INTRODUCTION

Geochemical mapping at the scale of 1:25 000 carried out in the Libiąż Map Sheet M-34-63-D-a area is a continuation of detailed cartographic survey that has been conducted in the Silesian-Cracow region by the Polish Geological Institute-National Research Institute since 1996. The project was ordered by the Ministry of the Environment and it was financed by the National Fund for Environmental Protection and Water Management. The purpose of the study is to assess environment pollution in the area of long-lasting hard coal and rock raw materials mining accompanied by other industries development.

The Libiąż Map Sheet is an area of a Pb–Zn–Cd assemblage geochemical anomaly found in soils, aqueous sediments and surface water (Lis, Pasieczna 1995a, b, 1997). The occurrence of the geological and anthropogenic anomalies is related to both the outcrops of ore-bearing dolomites with associated zinc-lead ore deposits as well as their historical mining and processing. Additional factors (geological and anthropogenic), causing chemical changes in the natural environment and landscape transformation, are the existence and extraction of other mineral deposits (hard coal, dolomites, clays and sands) and the activity of industrial plants.

The southern part of the map sheet is an industrial area (including industrial towns Chełmek and Libiąż) affected by significant changes in the terrain morphology. In the north there are parts of the Byczyna and Jeleń districts of Jaworzno city. Forest areas predominate in the western and central parts of the surveyed area. At the western boundary of the map sheet, there is a small part of the man-made Dziećkowice reservoir of drinking water, (which also plays recreational functions) as well as a number of fish ponds.

Most of the area is drained by the Przemsza River through the Byczynka Stream and Kanał Matylda Canal, whose drainage basin is characterised by a dense network of drainage ditches. The southern part of the study area is drained by small watercourses – tributaries of the Vistula River.

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

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

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

- **A. Pasieczna** − concept and project proposal, supervision and coordination of research, interpretation of research results;
- **P. Dobek, A. Dusza-Dobek, T. Kołecki** − sample collection;
- **P. Dobek, A. Dusza-Dobek, T. Kołecki, W. Markowski, A. Pasieczna** − databases;
- **A. Maksymowicz, P. Pasławski, E. Popiołek** − leadership and coordination of analytical works;

- **M. Cichorski, J. Duszyński, Z. Prasol** − mechanical preparation of samples for analyses;
- **I. Witowska** – chemical preparation of samples for analyses;
- **E. Górecka, I. Jaroń, M. Jaskólska, D. Karmasz, J. Kucharzyk, B. Kudowska, D. Lech, M. Liszewska, E. Maciołek, A. Maksymowicz, I. Wysocka** – chemical analyses;
- **W. Wolski, P. Dobek** – grain size analyses;
- **A. Dusza-Dobek, A. Pasieczna** − statistical calculations;
- **A. Pasieczna, A. Dusza-Dobek, T. Gliwicz** − construction of geochemical maps;
- **M. Szuwarzyński, A. Pasieczna** − characteristics of the map area;
- **M. Szuwarzyński** − geology and mineral deposits; human impact.

CHARACTERISTICS OF THE MAP AREA

Geographical and administrative setting. The Libiąż Map Sheet area is located at the Małopolska and Silesian Voivodeships borderland. The central and eastern part of the map area is located in the Małopolska Voivodeship (parts of Chrzanów, Babice, Libiąż and Chełmek commune). Part of the Jaworzno urban district (in the north of the map sheet) and a small part of the Lędziny–Bieruń district (Imielin urban commune) are located in the Silesian Voivodeship.

According to the physiogeographic subdivision of Poland (Kondracki, 2000), most of the study area is situated within the Silesian Upland (within a lower-order unit called the Pagóry Jaworznickie hills). The Grzbiet Tenczyński ridge, stretching in the south-east of the area, is a part of the Kraków–Częstochowa Upland.

Relief and geomorphology. The relief of the area reveals clear relationship with tectonic structures, which is expressed by the presence of longitudinal belts of hills and depressions, corresponding to horsts and basins, respectively (Siedlecki, 1952).

The north-eastern part of the map area is occupied by a belt of gently sloping hills (with an elevation exceeding 300 m a.s.l.), composed of Triassic deposits of the so-called Cezarówka Horst. A westerly inclined flat depression of the Chrzanów–Dąb Basin, which is an extension of the Krzeszowice graben, stretches parallel to the hills (Bogacz, 1967). The depression is filled with Cenozoic deposits, and the elevations fall within the range from 230 m a. s. l. in the Przemsza River valley to 270 m a. s. l. in the Kroczymiech area. To the south, there is another belt of hills associated with horst structures located on the extension of the so-called Płaza Block (Siedlecki, 1952). Meridionally-oriented Chechło River valley separates the hills from the block. The hills are composed of Upper Carboniferous and Triassic deposits and they reach an elevation of 300–330 m a. s. l. near the Libiąż town. In the southern part of the map area, there is a flat topographic low sloping towards the Vistula River valley. Its relief is composed of glacial sands (Buszman *et al.*, 2006).

The map sheet covers drainage basins of the Vistula River tributaries in its upper reach. The largest catchment, in terms of areal extent and runoff volume, is that of the Kanał Matylda Canal, a tributary of the Przemsza River. The Kanał Matylda Canal is recharged by small streams draining the northern and southern belts of hills. The north-western part of the map area is situated within the Byczynka Stream catchment. The south-eastern area is crossed by the Chechło River having no tributaries in this area, but recharged by several springs located on its right bank. The southern part of the map area is drained by small streams entering directly into the Vistula River.

There are several artificial reservoirs within the map sheet area. These are ponds formed during engineering works carried out at the Kanał Matylda Canal and Byczynka Stream, ponds located at Chełmek, settling ponds of the Janina coal mine and power plant (Zakład Górniczo-Energetyczny Janina) in Libiąż, water-filled brickyard pits in Byczyna, and part of the Dziećkowice drinking water reservoir in the Przemsza River valley.

Near Libiąż, there are wetland areas in topographic lows, located mainly in post-mining subsiding troughs above coal mine workings.

Land use. Non-built-up and rural areas occupy 76%, urban areas account for 20%, and industrial areas cover 4% of the map sheet. Urban and industrial areas of Chełmek and Libiąż towns are located in the south of the map sheet.

The degree of forestation in the surveyed area (57.9%) is almost twice as big as the national average forestation of 28% (Program..., 2005). Wasteland (27%) covers the southern and northern parts of the map area. Agricultural areas (5%) are of minor importance and concentrate around villages. Other forms of land use include: lawns (8.5%), allotments (1.1%) and parks (0.5%).

Economy. Libiąż is the major industrial centre where the following companies operate:

- ZGE Janina mining and power plant (Zakład Górniczo-Energetyczny ZGE Janina)

- Libiąż dolomite mine (Kopalnia Dolomitu Libiąż);

- Thermoplast company - manufacturer of windows, tools and plastic products;

- Libet cobblestone factory (Fabryka Kostki Brukowej Libet);

- Heat station (Nadwiślańska Spółka Energetyczna - Zakład Ciepłowniczy).

The Janina mining and power plant has mined hard coal since 1904. The company has a mining waste dump in the Moczydło district of Libiąż and two mine water settling ponds (one inside the waste dump and the other in the Kosówki). In settling ponds suspended coal particles precipitate and purified water from mine dewatering is discharged into watercourses.

A Triassic dolomite quarry, located in Kamienna Street in Libiąż, produces aggregate, structural elements and calcium-magnesium fertilizers. The company discharges wastewater and groundwater from the quarry to the sewerage system. A closed water reservoir is located in the quarry (Program…, 2005).

The Ocynkownia Śląsk galvanizing line operates in Kroczymiech. In the south-western part of the map area, there is an industrial zone of the former Chełmek leather industry factory (Południowe Zakłady Przemysłu Skórzanego PZPS Chełmek). In place of the PZPS Chełmek (follower of the Bata shoe factory, which was launched in 1932) a Municipal Economic Activity Zone is being created. Currently, 37 economic entities operate in the area, especially in the shoe sector, but there are also package, carpentry and construction industries. (Gmina..., 2008; Program…, 2008).

GEOLOGY AND MINERAL DEPOSITS

The study area is situated at the southern edge of the epi-Variscan platform called the south-western platform of Poland (Bukowy, 1974), and more precisely in the Upper Silesian Basin, in its part involved in the geological structure of the Carpathian piedmont. The region is composed of Mesozoic and Cenozoic rocks deposited upon the Upper Carboniferous basement (Żero, 1956; Szuwarzyńska *et al.*, 2001).

The oldest formation, exposed on the surface, is the so-called Kwaczała arkose representing the Upper **Carboniferous** (Rutkowski, 1972), whose outcrops are located in a belt of hills stretching near Libiąż and Żarki. In this area, the thick Cenozoic cover is underlain by the uppermost Westphalian Kraków sandstone series containing coal seams (Dembowski, 1972), playing an important role in the geological structure of the whole map area. The total thickness of the Upper Carboniferous deposits exceeds 1000 m. These deposits were folded during Variscan movements. The main structure of this age is the Chrzanów Trough (Bukowy, 1974). In late Palaeozoic and Mesozoic through Neogene times, the Carboniferous deposits were faulted creating a complex system of tectonic blocks (Buła, Kotas, 1994).

The Mesozoic succession consists mainly of **Triassic** deposits. **Jurassic** rocks occur as small isolated patches only in the eastern part of the map area. The Triassic section is represented by Buntsandstein and Muschelkalk carbonates (Szuwarzyński, 1984). This succession is about 160 m thick and is composed mainly of dolomites accompanied by marls and limestones. Its lowest and highest parts contain terrigenous interbeds. Over large areas, the dolomites (especially Zn–Pb ore-bearing and diplopora dolomites) are overlain by Cenozoic deposits or form extensive outcrops, which are parent rocks of soils.

The Cenozoic succession includes **Neogene** deposits (clays and marls typical of the Miocene section in the Carpathian Foredeep) and Quaternary sediments of varied depositional settings. Miocene deposits, reaching a thickness of more than 40 m, rarely outcrop in natural exposures, despite its widespread occurrence in the Kanał Matylda Canal valley. They are often exposed in various excavations. Outcrops of Miocene marine clays occur only in a topographic low extending south of Chełmek.

Quaternary deposits cover the most of the map sheet area, forming multilayered sequences of lithologically diverse sections. Their thickness varies from tens of centimetres, at hilltops to tens of metres in buried erosional valleys. They represent the effects of Pleistocene glacial and ice-marginal deposition (glaciofluvial sands and gravels, tills, ice-dammed lake muds) and periglacial phenomena (a range of weathering mantles) as well as Holocene deposits of various origin (dune sands, muds, clays, sands, travertines and peats).

Mineral deposits. Triassic ore-bearing dolomites were mined for **zinc and lead ores** from the 13th century to the beginning of World War I. The subjects of interest were small, platy ore bodies that follow the stratification of rocks, and the accompanying ore lenses or zones of vein mineralisation (Sass-Gustkiewicz, 1985, 2001; Dżułyński, Sas-Gustkiewicz, 1993; Górecka, 1993, 1996; Szuwarzyński, 1993). Extraction was carried out in the north-eastern part of the map area along the belt of dolomite outcrops near the Kąty, Cezarówka and Libiąż.

The mined ore was mainly calamine. The common ore minerals were smithsonite and galena, accompanied by cerussite, hemimorphite, hydrozincite, anglesite and vein minerals: dolomite, calcite, chalcedony and barite (Górecka, 1996; Szuwarzyński, 1996). In addition to calamine, limonite iron ore was mined near Libiąż. There were two types of occurrence of all these minerals: layered aggregates and earthy ores replacing carbonate rocks or *filling* the *voids* of *the rocks* (veins of various kinds, coatings and matrix of breccias). Dolomite was the host rock to the ore bodies.

Zn–Pb ore was mined above the groundwater level, locally using mine dewatering with short adits. For the same purpose drainage of nearby coal mines was used in the 19th century (Szuwarzyński, 2003). Until the early 19th century, galena had been mined providing material for lead smelting in the vicinity of mining sites. Calamine mining started in the 16th century. It was initially intended for the production of brass (exported to Sweden). In the late 18th century, iron ore extraction started in this region, which lasted until the mid-19th century. Processed ore was shipped to Chrzanów, Sucha Beskidzka and even to Moravia. After the beginning of zinc metal production (early 19th century), calamines were intensively exploited and transported, mostly to the Silesian smelters.

Extraction of Zn–Pb ores was carried out until the resources were exhausted in the mining fields exploited since the Middle Ages. Exploratory works conducted in the 1950s and 1960s revealed no possibility of ore mining from Triassic deposits in depressions (Kurek *et al.*, 1977).

Mining of **hard coal** deposits began in the second half of the 19th century around the Libiąż (Szuwarzyński, 2008). It is still being continued and seems to have long-term perspectives.

Two mining centres included in the Południowy Koncern Węglowy coal mining concern operate currently on the proven coal deposits: the Janina ZGE coal mining company in Libiąż and the ZGE Sobieski coal mining company in Jaworzno. The Janina ZGE coal mining company has its on-surface facilities within the map area, while the ZGE Sobieski coal mining company is represented only by a part of its mining area in the north of the map sheet. Both these companies extract coal from the Kraków sandstone series (ZGE Janina: coal seams Nos 113–119; ZGE Sobieski: coal seams Nos 207, 209 and 302). Within the map sheet limits, there are also parts of five proven and yet undeveloped coal deposits: Byczyna, Libiąż-Dąb, Libiąż-Janina, Libiąż III and Wisła I-Wisła II.

Extraction of outcropping Triassic **dolomites,** used as construction stone, has been conducted for at least 100 years. Currently, mining is carried out in the Libiąż deposit.

Until the mid-1970s extraction of Triassic **limestones** used as construction stone and raw material for burning lime for the local needs had been carried out. Miocene **clays** and

Quaternary **tills** were used as raw materials for the ceramic industry. **Sand** was mined for construction purposes.

HUMAN IMPACT

Natural environment of the study area is degraded due to historical mining of zinc-lead ores, modern mining of hard coal and rock materials, and long-lasting activities of many plants and enterprises. Some hazard is related to waste management and water sewage disposal.

Long-lasting exploitation of mineral deposits has led to a remarkable land transformation. It mostly includes abandoned workings (quarries, clay and sand open-pits) as well as tailings heaps and subsidence troughs associated with shallow mining of Zn–Pb ores. These old excavations have not been subjected to land reclamation and they are used in many cases as places of illegal disposal of various kinds of waste.

The Libiąż region is an area of terrain deformation including continuous (subsidence troughs) and discontinuous (thresholds, collapse sinks) landforms, which were formed due to the impact of coal mining, particularly longwall mining (Program..., 2005).

Terrain transformations are also caused by dumping of waste generated during mining and processing of mineral deposits. The largest landfills are managed by the ZGE Janina coal mining company and the Libiąż dolomite mine.

Atmospheric air. Most of the air pollution originates from power plants and other industries, public utility companies and from transportation sources. Emissions from individual furnaces are of minor significance due to its nature and dispersion.

The greatest contributors to the total quantity of pollutants emitted into the atmosphere are the ZGE Janina mining and power plant, Thermoplast company in Libiąż, Ocynkownia Śląsk galvanizing plant in Kroczymiech and Libiąż dolomite mine (Ocena.., 2005; Program..., 2005) emitting both gas and dust pollutants.

A serious source of the air contamination along transportation routes and city roads is engine exhaust fumes containing hydrocarbons, nitrogen dioxide and carbon oxide. They are sourced from local heavy traffic roads and the Libiąż and Chełmek towns.

Additional source of the air contamination is long-distance emission of pollutants from the western part of Upper Silesian Industrial Region, emitting more than 20% of dust and gas contaminants of the Poland's total emissions.

Surface water and groundwater. The most serious hazard to groundwater is coal extraction in the ZGE Janina coal mining company. Changes in groundwater conditions result from the drainage of multiaquifer formations by underground mining (the impact of the Libiąż dolomite quarry is negligible) and discharge of mine water. In the north-eastern part of the map area, Triassic formations are also affected by the drainage related to Zn–Pb ore underground mining in the adjacent map sheets and by the impact of groundwater intake in the Chrzanów region (Różkowski, Siemiński, 1995; Szuwarzyński, 2003).

Due to the high water inflow into the mines extracting hard coal from Kraków sandstone series, mining companies in the Chrzanów Trough are forced to pump up more than 100 m^3/min of water, which results in a vast drainage zone within Carboniferous deposits (Wilk, 2003). Locally it also affects the groundwater conditions in the Triassic deposits (Szuwarzyński, 2003).

Groundwater discharge by the coal mines is a continuous process. The extent of the predicted cone of depression, caused by the activity of the ZGE Janina coal mine, covers the areas of Chrzanów, Babice, Oświęcim and Chełmek. Transformations associated with land subsidence have caused the possibility of joining individual aquifers. An example of such situation is observed in the Libiąż commune, where terrain deformation (caused by longwall mining in the ZGE Janina coal mine) and the lack of impermeable beds resulted in merging subsurface waters and groundwaters, groundwater drainage and extensive drying land surface (Program…, 2005).

The source of groundwater contamination is waste dump in the ZGE Janina coal mine in Libiąż gathering mining wastes. This is a naturally sealed above-ground landfill, partly reclaimed for recreational use. Leachates from the landfill are captured by a special drainage system. Water monitoring conducted in piezometers in the vicinity of the landfill showed high contents of cadmium, lead and nitrogen compounds. Increased concentrations of sulphates were reported for water from the drainage system.

Discharge of highly mineralised mine water from the ZGE Janina coal mine directly to the surface water leads to deterioration of their quality. It results in the salinity increase of the water of the Kopalnianka and Rzepka streams and in a canal draining the area of mine shafts near Kosówki. It also brings the increase of sulphate and heavy metal concentrations in these streams and the disturbance of their natural recharge. Sewage discharge from other industrial plants and municipal sector cause increased water mineralisation, biological degradation and eutrophication.

The quality of surface water is affected also by engineering works in watercourses, discharge liquid municipal sewage, improper land reclamation as well as mining coal and Zn–Pb ore (in the Myślachowice and Chrzanów map sheets area)(Szuwarzyński, 2003; Wilk, 2003).

Soils. Soil degradation related to the impact of anthropogenic factors, involves decrease of quality and quantity of humus, changes of structure and acidity, leaching of basic cations and, consequently, fertility reduction. The most important soil-contaminating factors of anthropogenic origin are emissions of dust and gas from industrial and engine vehicle sources, waste disposal and inappropriate agricultural land use. Widespread use of pesticides and fertilizers results in the introduction of metals, nitrogen compounds, organophosphates and chlorinated hydrocarbons into the soil. Chemical degradation of soils occurs also due to the use of waste and sewage to fertilize as well as liming the soils.

Chemical pollution of soils, particularly by heavy metals, results mainly from the industrial and transportation activities. Locally, they are caused by mining activity and storage of industrial waste. Anomalous metal contents, especially of zinc, lead and cadmium, are observed in small areas and are related to the environmental impact of the historical Zn–

Pb ore mining and processing industry, as well as to the natural geochemical background in the areas of outcropping ore-bearing rocks.

An important evidence of soil transformation, although generally invisible in the surface, are the tracks of historical lead smelting – large amounts of lead oxides, so-called massicot (Szuwarzyński, 2008b).

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

Surface water samples were collected at the same sites as aqueous sediment samples. Specific electrical conductivity (EC) and acidity (pH) of water were measured on site. EC was measured using 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 last 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 in water extracts 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 waters was performed by the 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 the inductively coupled plasma atomic mass spectrometry (ICP-MS) method. All 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, Chrzanów Map Sheet M-34-63-D (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 Detailed geological map of Poland Chrzanów Sheet 1:50 000 (Żero, 1956). Individual elements of the geological map were digitized to create their vector images which were subsequently combined with the topographic base, producing the geological map at the scale of 1:25 000 (Plate 1).

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

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

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

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

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

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

The geochemical maps of soils were constructed using the analytical dataset created for the Libiąż Sheet and the datasets of 1:25 000 scale neighbouring sheets. Thus any disagreements at the sheet borders were avoided. After interpolation the Libiąż 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 Libiąż 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 limit values of metals, defined in the Regulation of the Ministry of the Environment (Rozporządzenie..., 2002), according to the recommendation that ’soil or land is considered polluted if the concentration of at least one substance exceeds the permissible limit value’.

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

For publication purposes, the geochemical maps were constructed by combining the maps into pairs: the topsoil maps is presented together with the aqueous sediments map, and the subsoil map 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 parent rocks of the soils in the study area are differentiated in terms of both lithology and age (Plate 1). It gave rise to a variety of soil types which clearly reflects the chemical composition of the bedrock.

The basement of the northern and southern areas of the map sheet is built from Triassic carbonates and results in *Rendzinas* formation development. *Podzols* and *Cambisols* developed on Quaternary glaciofluvial sandy deposits (Program.., 2005). Grasslands, common in the north-western part of the map sheet, are covered by *Histosols* occupying large areas of low land with a shallow groundwater level.

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

Soils rich in the clay fraction (<0.02 mm) and silt fraction (0.1–0.02 mm) are commonly characterised by high contents of individual elements and their low migration ability under hypergenic conditions. This soil property is usually taken into account when preparing standards and recommendations for their use, allowing higher limiting concentrations of elements for soils rich in the clay fraction and lower concentrations for soils rich in the sand fraction (Kabata-Pendias *et al*., 1995).

Within the Libiąż Map Sheet the most common are sandy topsoils (76%) developed on Pleistocene glaciofluvial sands and gravels and aeolian sands. Many of them contain more than 75% of the 1.0–0.1 mm fraction. In the east, there is a narrow belt of soils containing over 90% of the sand fraction. These soils are characterized by a low content of the silt (<5%) and clay (<5%) fractions.

Soils developed on the outcrops of Triassic carbonates are slightly enriched in the silt (0.1–0.02 mm) and clay (<0.02 mm) fractions. The silt fraction content ranges mostly from 10 to 15%.

An increased content of the clay fraction (5–10%) was recorded in the soils developed from some of Triassic carbonates, Miocene marine clays and Holocene muds in the southern part of the map area.

Acidity. Differentiation of the topsoil pH is related mostly to the soil use, which in turn is constrained by the bedrock lithology. Forest soils (developed from glaciofluvial sands and gravels) covering about 57% of the study area, are highly to moderately acidic (average pH 5.3). An especially large area of highly acidic soils (pH <5) occurs in the Kanał Matylda

Canal drainage basin. Urban soils of Libiąż are neutral and locally alkaline. Small patches of neutral soils are observed at the northern boundary of the map sheet.

The subsoils (0.8–1.0 m depth) in the central part of the map sheet are predominantly acidic, whereas in the north and south, neutral and alkaline soils predominate, which is associated with their development from Quaternary glaciofluvial sands and Triassic carbonate rocks, respectively.

Alkalinisation of soils in the Libiąż urban-industrial area can be related to both the occurrence of Triassic carbonate bedrock and the scattering of industrial dust rich in calcium and magnesium compounds. More important is the chemical composition of parent rocks, as evidenced by a larger area of alkaline soils at a depth of 0.8–1.0 m.

Geochemistry. Analysis of the distribution patterns of individual elements allow to determine the geochemical background variability and to identify anomalies.

The distribution of chemical elements in the soils indicates their strong relationship with the chemical composition of the parent rocks. The soils developed from Pleistocene glaciofluvial, aeolian and alluvial sands, characterized by the proportion of the sand fraction often exceeding 75%, contain the smallest amounts of aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, strontium, titanium and vanadium. This refers to both the topsoils and subsoils. Low contents of these elements in soils are associated with the poor chemical composition of the bedrock and acidic values of pH that favours leaching of the elements.

Soils that developed from Triassic carbonates and Neogene marine clays are characterized by particularly high calcium concentrations reaching a maximum of 13.80% in the topsoils and 10.13% in the subsoils. They are also rich in magnesium and manganese and enriched in most analysed elements. Such elements distribution pattern is especially noticeable in the subsoils.

The sources of anthropogenic-geological anomalies of cadmium, zinc and lead are: historical opencast extraction of calamine deposits carried out on Zn–Pb ore-bearing dolomite outcrops in the vicinity of Kąty, Cezarówka (north-eastern part of the map area) and near Libiąż, as well as mine water discharge from the historical Matylda Zn–Pb ore mine (in Kąty near Chrzanów) to the Kanał Matylda Canal (built along the former Śmidra Stream).

The concentrations of cadmium, lead, and zinc in the topsoils in the area between Kąty and Cezarówka Dolna, in the Moczydło district of Libiąż and in the Kanał Matylda Canal valley are >32 mg/kg, >250 mg/kg and >1000 mg/kg, respectively. The intensity of anomalies increases with depth, but their areal extent simultaneously decreases.

The cadmium, lead and zinc anomalies fade in the subsoils in the western part of the Kanał Matylda Canal valley. In the eastern part of valley their intensity is increased. Within the area of cadmium, lead, and zinc anomalies, the soils are also contaminated with silver (>1 mg/kg) and mercury (>0.1 mg/kg). These elements likely originate from mining wastes of the historical Matylda Zn–Pb ore mine (located outside the eastern boundary of the map sheet), which were transported to the west with the sediments and water of the Kanał Matylda Canal.

The topsoils of some sheet areas shows increased arsenic contents (20–40 mg/kg). In the area of historical mining of Zn–Pb ores, the maximum noted arsenic value was 2130 mg/kg, which also continues in the subsoil.

The most remarkable anthropogenic copper anomaly is proved near mine shafts and settling ponds of the ZGE Janina coal mine (in the south of Libiąż and near the western boundary of the town). The copper content varies within the limits of 40–80 mg/kg. In the same area, the soils are enriched in mercury, whose increased concentration was also observed in alluvial soils of the Chechło River valley.

The contents of elements determining soil fertility (organic carbon and phosphorus) are varied. The topsoil total organic carbon (TOC) content is 1.9% and the phosphorus content is 0.022%. TOC content in forest soils of the central part of the map sheet varies from 3 to 12%, sometimes exceeding this value. The maximum total organic carbon content (47.1%), recorded near the mine shafts of the ZGE Janina coal mine (west of Kosówki), is related to the presence of coal crumbs in the soil.

The parts of the sheet area contaminated to a different extent by cadmium, lead and zinc were estimated (Table 6). Most of the mapped area topsoil contains <4 mg/kg of cadmium, <100 mg/kg of lead and <500 mg/kg of zinc, whereas the subsoil commonly contains <1 mg/kg of cadmium, <25 mg/kg of lead and <100 mg/kg of zinc.

Estimation of the degree of contamination by metals was carried out for the soils from the 0.0–0.3 m depth interval, classifying them with respect to soil use into the groups A, B and C based on permissible limit values (Rozporządzenie…, 2002). The total classification was calculated using the rule that the sample is classified into a particular soil use group if the content of at least one element exceeds the permissible limit value. With respect to the concentrations of metals, 32.82% of the analysed samples were included into group A. Group B is represented by 34.36% of the samples, whereas 32.82% of the samples were classified into group C. The soils classified into group C are mainly found in the northern part of the map area along the outcrops of ore-bearing dolomites and in urban areas of Chełmek and Libiąż (Plate 63). The map shows the recommended land use in accordance to the guidelines of Rozporządzenie...(2002). In many cases, the present-day land use is inappropriate and needs to be monitored. Locally, the area requires land reclamation. Concentrations of some metals in the soils of forests, arable land, meadows and gardens are so high that the area should be used only for industrial purposes. The soils that are classified into groups A and B meet the requirements of multifunctional use. The most significant pollutants in the soils are zinc, cadmium and lead (Table 7).

AQUEOUS SEDIMENTS

Aqueous sediment samples were collected from the following watercourses: Kanał Matylda Canal and Byczynka Stream and their catchments, Chechło River (in its lower reach), a small section of the Przemsza River, small unnamed streams and ditches, a number of fish ponds and from the eastern part of Dziećkowice artificial reservoir. A few samples represent sediments of small stagnant water reservoirs (ponds). The main feature of the geochemistry of the aqueous sediments is the dominance of anthropogenic factors over natural ones with respect to concentrations of metals.

Kanał Matylda Canal and its catchment. The Kanał Matylda Canal (formerly Śmidra Stream) catchment covers the central part of the map sheet area. Alluvial sediments of the canal are highly contaminated by cadmium, lead and zinc and enriched in silver, copper and mercury (Table 4).

The highest concentrations of cadmium, lead and zinc were observed in sediments of the upper reach of the Kanał Matylda Canal. The average and maximum values are, respectively: 60 mg/kg and 430 mg/kg for cadmium, 1400 mg/kg and 16 100 mg/kg for lead and 6400 mg/kg and 49 500 mg/kg for zinc. Considerable contamination by these elements is confirmed by the studies conducted by Aleksander-Kwaterczak *et al.* (2010). The average concentrations of cadmium, lead and zinc in sediments of the canal measured between Kąty and Staw Dolny are 130.7 mg/kg, 5728 mg/kg and 18 627 mg/kg, respectively.

Significant enrichments with silver (2–6 mg/kg), arsenic (20–40 mg/kg) and copper (20–70 mg/kg) occur in sediments of the eastern part of the canal. Along the entire length of the watercourse, its sediments contain elevated mercury values (0.20–0.40 mg/kg).

The contamination of sediments with metals is related to the drainage of old mine dumps of the Matylda Zn–Pb ore mine, located outside the eastern boundary of the map sheet in the upper reach of the canal. Two mining waste dumps were left after completion of mining (in 1972): an "ore" pile and a former tailings pond of waste material of the ore processing. In both cases, the waste was considered as potential zinc-bearing raw material, but tests carried out in the Miasteczko Śląskie zinc smelter proved that it has no economic value (Szuwarzyński, 2008). The area of the former landfills has been partially developed, but it is still a source of metals penetrating into the environment.

Aluminium, barium, calcium, cobalt, chromium, iron, manganese, nickel, phosphorus, titanium and vanadium are geogenic elements in origin. The contents of aluminium, arsenic, calcium, iron, magnesium, manganese, nickel, strontium and vanadium are slightly higher in sediments of the upper reach of the Kanał Matylda Canal than in its lower reach. The smallest amounts of these elements were noted in sediments of the Staw Duży Pond. They are contaminated only by lead and zinc.

Chechło River and its catchment. Sediments of the Chechło River are contaminated by cadmium, lead and zinc. They also contain increased amounts of silver, mercury and sulphur. The average concentrations of cadmium, lead and zinc (expressed as the median values) are 63 mg/kg, 1030 mg/kg and 9200 mg/kg, respectively (Table 4). The mercury, silver and sulphur contents are <0.05–1.57 mg/kg, 2–3 mg/kg and 0.016– 0.830%, respectively.

Sediments of the Chechło River are contaminated mainly by the activity of the Trzebionka Zn–Pb ore mining company (Zakłady Górnicze ZG Trzebionka) located in the area of the Myślachowice and Chrzanów map sheets (Ciszewski, 1994, 1996; Bellok, 1996; Bellok *et al.*, 1997). Leachates from a tailings pond as well as mine water from the mine facilities are discharged into the Chechło River through the Luszówka Stream, supplying water and suspensions contaminated with metals. An additional source of sediment pollution is the discharge of water contaminated with metals brought into the Chechło River through the Pstrużnik Stream from the facilities of the metallurgical pant (the former zinc smelter) and the oil refinery in Trzebinia.

Geogenic elements of the Chechło sediments include aluminium, barium, calcium, cobalt, chromium, iron, manganese, nickel, phosphorus, titanium and vanadium. The contents of these elements remain within the limits of the regional geochemical background and slightly vary along the considered river section.

Sediments of the Młynówka canal (located in the horseshoe of the Chechło River) are strongly contaminated with heavy metals. The concentrations are as follows: 23 mg/kg of silver, 262 mg/kg of arsenic, 78 mg/kg of chromium, 980 mg/kg of copper, 14.23 mg/kg of mercury, 4670 mg/kg of lead and 16 300 mg/kg of zinc. These metals were probably deposited in depressions of the Chechło River valley during periodic floods.

Byczynka Stream and its catchment. Most of the analysed sediments contain small amounts of geogenic elements (aluminium, barium, calcium, cobalt, chromium, iron, manganese, nickel, phosphorus, titanium and vanadium) due to the nature of the catchment bedrock that consists of Quaternary glaciofluvial sands and muds (silts, clays and sands). Sediments enrichments in cadmium (up to 110 mg/kg), cobalt (up to 116 mg/kg), iron (up to 9%), manganese (up to 16 500 mg/kg), lead (up to 300 mg/kg) and zinc (up to 7900 mg/kg) were recorded in the areas of periodically drying right-bank tributaries of the Bryczynka Stream (north of the Belnik ponds). The metals probably come from the outcrops of Triassic Zn–Pb ore-bearing dolomites in the vicinity of Podkamieniec.

Other watercourses and lakes. Sediments of the Rzepka and Kopalnianka streams, draining the southern part of Libiąż, contain small amounts of the analysed elements. Only the Kopalnianka Stream sediments show elevated contents of barium and strontium due to discharges of mine water from the ZGE Janina coal mine. In the neighbourhood of Córeczka village, sediments of an unnamed stream, draining the area of the coal mine's former settling ponds, are enriched in cobalt, iron, manganese, nickel, sulphur and strontium probably derived from weathering of Carboniferous barren rocks dumped in piles.

Sediments of Dziećkowice artificial reservoir are poor in all the elements analysed. At a short section of the Przemsza River round the reservoir, flowing here in an artificial channel, sediments are contaminated significantly. The following concentration values were measured: silver up to 6 mg/kg, arsenic up to 70 mg/kg, chromium up to 90 mg/kg, copper up to 220 mg/kg, iron up to 4.80%, mercury up to 1.50 mg/kg, phosphorus up to 0.65%, lead up to 2800 mg/kg, sulphur up to 1.70%, and zinc up to 7200 mg/kg.

SURFACE WATER

Kanał Matylda Canal and its catchment. The acidity of water is neutral and slightly alkaline (pH 7–7.5). The amount of total dissolved solids in the water, expressed by the electrical conductivity, varies from 0.22 to 1.21 mS/cm (median 0.63 mS/cm). Increased EC values (0.70–1.20 mS/cm), indicating significant mineralisation, were observed in the unnamed stream, which is contaminated by sewage discharged from the sewage treatment plant in Libiąż. It is also the source of elevated contents of chlorine, cobalt, potassium, sodium, phosphorus, rubidium, and sulphates in the stream water.

The water of the unnamed right-bank tributary of the Kanał Matylda Canal is contaminated by silver (0.50–0.60 μg/dm^3) and lead (1112 μg/dm^3). Lead and silver anomalies were observed also in the drainage basin soils of this watercourse. These elements can be extensively leached from the soils (characterized by acidic pH) by infiltrating rainwater.

The group of elements showing increased contents (arsenic, calcium, cadmium, lithium, magnesium, lead, sulphates, antimony, uranium and zinc) recorded in the upper reach of the Kanał Matylda Canal, is sourced from the drainage of old Pb-Zn ore mining waste piles near Kroczymiech and discharges of wastewater from the Ocynkownia Śląsk galvanizing plant.

High concentrations of aluminium (up to 1400 μg/dm^3), arsenic (4-7 μg/dm^3), cadmium (6.6 μg/dm^3), cobalt (8.8 μg/dm^3), iron (1.5-2.0 mg/dm^3), manganese (400-600 μg/dm^3) and silica (10-20 mg/dm^3) occur in the water of ditches draining the areas around the Staw Duży Pond located in a forest area covered with mud-peat soils. These elements are easily adsorbed in soils rich in organic matter, clay minerals and iron hydroxides, and can be released under favourable physicochemical conditions to penetrate into the water and sediments.

Chechło River and its catchment. The river water shows equalised pH values (7.3-7.6) and electrical conductivity within the limits of 0.95-1.03 mS/cm (Table 5), proving its considerable mineralisation associated with long-term transport of sediments and water polluted with sewage from a tailings pond and mine water from the ZG Trzebionka Zn-Pb ore mine. The Chechło River water contains elevated amounts of arsenic (2-3 μg/dm^3), thallium (0.21-0.33 μg/dm^3), uranium (0.76-0.94 μg/dm^3) and zinc (250-580 μg/dm^3), and is also enriched in boron, chlorine, lithium, magnesium, sodium, rubidium, strontium and sulphates.

Byczynka Stream and its catchment. The water of the stream and its tributaries is characterized by pH values ranging from 7.0 to 8.5. The highest pH values (>8) were measured in the fish pond near the A4 motorway and in the Staw Belnik Pond. Electrical conductivity of the drainage basin water ranges from 0.28 to 2.46 mS/cm (Table 5).

The EC values >1 mS/cm was recorded in the water of the upper reach of the Byczynka Stream and small streams recharging the Stawy Belnik Ponds. Such electric conductivity proves strong degradation of water since EC values above 1 mS/cm indicate considerable contamination (Witczak, Adamczyk, 1994). The water contain significant amounts of barium (130-140 μg/dm^3), calcium (100-110 mg/dm^3), chlorine (200-300 mg/dm^3), potassium (20-26 mg/dm^3), sodium (100-180 mg/dm^3), phosphorus (1-2 mg/dm^3), rubidium (26-28 μg/dm^3), strontium (200-290 μg/dm^3) and uranium (0.9-2.0 μg/dm^3) probably originating from municipal wastewater discharges in Byczyna.

Other streams and lakes. The Kopalnianka Stream is a receiver of highly mineralised mine water from the ZG Janina coal mine. Electrical conductivity of the water is 4.3-4.4 mS/cm, and the pH 7.8-7.9. The Kopalnianka Stream water contains high concentrations of boron (>2500 μg/dm^3), chlorine (>1500 mg/dm^3), potassium (>36 mg/dm^3), lithium (>140 μg/dm^3), molybdenum (>19 μg/dm^3), sodium (>970 mg/dm^3), rubidium (>40 μg/dm^3) and antimony (8-12 μg/dm^3). It is also enriched with calcium, magnesium, sulphur, uranium and strontium. Elevated contents of these elements occur also in the water of the Rzepka Stream (draining the south-western part of Libiąż), the Przemsza River and a stream draining the area of old settling ponds of the ZG Janina coal mine.

CONCLUSIONS

1. Chemical composition of the parent rocks of the soils is the most important factor affecting their geochemistry. The soils that developed from Pleistocene glaciofluvial and aeolian sands are characterised by low contents of aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, strontium, titanium and vanadium. It refers to both the topsoils and subsoils. The soils that developed on Triassic carbonates and Neogene marine clays distinguish by high content of calcium, magnesium and manganese as well as enrichment in most of the elements analysed.

2. The soils of the areas composed of the Triassic carbonates are polluted with cadmium, lead and zinc. These metals, locally with an admixture of arsenic, are observed mainly within the topsoil. The areas of anomalies diminish at the depth of 0.8–1.0 m, however their intensity simultaneously increases. Natural (geological) sources of these metals are outcrops of Triassic Zn–Pb ore-bearing dolomites. The highest concentrations of toxic elements were observed in soils of forest and industrial land, fortunately not in agricultural areas, which reduces the risk of food contamination.

3. Soils acidity is variable and constrained largely by land use. The soils of industrial areas are commonly neutral, rarely slightly alkaline, whereas forest soils are acidic.

4. Anthropogenic pollution of the environment originates from historical exploitation and processing of Zn–Pb ores and coal mining, especially from old mining waste dumps.

5. Contamination of aqueous sediments and surface water is related to human impact. It is sourced from mining waters of the ZG Janina hard coal mine, industrial and municipal sewage and eluates from mine waste dumps.

6. Aqueous sediments are polluted by cadmium, lead and zinc and to a lesser extent also by silver, copper and mercury.

7. The surface water is characterised by high variability in the contents of individual elements, acidity and electric conductivity. Salinity of most of the watercourses is related to the discharges of mineralized mining water. Waters of the watercourses draining old mining waste dumps in the areas of Zn-Pb ore mining and the outcropping of Triassic carbonates are enriched in arsenic, calcium, cadmium, lithium, magnesium, lead, sulphates, antimony, uranium, thallium and zinc. Wastewater discharges from coal mine result in contamination of surface water by boron, chlorine, potassium, lithium, molybdenum, sodium, rubidium and antimony.

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