remaining part of the area is occupied by the Chrzanów Triassic a fissure-karst groundwater basin characterised by low resistance to contamination.

**Soils.** Chemical degradation of soils is caused by industrial activity, transport, waste disposal and improper farming. Anthropogenic pollution reduces the amount of humus in the soil, changes acidity and decreases soil fertility. Fallout of atmospheric dust and processes of chemical degradation due to improper waste and sewage management play an important role in soils contamination. According to ecological valorisation of agricultural land (Program..., 2003), it is necessary to apply selective cultivation and appropriate agricultural practices because of local concentrations of heavy metals and high contents of sulphur in the air.

Due to the impact of historical mining and processing of Zn-Pb ores and high values of the geochemical background of these metals in the soils developed on Triassic carbonates, soils of the Jaworzno region contain high amounts of metals: up to 5500 mg/kg of zinc, up to 2200 mg/kg of lead and up to 35 mg/kg of cadmium (Lis, Pasieczna, 1997).

Mechanical transformation of soils is caused by the land development, surface hardening, baring of the soil cover or mixing it with extraneous elements (crushed brick, scrap) and by the foundation trenches, embankments and surface levelling. The specific form of soil degradation is disturbance of hydrogeological conditions in mining areas. In river valleys the source of soil contamination are floods.

## MATERIALS AND METHODS

The 2005–2008 researches included studying published and archival materials, selecting sampling sites in topographic maps at the scale of 1:10 000, collecting samples, coordinate surveying at sampling sites, chemical analyses of samples, setting up field and laboratory databases, preparing a vector topographic map, statistical calculations, constructing geochemical maps and a geological map, and finally interpretation of results. The sequence of activities is shown in Figure 1.

## FIELD WORKS

Soil samples were collected at a regular grid of 250x250 m (16 samples per 1 $km^2$). The total number of soil sampling sites was 1289. At every site, two samples were collected from two depths: 0.0–0.3 (topsoil) and 0.8–1.0 m (subsoil). If the parent rock was found shallower in the soil profile the subsoil sample was collected at a smaller depth. Soil samples (ca. 500 g) were collected using a 60-mm hand probe, put in linen bags labelled with numbers, and pre-dried on wooden pallets at a field storage site.

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

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

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

## LABORATORY WORKS

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

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

All the archive samples are stored 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$^{o}$C in the aluminium heating block thermostat.

Contents of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in the soil and aqueous sediment samples were determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES) method. Mercury content was measured using a cold vapour atomic absorption spectrometry (CV-AAS) method. Soil pH was measured by water extractions using a pH-meter. Organic carbon content was measured using a coulometric method. Determination of Al, B, Ca, Fe, K, Li, Mg, Na, P, $SiO_2$, Ti and Zn in surface water was performed by an ICP-AES method. Contents of Ag, As, Ba, Cd, Cl, Co, Cr, Cu, Mn, Mo, Ni, Pb, Rb, Sb, $SO_4$, Sr, Tl and U were analysed using an inductively coupled plasma atomic mass spectrometry (ICP-MS) method. The applied analytical methods and the detection limits of measured elements are shown in Table 1.

Quality control was performed through analysis of duplicate samples (about 5% of all samples), analysis of reference materials with certified content of elements studied (2% of all samples) and analysis of laboratory control samples confirming correct instrument calibration (5% of all samples). ’Reagent blank samples’ and ’preparation blank samples’ were used. Purity of reagents and vessels was controlled with ’reagent blank samples’. ’Blank samples’ (*sea sand extra pure Merck*) were used to monitor for possible contamination introduced during the sample preparation procedure.

For the solid samples, analytical precision is ±10–15%. For the surface water samples, analytical precision is about ±10–20% (depending on the element’s concentration).

**Grain size analyses** of topsoils (0.0–0.3 m) samples were carried out in the Hydrogeology and Engineering Geology Laboratory of the Polish Geological Institute-National Research Institute in Warsaw, using a laser particle size analyzer. Direct use of laser method results does not allow soil classification according to pedological criteria. However, the data are very useful for interpretation of geochemical analyses.

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

## DATABASES AND GEOCHEMICAL 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 the 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 (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**. Separate databases were prepared for: topsoil (0.0–0.3 m), subsoil (0.8–1.0 m), aqueous sediments and surface water.

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

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

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

**Maps construction.** The following maps were produced for the Jaworzno Sheet (Plates 2–63): land development, land use, contents of organic carbon and grain size of topsoil (sand, silt and clay fractions ); acidity of topsoil and subsoil; contents of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in topsoil, subsoil and in aqueous sediments; acidity, specific electrical conductivity and contents of Ag, Al, As, B, Ba, Ca, Cd, Cl, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, $SiO_2$, $SO_4$, Sr, Ti, Tl, U and Zn in surface water; topsoil classification indicating appropriate soil use.

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

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

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

The geochemical maps of soils were constructed using the analytical dataset created for the Jaworzno Sheet and the datasets of 1:25 000 scale neighbouring sheets. Thus any disagreements at the sheet borders were avoided. After interpolation the Jaworzno 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 Jaworzno Sheet area only. They were constructed as dot maps with the circle diameters corresponding to individual classes, most often according to geometric progression.

While constructing the map of soil classification (Plate 63), indicating appropriate soil use, the results of geochemical analyses were referred to the permissible levels of metals, defined 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 the case of equal permissible limit values for classes A and B (for arsenic, barium and cobalt), the soil was categorized into class A, which is more advantageous to the user and enables multifunctional land use.

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

## RESULTS

## SOILS

The analysed soils were formed by natural processes and modified by anthropogenic processes of industrialization and urbanization. The processes of the soil degradation, occurring primarily in the areas of new housing development, transportation routes, industrial facilities and landfills, are manifested by changes in the soil profile and physicochemical properties.

Accumulation of chemical elements in the soils occurred as a result of geological (outcrops of rock formations, geochemical barriers) and anthropogenic (mining water and sewage discharge, eluates from post-mining waste dump sites and settling ponds, coal combustion) factors. The most common soil types are*Rendzinas* developed on carbonate rocks. *Podzols* and *Cambisols* developed on tills and sands (Program ..., 2003). In forested areas located mainly in large depressions, *Podzols* developed on glaciofluvial sands. River valleys are the areas of common boggy and muddy soils. River valleys are covered with alluvial soils (*Fluvisols*) while topographic lows (near Szczakowa) are occupied by *Gleysols*.

**Grain size.** Almost all chemical and physical properties of soils result either directly or indirectly from their mechanical composition. By determining the grain size of soil particles, we can infer about the soil origin and its vulnerability to contamination. This is one of the most important parameters controlling migration ability of elements within the soil profile. Grain size composition of soil is one of the factors determining content of chemical elements. Soils rich in the clay fraction (<0.02 mm) and silt fraction (0.1–0.02 mm) are commonly characterized by the biggest content of many elements and their low migration ability under hypergenic conditions. The standards and recommendations on permissible limits of elements in soils commonly take account of this soil property, allowing higher limiting concentrations for clay fraction-rich soils and lower limiting concentrations for sand fraction-rich soils (Kabata-Pendias *et al.*, 1995).

Grain size variability of the soils in the Jaworzno Map Sheet is clearly dependent on the parent rock lithology. The most frequent (67%) are sandy soils, that developed on glaciofluvial sands and gravels and aeolian sands). Much of them contain over 75% of the 1.0–0.1 mm fraction (over 90% in the north-east). These soils are characterised by a small proportion of the silt fraction (<5%) and clay fraction (<5%). Soils that developed on Triassic carbonates are greatly enriched in the silt fraction (0.1–0.02 mm) and clay fraction (<0.02 mm). The proportion of the silt fraction in these soils commonly varies between 10 and 30%, and the proportion of the clay fraction ranges from 5 to 10%.

**Acidity.** The topsoils are mainly neutral (42%) and alkaline (41%), which is related to their development from Triassic carbonates and large proportion of anthropogenic grounds. Neutral soils (pH 6.3–7.4) occur in the north-eastern and southern parts of the map area. The north-western part is covered by alkaline soils. The highest pH (> 8) was measured in soils of the Szczakowa industrial area (in the vicinity of the former cement works, glass works and dolomite quarry). Such a high acidity is associated with a scattering of dust and waste during long standing mining of carbonate rocks. The largest area of acidic soils (pH <6.3), developed on Quaternary sands, occurs in forests and meadows of the southern part of the Łużnik Stream catchment and near barren rock piles of the Jaworzno coal mine, located between the Bory and Stara Huta.

At the depth 0.8–1.0 m areas of neutral and alkaline soils occur in a hilly terrain composed of Triassic carbonates and in the vicinity of industrial objects in Szczakowa. Acidic soils were noted only in a small part of the Łużnik Stream catchment.

In urban and industrial districts, soil alkalinisation can be related to both the Triassic carbonates in the bedrock and the dispersion of industrial dust rich in calcium and magnesium compounds. More important is the chemical composition of parent rocks, as evidenced by the large area occupied by alkaline soils at a depth of 0.8–1.0 m (62%).

Comparison of the average acidity values of the topsoil in areas of different land use (Table 2) shows a clear relation of soil alkalinisation to the fallout of dust from fuel combustion and industrial processes. In non-built-up areas, the median pH value is 7.0 and it increases to 7.6–7.7 in urban and industrial areas.

**Geochemistry.** Depending on the physicochemical conditions of the environment, soil-formation processes have led to diversified intensity changes in the chemical composition of soils in relation to the parent rocks, but the most basic geochemical features of the original rock are easily decipherable.

Analysis of the chemical composition of soils show a clear relationship between the spatial distribution of several elements (aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, strontium, titanium and vanadium) and the geological structure of the bedrock. Soils that developed on the outcrops of Triassic carbonates are characterized by elevated contents of these elements. The soils enriched in these elements extend in the south from Koźmin and Cezarówka through the Jaworzno-Śródmieście district to Długoszyn, and in the North from Ciężkowice through Pieczyska to Szczakowa and Długoszyn.

The lowest contents of aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, strontium, titanium and vanadium were noted in soils developed on Pleistocene sands of alluvial fans covering the Łużnik Stream drainage basin and in the north-eastern part of the map area. The observation refers to both the topsoil and subsoil. Low contents of the elements are associated with a poor chemical composition of sandy parent rocks and their acidity, which favours the leaching of many elements.

The topsoils are enriched in some elements (barium, calcium, chromium and strontium), which is related to anthropogenic factors. The content of barium in subsoil rarely exceeds 120 mg/kg. In the topsoil, vast areas exceeding this value occur in the industrial districts of Jaworzno (near a tailings pile of the KWK Jaworzno coal mine as well as around Galmany, Warpie and Szczakowa). The anthropogenic source of barium is probably the tailings pile of

Carboniferous rocks and wastes after historical mining of Zn–Pb ores in the Galmany, Warpie and Piaskowa Góra.

In the vicinity of a dolomite quarry located between Pieczyska and Dobra geological-anthropogenic anomalies of calcium with the maximum of 15.20%, and of strontium with the maximum of 380 mg/kg were revealed in the topsoils. Considerably stronger intensity and extent of these anomalies observed at a depth of 0.0–0.3 m is related to long lasting extraction and dissipation of dolomite waste and dust from a former cement plant. The increase of calcium (and magnesium) content in the soils is favourable for the environment because these elements enhance the alkalinity and favour heavy metals immobilization.

The source of the alluvial topsoils enrichment in chromium at Długoszyn in the Kozi Bród Stream valley is discharge of sewage from the Szczakowa tannery.

Anomalies of cadmium, zinc, lead and arsenic observed in the southern and western parts of the map area are associated with Zn–Pb ore mining. In the topsoil near the area Galmany–Warpie–Sodowa Góra–Długoszyn, in the eastern part of Ciężkowice and Jeziorki, the concentrations of cadmium, lead and zinc were; >8 mg/kg, >250 mg/kg and >1000 mg/kg, respectively. Strong anomalies of cadmium and lead were also recorded in the area located to the north of the Bory district of Jaworzno. Cadmium, lead and zinc are concentrated mainly in topsoil. There is a reduction in the area of these anomalies at a depth of 0.8–1.0 m (Table 6) and a simultaneous increase in their intensity. The maximum concentrations of cadmium, lead, arsenic and zinc in subsoils are 197 mg/kg, 22 000 mg/kg, 319 mg/kg and 43 100 mg/kg, respectively. Contamination of soils by silver, arsenic, mercury, copper and sulphur is related to anthropogenic factors.

The source of point silver anomaly (with the maximum of 28 mg/kg) in forest soil to the north of Ciężkowice is probably an illegal waste dump.

An arsenic anomaly (up to 1260 mg/kg) observed in the alluvial topsoils in Szczakowa is caused by the presence of arsenic compounds in wastewater discharges from the tannery. The anomaly area is small (about 1 $km^2$), but should be of concern to local authorities due to toxic properties of arsenic, causing various diseases (Charlet, Polya, 2006; Hopenhayn, 2006; Seńczuk, 2002).

High copper concentrations were observed in the topsoil near the Jaworzno-Szczakowa railway station, around a waste dump in a former dolomite quarry south of Pieczyska, and near a mining waste dump of the KWK Jaworzno coal mine. The most significant anomaly (up to 530 mg/kg of copper) was recorded in Upadowa Street area in Chropaczówka. The subsoil in the KWK Jaworzno coal mine contains 1160 mg/kg of copper (near a transport base and railways at Rzemieślnicza Street). It is possible that this element originates from leachates of mining waste dumps and storage of scrap metal and cables.

A strong mercury anomaly (with the maximum of 9.96 mg/kg) occurs in the topsoil around the Organika-Azot chemical plant. The pollution continues down to a depth of 0.8–1.0 m, reaching the maximum of 0.80 mg/kg of mercury. The source of the pollution are certainly the compounds of mercury used to produce plant protection chemicals. Worth noting is another mercury anomaly observed in the vicinity of waste piles of the Jaworzno coal mine, which is more intense (up to 17 mg/kg) at a depth of 0.8–1.0 m.

The sulphur content in soils of the map area rarely exceeds 0.16%. Its increased contents occur near waste piles of the Jaworzno coal mine and the Huta Szkła Szczakowa glasswork: up to 2.55% in topsoil and up to 2.03% in subsoil.

The organic carbon content (TOC) in topsoil is usually within the range of 0.70–3.00%. In meadow soils of the Kozi Bród and Łużnik catchments, the content of TOC is higher (3.00–12.00%) and locally reaches 24.00%. The maximum TOC content (45.9%) was recorded in anthropogenic soils with chips of coal near the waste pile of the KWK Jaworzno coal mine.

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 Jaworzno Sheet were classified applying current guideline values (Table 7) established by the Polish Ministry of the Environment (Rozporządzenie…,2002). The guideline values are based on the average of particular elements in soils for Poland as a whole and also on the assessment if the content of a particular element may have negative influence on the ecosystem or on human health. Guideline values are applied for three-level scale: A (protected areas), B (agricultural, forest and residential areas) and C (industrial areas). The total classification was calculated using the rule that the sample is classified to a particular soil use group if the content of at least one element exceeded the permissible limit value.

With respect to the concentrations of metals, 14.12% of the soils were included into group A, 30.26% of the samples were classified into group B and 55.62% of the soils into group C (Table 7). Soils classified into groups A and B meet requirements of multi-purpose use. Zinc, cadmium and lead are the main pollutants of the soils classified into group C which occur in the southern and western parts of the map sheet in areas of industrial facilities and outcrops of Triassic carbonates (Plate 63). The map shows the recommended land use according to the guidelines provided in Rozporządzenie... (2002). Much of the soils are currently improperly used and require monitoring or reclamation. Concentrations of metals in soils of some forest, agricultural, grassland and garden areas are so high that the land should be used for industrial purposes.

## AQUEOUS SEDIMENTS

Analysed sediments were collected from the Kozi Bród, Łużnik and Wąwolnica streams and their tributaries (mainly drainage ditches), the Kanał Główny Canal and the Sosina artificial reservoir.

**Kozi Bród Stream and its catchment**. Aluminium, arsenic, barium, calcium, cobalt, chromium, iron, manganese, nickel, phosphorus, titanium and vanadium contents show slight variations within the catchment. The median values of these elements are close to the median for the entire map area (Table 4). The median values of calcium, iron and magnesium are 0.78%, 1.21% and 0.23%, respectively.

Sediments of the watercourses in the area between Ciężkowice and Pieczyska (the Kozi Bród Stream tributaries) are polluted by arsenic (up to 80 mg/kg), cadmium (up to 98 mg/kg), lead (up to 1090 mg/kg) and zinc (up to 9700 mg/kg). The likely sources of these elements are related to wastes of historical opencast extraction and processing of Zn–Pb ores at Ciężkowice. Sediments of this part of the catchment are also enriched in cobalt, copper, manganese, nickel and vanadium. The phosphorus, sulphur, titanium and strontium contents in the sediments, draining Quaternary muds of the Kozi Bród Stream valley, are several times lower as compared to those of alluvial sediments of this stream.

Contamination of sediments in the lower section of the Kozi Bród Stream is caused mainly by discharge of sewage from industrial plants and drainage tailings piles of glassworks, dolomite plant, cement factory and tannery.

In the upstream section of the Kozi Bród Stream the silver content of the sediments does not exceed 1 mg/kg. In Szczakowa the sediments are enriched in silver (up to 21 mg/kg), which may be related to sewage discharges from the Vitroform metal processing plant (Plan..., 2003).

In the upper section of the Kozi Bród Stream sediments are contaminated by chromium from the Szczakowa tannery sewage discharge. The concentration of this element in some samples exceeds 1000 mg/kg, reaching the maximum of 2200 mg/kg.

Along the entire course of the Kozi Bród Stream sediments are enriched in mercury. The median value of it is 0.20 mg/kg, and the maximum concentration achieves 0.43 mg/kg.

**Łużnik Stream and its catchment.** Sediments of the Łużnik Stream drainage basin are the least contaminated. Median values of all the analysed elements are much smaller than in the other drainage basins of the map area (Table 4).

The lowest contents of many elements (aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, sulphur, titanium and vanadium) were recorded in the lower reach of the stream that drains Pleistocene sandy sediments of poor chemical composition. The bedrock of Łużnik Stream tributaries in the southern part of its catchment is composed of outcropping Triassic carbonate-clay deposits, the weathering of which releases some of the elements, causing an increase in their amount in alluvial sediments. Increased contents were recorded for aluminium, cobalt, iron, manganese, strontium and vanadium. Aqueous sediments of this part of the drainage basin are also enriched in elements associated with Zn–Pb sulphide mineralisation: arsenic, cadmium, lead and zinc. The average arsenic content is tens of mg/kg while in the lower reach of the Łużnik Stream, it rarely exceeds 5 mg/kg. The maximum concentrations of cadmium, lead and zinc are 67 mg/kg, 450 mg/kg and 2800 mg/kg, respectively.

**Kanał Główny Canal and its catchment.** The Kanał Główny Canal (also known as the Kanał Szczakowski Canal) was built to discharge water from the Szczakowa open-cast sand mine founded in the mid-1950s. The canal has many tributaries (smaller canals and ditches). The Kanał Główny Canal drains the areas that have been subjected to land remediation for many years.

Sediments of the Kanał Główny Canal are characterized by enrichment in aluminium, chromium, sulphur, strontium, titanium and vanadium.

In sediments of small watercourses draining a wetland area south of the Sosina artificial reservoir arsenic and barium contents were 154 mg/kg and 2770 mg/kg, respectively. Additionally, significant amounts of cadmium, cobalt, iron, manganese, nickel, titanium, vanadium, sulphur and strontium were noted. The enrichments are probably associated with the dumping wastes of various origin (mainly from the Siersza power plant) in the area of reclaimed old mine workings of the Szczakowa sand mine. Reclaimed land covered by *Histosols*, is convenient for sorption of elements due to the abundance of iron oxides and hydroxides, while the wastes are the source of metals.

**Wąwolnica.** The upstream section of the stream drains the south-western part of the map sheet. Its sediments show high concentrations of metals (copper, mercury, lead, zinc) and sulphur in the area of the Organika-Azot chemical plant. The copper, lead, sulphur and zinc contents are up to 150 mg/kg, 21 670 mg/kg, 7.40% and 2270 mg/kg, respectively. The most hazardous anthropogenic pollution is the mercury concentration of 182 mg/kg, being a great danger to plants and animals. There is also a slight enrichment in silver (2–3 mg/kg). The contamination of sediments is associated with long-lasting production of various chemicals by the Organika-Azot chemical plant. In the 1930s, the factory produced copper sulphate, calcium cyanide, ferrocyanide and other products, and, after World War II, the mercury electrolysis method was introduced into the production processes (Proksa, 2008) and lead compounds were used for the production of plant protection chemicals.

## SURFACE WATER

**Kozi Bród Stream and its catchment**. The pH of the drainage basin water varies from 6.8 to 8.6 (Table 5). Most of the water is slightly alkaline. Its electrical conductivity (EC) ranges from 0.20 to 2.35 mS/cm. Water of unnamed streams of the upper part of the drainage basin is characterized by EC values of 0.30–0.70 mS/cm while in the Kozi Bród Stream it is commonly 0.80–0.90 mS/cm. The highest mineralisation (EC 1–2 mS/cm) was recorded in the Kozi Bród Stream water downstream of the Szczakowa tannery sewage discharge site. It should be emphasized that the water conductivity exceeding 1 mS/cm indicates that the water is significantly polluted (Witczak, Adamczyk, 1994).

The Kozi Bród Stream water contains significant amounts of boron, chlorine, potassium, lithium, magnesium, molybdenum, sodium, thallium sulphate, and also calcium, rubidium and antimony. Enrichments with the same elements occur also in the upper reach of the stream in the neighbouring Myślachowice Map Sheet. The elements originate from discharges of cooling water from the Siersza power plant located in the upper part of the catchment. The power plant draws water for technological processes from, inter alia, the abandoned Arthur shaft of the Siersza coal mine. The average boron concentration in the Kozi Bród Stream water (911 $\mu g/dm^3$) is several times higher than in other watercourses of the Jaworzno Map Sheet (Table 5). The very characteristic feature are similar chlorine and sodium distribution patterns. Upstream of the confluence with the Łużnik Stream, chlorine and sodium contents in the Kozi Bród Stream are 50–to 60 $mg/dm^3$, and 30–40 $mg/dm^3$, respectively. After receiving significantly less mineralised water of the Łużnik Stream, the contents of these elements decrease to 30 mg/dm$^3$ and 20 mg/dm$^3$, respectively. A rapid increase in the concentration of chlorine (up to 390 mg/dm$^3$) and sodium (up to 433.2 mg/dm$^3$) were observed downstream of the Szczakowa tannery sewage discharge.

**Łużnik Stream and its catchment.** The water of the catchment is characterized by neutral pH (7.1–7.2) and low electrical conductivity (0.26 mS/cm) (Table 5).

The upper part of the drainage basin of the Łużnik Stream and its tributaries is located in the area of shallow-seated Triassic carbonate rocks mineralised with lead and zinc sulphides, and of Upper Carboniferous rocks weakly mineralised with uranium in near-fault zones (Sałdan, 1965). Enrichment of water in cadmium, copper, thallium, uranium and zinc in this area is associated with drainage of rocks supposedly rich in compounds of these elements.

The water of the left-bank tributaries of the Łużnik Stream (especially in the area located north of Jeziorki village) shows high concentrations of aluminium (up to 2800 μg/dm$^3$), arsenic (up to 13 μg/dm$^3$), iron (up to 10 mg/dm$^3$), titanium (up to 11 μg/dm$^3$) and thallium (up to 0.65 μg/dm$^3$). These elements may migrate from organic matter, clay minerals, soils and sediments to surface waters under favourable physicochemical conditions. It is a marshy area composed of glaciofluvial sands and pra-Przemsza valley deposits, locally peats. The organic carbon content in soils of the area exceeds 24%..

**Kanał Główny Canal and its catchment.** Water of this drainage basin has neutral pH values (pH 7.2). Low mineralisation of water (average EC 0.40 mS/cm) suggests its natural composition and insignificant contamination.

The water of Sosina artificial reservoir and its southern tributaries contain significant amounts of boron (400–1000 μg/dm$^3$) and cobalt (> 1.6 μg/dm$^3$) and is enriched in cadmium (often >3 μg/dm$^3$), nickel (6–16 mg/dm$^3$), copper (>40 μg/dm$^3$), molybdenum (>4 μg/dm$^3$) and sulphates (>200 mg/dm$^3$). The bedrock of the drainage basin is represented by Quaternary sandy sediments of poor mineral composition. Water pollution can therefore be related to anthropogenic factors (leaching of elements from waste dumps located in abandoned excavations of the Szczakowa open-pit sand mine).

**Wąwolnica.** The acidity of the Wąwolnica Stream water varies from 2.9 (near the mining waste pile of the KWK Jaworzno coal mine) to 9.0 (around the Organika-Azot chemical plant). The average electrical conductivity reaches 2.5 mS/cm. The concentrations of boron (>1000 μg/dm$^3$), chlorine (500 mg/dm$^3$), potassium (20–25 mg/dm$^3$), lithium (50–100 μg/dm$^3$), magnesium (90 mg/dm$^3$), sodium (300 mg/dm$^3$), rubidium (30 μg/dm$^3$), sulphates (300–400 mg/dm$^3$), strontium (1600 μg/dm$^3$), and probably cadmium (up to 51 μg/dm$^3$) and copper (up to 50 mg/dm$^3$) are related to run-off of leachates from waste heaps of the Jaworzno coal mine.

## CONCLUSIONS

**1.** Both the topsoils and subsoils are significantly contaminated with heavy metals in areas of Triassic carbonates (the western and southern parts of the map area). Heavy metals (especially cadmium, lead and zinc) are concentrated mainly in topsoil. At a depth of 0.8–1.0

m, there is a reduction in the area of these anomalies and a simultaneous increase in their intensity.

**2.** The natural (geological) sources of zinc, cadmium and lead, and also arsenic and thallium, are the outcrops of Triassic Zn–Pb ore-bearing deposits.

**3.** The anthropogenic source of contamination by metals is historical mining and processing of Zn–Pb ores, particularly the influence of wastes from old mine dumps.

**4.** Contamination of aqueous sediments and surface water is mainly anthropogenic in origin. It is caused by sewage discharges from industrial plants (mostly inactive at present), by leachates from waste dumps and landfills, and by improperly managed land reclamation of sand excavations pits.

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