# INTRODUCTION

Geochemical mapping at the scale of 1:25 000 at the Olkusz Sheet M-34-64-A-a (82.5 $km^2$) is a continuation of detailed mapping works initiated in years 1996–1999 by a pilot elaboration entitled “Detailed geochemical map of Upper Silesia 1:25 000 – Sławków map sheet M-34-63-B-b” (Lis, Pasieczna, 1999).

The project was ordered by the Ministry of the Environment and it was financed by the National Fund for Environmental Protection and Water Management.

The area of Olkusz Sheet M-34-64-A-a is located in the eastern part of the most polluted region of Poland – Cracow-Silesia Upland. Distinct geochemical anomalies of Pb–Zn–Cd occur in soils, aqueous sediments and surface water in this region (Lis, Pasieczna, 1995 a, b; 1997). In the area of Olkusz Sheet the main source of geologic-anthropogenic anomalies are ore-bearing dolomites which hosts zinc-lead ores, their exploitation and treatment.

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

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# CHARACTERISTICS OF THE MAP AREA

**Geological and administrative setting.** The area of the Olkusz Sheet belongs in terms of administrative setting to the North-western part of the Małopolska voivodeship. It comprises central part of the Olkusz district (communes: Olkusz and Klucze as well as a small part of the Bukowno commune – south-western part of the map sheet).

Most of the area under study belongs to the Cracow-Częstochowa Upland, and its north-western part belongs to the Silesia Upland (Kondracki, 2000).

The area of the Olkusz Sheet is located in the Biała Przemsza River catchment (the upper Vistula River tributary). The main watercourses are streams: Baba and Witeradówka, and Roznos (Dąbrówka) Canal. The water quality and character of stream-beds were highly changed due to mining drainage and exploitation of groundwater for water supply systems (Adamczyk, 1990).

**Relief and geomorphology.** The area of the Olkusz Sheet is a strongly flattened plateau with altitude up to 400–460 m a.s.l. Western boundary of the plateau is a denudation cuesta with meridian extension (about 100 meters high) formed on outcrops of Jurassic and Triassic carbonate rocks (Plate 1). The cuesta is a regional unit, tectonic in origin (Górecka, 1993). In the north-western part of the Olkusz Sheet (in the Silesia Upland area), there is a denudation formed in Keuper rocks and filled with the Middle Polish Glaciation glaciofluvial sands (Bogacz, Kawulak, 2004). Above the flattened area (300–330 m a.s.l.) there are hill-like elevations built up of Triassic carbonate rocks.

The relief of the Olkusz Sheet is strongly changed in many places. Common forms are historical open-pits and mining shafts of zinc-lead ores and open-pits of rock raw materials. Mining subsidence, mine and post-production waste dumps were formed in the mining areas of the Pomorzany zinc-lead ores mine and former Olkusz zinc-lead ores mine. At the western boundary of the Olkusz Sheet there is a part of the post-flotation pond of the Bolesław Mining and Metallurgy Company producing zinc concentrates from zinc-lead ores. Not long time ago in the western part of the map there were open-pit sand mines, currently wooded.

**Land use.** Essential role in the land usage is played by forests (Plate 3) covering 61% of the area. Due to the natural values the forests are under preservation. The Orle Gniazda Park and numerous monuments of nature were established there (Program..., 2004a, b). The park protects landscape developed on Jurassic rocks (isolated rocks, deep valleys, caves and limestone endemic flora). A characteristic feature of the Park are medieval castles and fortresses, among others ruins of the Rabsztyn castle.

Wastelands and cultivated fields are located in the central and southern part of the Olkusz Sheet, covering 22% and 6% of its area respectively. Areas with industry buildings are located in the Olkusz town area (Plate 2).

**Economy.** Economy in the area of the Olkusz Sheet is based mainly on industry. Only minor part of the area is used for agriculture.

The biggest industrial plant is the Bolesław Mining and Metallurgy Company located in Bukowno – with Olkusz-Pomorzany zinc-lead mines, zinc-lead ores treatment plants and zinc smelter. Other important plants are: enamel factory Emalia, paper factory Klucze and glass factory Jaroszowiec (Program..., 2004b).

Minor companies are owned by private sector and their activities concentrate on trade and services, civil engineering, real estate consultancy, transport, stock management, and communication.

## GEOLOGY AND MINERAL DEPOSITS

Geological structure of the Olkusz Sheet area comprises two structural units: Palaeozoic basement, folded during Variscan orogen, and platform Mesozoic cover.

Devonian and Carboniferous rocks are known from boreholes only.

Plate-like Mesozoic cover (the Silesia–Cracow Monocline) is built of Triassic and Jurassic carbonate rocks (Plate 1). During Alpine orogen, due to formation of the Carpathians, the plate was highly tectonically deformed, mainly cutting by faults.

**Triassic.** Lower Triassic deposits are known from boreholes only. Middle and Upper Triassic rocks are exposed locally on the surface (Kurek, Preidl, 1992). The most common deposits of the Lower Triassic (Buntsandstein) are sandstones and variegated clays, whereas upper ones (Roetian) are dolomites, cavernous limestones and marls. The Middle Triassic (Muschelkalk) rocks comprise limestones, diplopora dolomites and ore-bearing dolomites hosting zinc-lead ores. The latter are epigenetic dolomites (crystalline and cavernous) comprising various units of the Lower Muschelkalk deposits with thicknesses from several meters to about 65 m. The Upper Triassic rocks (claystones, siltstones and Keuper marls) occur in the central part of the Olkusz Sheet area (Plate 1).

**Jurassic** rocks occur in the central and eastern part of the Olkusz Sheet (op. cit.). They comprise conglomerates, sandstones, limestones and marls in the lower units, whereas the upper ones comprise platy limestones, marls and massive limestones.

Lithology of **Quaternary** deposits is highly diversified. Pleistocene sands of the Middle Polish Glaciation with thicknesses up to several tens of meters are dominant in the western part of the Olkusz Sheet area. The North Polish Glaciation deposits are sands filling wide waterless valleys. In the western part of the map area glaciofluvial sands fill the old Pleistocene valley of Pra-Przemsza river (Paulo, Krobicki 2001). Quaternary deposits – rock debris, sands and colluvial tills as well as eolian sands occur locally. Muds, clays, sands, and sometimes peats occur in the bottom of stream valleys.

**Lead-zinc ore deposits.** The area of the Olkusz Sheet has considerable mineral resources. Mining and metallurgy of zinc-lead ores in the Olkusz Sheet area have long traditions since the 11th century (Grzechnik, 1978; Przeniosło, 1995; Paulo, 2001). Since the 12th century until the end of the 18th century the main object of exploitation was galena – the source of lead and silver.

At the beginning exploitation was carried out above groundwater table (Niedzielski, Szostek, 1977; Adamczyk, 1990). Beginnings of drainage of the Triassic rocks date back to the 16th century when several drain adits were built. Underground exploration of zinc-lead ores started in the 19th century; oxidized zinc-lead ores and limonitic iron ore as well as iron sulfides were exploited. Exploitation of sulfide zinc-lead ores was far lower (Liszka, Świć, 2000).

In the 1950's the Bolesław zinc-lead ore mine was extended on reserves of sulfide ores. It existed until 1998. Next discoveries of sulfide ores made the Olkusz mine open in 1968 and the Pomorzany mine in 1974. Since 1979 they have been existing as one plant – Olkusz-Pomorzany.

The zinc-lead ores are hosted by the Middle Triassic ore-bearing dolomites. Ore bodies are irregular nests and lenses of different size, reaching up to several hundred meters length and dozens meters thick (Sass-Gustkiewicz, 1985, 2001). In general the ores fill empty spaces in the rocks (pores, caverns, fissures) in the form of crusts and veins. Tectonic and karstic ore breccias of zinc sulfides (sphalerite, wurtzite, brunckite), lead (galena) and iron (marcasite, piryte, melnikovite) are cement of carbonate rocks. They are accompanied by carbonates (calcite, dolomite) and barite. Today only sulfide zinc-lead ores are exploited which contain average 4.2% of Zn and 1.4% of Pb as well as Cd, Ag and other minor elements (Ney, Smakowski, eds., 2004). Exploited zinc-lead ores are used to produce the zinc concentrate.

Recoverable resources of the Pomorzany deposit are 15.92 mln tons, and the Olkusz deposit – 2.05 mln tons. The mine operating is planned until the year 2013 (Przeniosło, ed., 2005).

**Rock raw materials.** The Olkusz Sheet area is a potential base for rock raw materials such as carbonate rocks, mainly Jurassic limestones, but also Triassic dolomites. Less important are sands and tills. These deposits were exploited in numerous open-pits for local needs.

## HUMAN IMPACT

Natural environment of the Olkusz Sheet is the most degraded part of the Małopolska voivodeship. The source of the pollution is exploitation and treatment of zinc-lead ores (current and historical), industry – concentrated mainly in town Olkusz, local transportation as well as communal economy.

**Atmospheric air pollution.** The most polluting factories are the Bolesław Mining and Metallurgy Company with the Factory of Sulfuric Acid and enamel factory Emalia. The air conditions are also determined by far-reaching emissions coming from the industry located in the Silesia voivodeship (Jaworzno Power Station Group and Katowice Steel Plant – Mittal Steel Polska) and in the Chrzanów district (Siersza Power Plant). There are some pointed sources of pollution – individual furnaces emitting mostly PM 10 dust, whose concentrations exceed standard levels (Ocena..., 2005). The most serious source of pollution is combustion of fuel oil in automobile and truck engines with emission of hydrocarbons, sulphur oxides, nitrogen oxides and metals to the atmosphere.

**Surface water and groundwater pollution.** Exploitation of zinc-lead ores as well as their treatment and zinc smelting at the Bolesław Mining and Metallurgy Company are the biggest hazards for surface water and groundwater (Różkowski, Siemiński, eds., 1995; Liszka, Świć, 2000; Paulo, Krobicki, 2001). Areas currently occupied by this industry have become seriously reduced in relation to the past by using modern, more environmentally friendly technologies (Lis, Przeniosło, 1999). However post-flotation wastes stored in post-flotation pond (near the western border of Olkusz Sheet) are still hazard for environment. Some water from the post-flotation pond is recycled, however, some water infiltrates the pond basement. Waters infiltrating the basement are enriched in sulphates, iron, zinc, lead, cadmium, copper, calcium, and magnesium ions and can migrate into the groundwater (Program..., 2005). Fortunately carbonate rocks of the basement are a natural barrier for wide migration of heavy metals.

Mining activity contributed to forming a vast cone of depression in Triassic and Jurassic water horizon (Adamczyk, 1990).

As a result of intensive drainage of Triassic deposits in years 1974–1986 some streams have been drained. Mining drainage makes pollutants easy to migrate into groundwater from the post-flotation waste pond (Adamczyk, Haładus, 1994), metallurgic waste dump of Bukowno smelter, not isolated communal dump in the former Ujków zinc-lead ore mine (located at the adjacent Sławków Sheet) and liquid wastes from the Klucze paper faktory (Adamczyk, Haładus, 1994; Adamczyk, Motyka, 2000).

Mining of zinc-lead ores in the Olkusz sheet area is about being closed down. After closing down of the mines a restoration of natural water relations is planned in some regions. After restoration of natural water net old springs can regenerate. However, it may cause a danger of local floods (mainly in river valleys) and appearing collapse troughs at locations of mine excavations.

Quality of surface water in the area of the Olkusz Sheet is not satisfactory. Stream water is polluted mainly by nitrates, heavy metals (zinc and lead) and it is also bacteriologically contaminated. The main source of contamination is disposal of communal and industrial sewages into the streams and soil. The biggest watercourse – the Baba Stream is polluted by the discharge of mine water, not-treated sewage from the Olkusz Heat and Power Company and rain water from the Olkusz town. The Olkusz town is sewaraged in 87% (Program..., 2004d).

**Soil pollution.** In soil of the Olkusz Sheet area high concentrations of metals (especially zinc, lead, cadmium and arsenic) have been reported for many years. This pollution is related to mining and smelting-treatment industry of zinc-lead ores as well as to naturally high geochemical background (in soils developed from ore-bearing dolomites). Some degraded areas of previous exploitation of sands and zinc-lead ores are wooded.

## MATERIALS AND METHODS

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

### FIELD WORKS

Soil samples were collected at the regular grid 250x250 m (16 sites per 1 $km^2$). The total number of soil sampling sites was 1364. At every site two samples from depths: 0.0–0.3 m (topsoil) and 0.8–1.0 m (subsoil) were collected. In case of shallow deposited parent rocks the subsoil sample was collected from shallower depth. Soil samples (of about 500 g) were collected by means of a hand probe and were initially dried at the field storage.

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

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

Location of all sampling sites was defined with GPS. Direct measurement with GPS equipment GS 20 Leica has accuracy of ±2–10 m. A GS 20 Leica was equipped with external antenna and system which can register not only coordinates but also additional information (pH and EC of sampled water, data on land development and land use as well as type of soil and aqueous sediment). Coordinates of soil sampling sites were put into read-only memory of GPS equipment, before going out in the field and the sites were next found in the field. For safety reasons all the field data was noted on sampling card (Fig. 2).

### LABORATORY WORKS

#### Chemical analyses

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

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

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

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

The determination of Al, B, Ca, Fe, K, Li, Mg, Na, P, $SiO_2$, Ti and Zn content in surface water samples was done by ICP-AES while the content of Ag, As, Ba, Cd, Cl, Co, Cu, Mn, Ni, Pb, Rb, Sb, $SO_4$, Sr, Tl and U was determined by inductively coupled plasma-mass spectrometry (ICP-MS).

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

The quality control of the analysis was performed by:

– analysis of duplicate samples (5% of total samples),

– analysis of reference materials with certified content of elements studied (2% of total samples),

– analysis of laboratory control samples confirming correct instrument calibration (5% of total samples),

– blank samples (5% of total samples).

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

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

### Grain size analyses of topsoil

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

## DATABASES AND GEOCHEMICAL MAPS PRODUCTION

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

**Geological map** was constructed using Detailed geological map of Poland 1:50,000 Olkusz Sheet (Kurek, Preidl, 1992). Particular vector layers of geological map were combined with topographic base map producing a geological map at the scale of 1:25 000 (Plate 1).

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

Separate databases were prepared for: topsoil, subsoil, aqueous sediments and surface water.

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

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

**Statistical calculations.** Statistical parameters were calculated (average, median, minimum and maximum values) both for the whole sets and subsets of soil, sediments and surface water (Tables 2–6). Subsets for statistical calculations were distinguished according to different media criteria, for example: concentrations of elements in soils under cultivation, forest soils, urban soils and elements content in sediments and water of particular bodies of water.

In the case of some elements (for example Ag, As, Cd, Hg, *etc.*) with the content lower than the value of detection limit for the applied analytical method, all values were converted to half of the detection limit value before making statistical calculations and map production.

**Geochemical maps production.** The following maps were made for the Olkusz Sheet: geological map, land development and land use, the content of organic carbon and grain size of topsoil (1.0–0.1 mm, 0.1–0.02 mm and <0.02 mm); acidity of topsoil and subsoil; acidity and electrical conductivity of surface water; the content of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in topsoil, subsoil and aqueous sediments; the content of Ag, Al, As, B, Ba, Ca, Cd, Cl, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, $SiO_2$, $SO_4$, Sr, Ti, Tl, U and Zn in surface water.

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

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

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

Taking into account comfort of usage by potential customers maps were printed out in slightly smaller format (A3) in relation to the 1:25 000 scale. This operation did not cause omitting any important details of maps.

## RESULTS

### SOILS

Development of soils in the area of the Olkusz Sheet was influenced by multicenturial exploitation of zinc-lead ores which changed their chemical composition and made the area drained.

**Grain size.** Grain size is an important factor influencing the content of chemical elements in soils. Soils of high contribution of clay (<0.02 mm) and silt fractions (0.1–0.02 mm) are usually characterized with high content of many elements and their lower mobility in hypergenic conditions. In the standards and recommendations defining permissible concentrations of metals in soils usually this feature is included accepting higher permissible limits for soils with high contribution of clay fraction and lower concentrations for soils of high content of sand fractions (Kabata-Pendias *et al.*, 1995).

The grain size distribution of topsoil is expressed as fractions: 1.0–0.1 mm – sand, 0.1–0.02 mm – silt, <0.02 mm – clay (Plates 4–6).

Diversity of grain size of topsoil at the Olkusz Sheet M-34-64-A-a is related to geological structure. Very sandy soils (containing >90% of sand fraction 1.0–0.1 mm) are in the areas where parent rocks are Quaternary deposits, mainly Pleistocene fluvioglacial sands and eolian sands (Plate 4). These soils are characterized by small amount (<5%) of silt (0.1–0.02 mm) and clay fractions (<0.02 mm).

In soils developed on pre-Quaternary formations sand fraction content ranges between 50% and 90% (Plate 4). More important in terms of their composition are silt (5–10%; Plate 5) and clay fractions (5–10%; Plate 6).

**Acidity.** Samples of acidic reaction (<6.3) make 36.3% of the topsoils. These are mainly forest and wasteland soils. Soils of neutral reaction make 44.2%, and 19.6% of those soils has alkaline reaction. Forest soils are mainly acidic, rarely strongly acidic or of neutral reactions. Soils of cultivated fields, meadows and wastelands have neutral reaction. Alkaline reaction in topsoil is observed in the town area of Olkusz and ranges up to the mining area of the Zn–Pb ore mine Olkusz in the west, and to outcrops of Jurassic limestone formations in the south (area between Witeradów and Żurada).

Alkaline reaction in subsoil additionaly exists in Jurassic limestone formations in the area of Sieniczno and Olewin, in the region between Olkusz and Klucze, in the neighbourhood of post-flotation waste pond of the ZGH Bolesław and the Pomorzany mine area. In the subsoil percentage of samples of acidic (29.5%) and neutral reactions (41.5%) is lower, however, percentage of samples of alkaline reaction increases (29.0%). A considerable percentage of strongly alkaline samples (pH >8) is observed in the eastern area of the Olkusz town.

**Geochemistry.** Diversification of geochemical background and distinguishing local anomalies of elements is related to spatial distribution of elements inherited after parent rocks in the area of Olkusz Sheet.

The main source of aluminium, barium, calcium, cobalt, chromium, iron, manganese, nickel, and strontium for soil of the Olkusz Sheet area are parent rocks. Spatial distribution of these elements in soil points out on a strong relationship with chemical composition of the bedrock. In the topsoil (and more clearly in the subsoil) high concentrations of the mentioned elements are in soils developed from Triassic and Jurassic rocks. There is a strong correlation between high content of these elements and the pre-Quaternary formations outcrops. High concentration of the elements, reflecting a character of the bedrock chemistry, are clearer visible in geochemical maps of subsoil. Topsoil and subsoil developed on Pleistocene sandy glaciofluvial deposits and eolian sands are characterized by low content of aluminium, barium, calcium, cobalt, chromium, iron, manganese, nickel, and strontium It is connected with poor chemical composition of the bedrock and acidic reaction which makes them leach.

High content of cadmium, zinc, lead, silver, arsenic, copper, mercury, manganese and sulfur were noted in soils in the areas of outcrops of ore-bearing dolomites and close to mines and smelting factories of zinc-lead ores. The highest concentration of these elements was found in topsoil mainly. A very strong reduction of area occupied by soils of anomalous concentration of these elements occurs at the depth of 0.8–1.0 m. This regularity is the most distinct for cadmium, zinc and lead (Table 7).

Industrial activity, both modern and historical, plays significant role in contamination of surface soil by metals. It is well documented by comparison of area sizes occupied by soils of various content of cadmium, zinc, and lead in the subsoil in relation to the topsoil (Table 7). High concentrations of those metals in the subsoil were only found within close existence of ore-bearing rocks or in places of intense metallurgic activity. In the latter case it leads to a very heavy contamination probably quite deeply in the ground both in the area of the Olkusz Sheet and in neighbouring areas (Lis, Pasieczna, 1997).

In the topsoil high anomalies of silver (>2 mg/kg), arsenic (>20 mg/kg), cadmium (>8 mg/kg), copper (>20 mg/kg), mercury (>0,2 mg/kg), lead (>500 mg/kg), and zinc (>1000 mg/kg) are observed in the town area of Olkusz, in the village of Stary Olkusz, at the southern edge of the Pomorzany village and in the area of shafts of the Pomorzany and Olkusz zinc-lead mines. These anomalies are mixed, anthropogenic-geogenic. One of the most important sources of soil contamination by metals are mine waste dumps. Anthropogenic anomaly (vanishing at the depth of 0.8–1.0 m) also occurs in the area of grouped industrial plants in the south-west of the Olkusz town.

Occurrence of intense anomalies of many elements have been noted in the area of Bolesław Mining and Metallurgy Company post-flotation pond, whose eastern part is located within the Olkusz Sheet boundaries. The topsoil and subsoil contains particularly high concentrations of calcium (up to 14.57% and 13.60%), magnesium (up to 5.43% and 5.22%), iron (up to 12.13% and 8.68%), sulphur (up to15.30% and 9.78%), silver (up to 10 mg/kg and 9 mg/kg), arsenic (up to 954 mg/kg and 808 mg/kg), cadmium (up to 142 mg/kg and 81mg/kg), manganese (up to 1220 mg/kg and 1104 mg/kg), mercury (up to 0,36 mg/kg and 0,34 mg/kg), lead (up to 10,200 mg/kg and 7500 mg/kg), and zinc (up to 34,800 mg/kg and 21,300 mg/kg) respectively.

The heavy metal contamination of soils is a problem for the municipal authorities and should be discussed with respect to the land usage. To fit the geochemical data to local authorities needs topsoils of the Olkusz Sheet were classified applying current guideline values (Table 8) established by the Polish Ministry of the Environment (Rozporządzenie…, 2002). The guideline values are based on the average of particular elements in soils for Poland as a whole and also on the assessment if the content of a particular element may have negative effects on the ecosystem or the human health. Guideline values are applied for three-level scale: A (protected areas), B (agricultural, forest and residential areas) and C (industrial areas).

The rule of the classification is that the sample is classified to a particular soil use group if the content of at least one element reaches or exceeds the permissible limit values of this group. Using this classification method, 26.69% of the topsoil samples were classified into group A, 26.17% into group B, and 47.14% into group C (Table 8). Soils of group C occur within areas of high-density housing in the town of Olkusz, on the outskirts of Olkusz, in the area of the Olkusz and Pomorzany Zn–Pb mines, and also in the area of the post-flotation dump. Soils of groups A and B occur mainly in forested areas.

## AQUEOUS SEDIMENTS

Hydrographic net at the Olkusz Sheet area is poor, and some of previously existent watercourses became drained. Mining drainage as well as exploitation of groundwater for water supply systems caused serious disturbances in natural water relationships. The watercourses are receivers of sewage mainly which makes them canals. Reservoirs of stagnant surface water non occure in the area of the Olkusz Sheet. Only a few separate ponds and marshes originated from specific geological framework of the basement and relief are known.

**Roznos (Dąbrówka) Canal.** Water from drained shafts of the Olkusz-Pomorzany Zn–Pb ore mine, post-flotation water (due to treatment of the ores), and sewage treatment plant of the city Olkusz are drained by the Roznos Canal to the Biała River (belonging to the Biała Przemsza River catchment) (Program..., 2004c).

The main feature of geochemistry of the Roznos Canal sediments is high concentration of numerous elements, especially metals and sulphur due to long term activity of mining-processing industry of the Zn–Pb ores.

The most contaminated sediments are those of the upstream of the Roznos Canal. They contain significant amount of lead (up to 33.631 mg/kg; median 19.280 mg/kg), silver (up to 52 mg/kg; median 43 mg/kg), arsenic (up to 670 mg/kg; median 509 mg/kg), cadmium (up to 2251 mg/kg; median 1630 mg/kg) and zinc (up to 394.400 mg/kg; median 292.000 mg/kg). The sediments are also rich in calcium (up to 12.80%; median 2.00%), magnesium (up to 4.10%; median 0.70%), iron (up to 5.80%; median 4.00%) and sulfur (up 13.301%; median 11.200%) – Table 4. The same set of elements of similar concentrations is found in the sediments of the canal in the downstream as well as in alluvial sediments of the Biała River, below the mouths of the Roznos Canal in the Sławków Sheet (Lis, Pasieczna, 1999).

**Baba Stream.** Water from drainage of mine excavations of the Zn–Pb ores flow into the Baba Stream at 179 m3/min. They contain among others: suspension matter, sulphates, chlorides, zinc, lead, cadmium, iron and not cleaned technologic sewage from the Heat & Power Company (Program ..., 2004b). The Baba Stream sediments are contaminated with different chemical compounds (excluding its upper stream above the mouths of the Witeradówka Stream). Just below industrial district of the Olkusz town the stream sediments at the length of about 2.5 km are enriched in silver (up to 10 mg/kg), cadmium (up to 94 mg/kg), cobalt (up to 39 mg/kg), chromium (up to 77 mg/kg), copper (up to 86 mg/kg), nickel (up to 96 mg/kg), lead (up to 1242 mg/kg), and titanium (up to 689 mg/kg). The contamination can be related to the sewage coming from: the enamel factory Olkuska Fabryka Naczyń Emaliowanych Emalia S.A., factory of ventilators, Heat & Power Company, factories of metals, renovation companies, transportation base and others.

High increase of elements content in the Baba Stream sediments is observed below the mouths of the canal with drained water from the Olkusz Zn–Pb mine. The sediments contain high amount of zinc (median 34.000 mg/kg; maximum 322.600 mg/kg) and lead (median 8500 mg/kg; maximum 14.791 mg/kg). They are also enriched in numerous other elements such as: arsenic (up to 269 mg/kg), barium (up to 382 mg/kg), calcium (up to 17.03%), cadmium (up to 369 mg/kg), cobalt (up to 50 mg/kg), iron (up to 4.10%), magnesium (up to 5.57%), manganese (up to 2727 mg/kg), sulfur (up to 3.40%), and strontium (up to 155 mg/kg). High concentration of the mentioned elements was also reported in the case of the Baba Stream sediments and the Sztoła River at the neighbouring Sławków Sheet (Lis, Pasieczna, 1999).

**Witeradówka Stream.** Sediments of the Witeradówka Stream are characterized by low content of elements studied (Table 4). They are only enriched with lead (21–300 mg/kg; median 90 mg/kg) and zinc (68–1222 mg/kg; median 194 mg/kg) – Table 4. The source of metals in the whole catchment of the Witeradówka Stream is probably surface runoff from soils enriched in lead and zinc due to migration of metal-bearing dusts from industrial areas.

**Unnamed little water bodies.** Increased values of cadmium, lead and zinc were found in some sediments of little watercourses without drainage.

In the sediments of little unnamed watercourses and small reservoirs (ponds) in the central part of the Olkusz Sheet (Olkusz, Pomorzany area) content of the elements studied is diversified and usually quite high. The sediments contain arsenic (up to 517 mg/kg), barium (up to 380 mg/kg), calcium (up to 7.43%), cadmium (up to 72 mg/kg), copper (up to 117 mg/kg), iron (up to 7.50%), manganese (up to 2207 mg/kg), lead (up to 5362 mg/kg), strontium (up to 107 mg/kg) and zinc (up to 13.348 mg/kg). Contamination of the sediments with metals originates both from natural sources (erosion of Triassic rocks) and anthropogenic ones (surface runoffs from the mine waste dump areas).

Increased values of cadmium (up to 54 mg/kg), zinc (up to 3256 mg/kg), and lead (up to 615 mg/kg) is observed in the northern part of the Olkusz Sheet in the sediments of ponds developed after disappearing Biała River.

## SURFACE WATER

Water of particular reservoirs differ with characteristic composition of elements and their concentration. Water is slightly alkaline, generally equal pH – 7.5. Slightly acidic (pH 6.1–6.4) and strongly acidic waters (pH 2.9) were found only in two little watercourses with no mouths in the southern part of the Olkusz Sheet area.

Similarly to their sediments the water of Roznos Canal and Baba Stream are very polluted.

**Roznos (Dąbrówka) Canal.** Roznos Canal is one of the most polluted watercourses. Its mineralization expressed by electrical conductivity is high and stable in the whole its part studied (EC 0.68–0.96 mS/cm; median 0.90 mS/cm). The characteristic composition of elements is related to the exploitation and treatment of zinc-lead ores: cadmium (up to 1.8 µg/dm$^3$; median 0.5 µg/dm$^3$), lead (up to 34.4 µg/dm$^3$; median 12.0 µg/dm$^3$), zinc (up to 1116 µg/dm$^3$; median 143 µg/dm$^3$), magnesium (up to 46.8 mg/dm$^3$; median 20.7 mg/dm$^3$), iron (up to 1.15 mg/dm$^3$; median 0.05 mg/dm$^3$), sulphates (up to 290 mg/dm$^3$; median 142 mg/dm$^3$), molybdenum (up to 8.58 µg/dm$^3$; median 8.37 µg/dm$^3$), nickel (up to 14 µg/dm$^3$; median 8 µg/dm$^3$), antimony (up to 5.46 µg/dm$^3$; median 4.88 µg/dm$^3$), and thallium (up to 3.78 µg/dm$^3$; median 0.38 µg/dm$^3$). Maximum concentration of arsenic (20 µg/dm$^3$) was found in the area of the Dąbrówka shaft.

Another set of the elements in the water of the Roznos Canal includes: boron (up to 714 µg/dm$^3$; median 669 µg/dm$^3$), chlorine (up to 104 mg/dm$^3$; median 91 mg/dm$^3$), potassium (up to 19.0 mg/dm$^3$; median 17.9 mg/dm$^3$), lithium (up to 24 µg/dm$^3$; median 22 µg/dm$^3$), sodium (up to 95.3 mg/dm$^3$; median 89.9 mg/dm$^3$), phosphorus (up to 3.21 mg/dm$^3$; median 2.90 mg/dm$^3$), rubidium (up to 21.2 µg/dm$^3$; median 18.6 µg/dm$^3$), sulphates (up to 290 mg/dm$^3$; median 142 mg/dm$^3$), and manganese (up to 370.4 µg/dm$^3$; median 52.9 µg/dm$^3$). The main source of this assemblage of elements is sewage from the sewage treatment plant in Olkusz. The increased concentration is also caused by disposing post-production liquid waste from Klucze paper factory, which contaminated soils in the northern part of the Olkusz Sheet (Adamczyk, Motyka, 2000). The components of the waste penetrated the ground with rain waters, reached the Pomorzany mine, and next with mine water were discharged into the Roznos Canal.

**Baba Stream.** The water mineralization of the Baba Stream is diversified. The EC values in the upstream range 0.64–0.80 mS/cm. In the area of discharge of water from the Olkusz-Pomorzany mine the EC values increase (above 1 mS/cm), and in downstream the EC values decrease down to 0.55 mS/cm.

The diversity of mineralization of water from the Baba Stream is shown in their chemical composition. In water of the middle part of the Stream (below industrial district) serious values of boron (up to 541 µg/dm$^3$), calcium (up to 125.9 mg/dm$^3$), chlorine (up to 110 mg/dm$^3$), cobalt (up to 3.1 µg/dm$^3$), copper (up to 1.8 µg/dm$^3$), potassium (up to 11.5 mg/dm$^3$), lithium (up to 16 µg/dm$^3$), magnesium (up to 23.3 mg/dm$^3$), manganese (up to 612 µg/dm$^3$), sodium (up to 112 mg/dm$^3$), phosphorus (up to 1.23 mg/dm$^3$), rubidium (up to 10.6

μg/dm$^3$), silica (up to 10.5 mg/dm$^3$), and strontium (up to 199.7 μg/dm$^3$) were noted. The source of this pollution is mainly not-treated technological sewage from the Heat and Power Company in Olkusz.

Chemical composition of water in the Baba Stream changes below discharge area of waters from the Olkusz–Pomorzany mine. The main metals contaminating the water are cadmium (up to 1.9 μg/dm$^3$), cobalt (up to 1.4 μg/dm$^3$), magnesium(up to 21.4 mg/dm$^3$), molybdenum (up to 3.98 μg/dm$^3$), nickel (up to 6.7 μg/dm$^3$), lead (up to 27.7 μg/dm$^3$), antimony (up to 2.19 μg/dm$^3$), thallium (up to 0.7 μg/dm$^3$), and zinc (up to 528 μg/dm$^3$). Very characteristic feature is the equal concentration of the elements which means they are derived from the point source.

**Witeradówka Stream.** Water of the Witeradówka Stream is slightly mineralized (EC is within 0.38–0.40 mS/cm) and contain low values of all components studied.

**Unnamed little water bodies.** In the water of little unnamed streams and small reservoirs (ponds) of stagnant waters in the central part of the Olkusz Sheet values of the elements studied are diversified and usually low. In some reservoirs increased values of barium (up to 224 μg/dm$^3$), calcium (up to 142.6 mg/dm$^3$), lithium (up to 14 μg/dm$^3$), strontium (up to 337.9 μg/dm$^3$), and uranium (up to 14.48 μg/dm$^3$) were found. They may originate both from natural sources (erosion of Triassic rocks) and anthropogenic ones (runoffs from mine waste dumps).

Increased values of boron (up to 525 μg/dm$^3$), calcium (up to 2140.4 mg/dm$^3$), copper (up to 2.4 μg/dm$^3$), iron (up to 9.15 mg/dm$^3$), and sodium (up to 121.1 mg/dm$^3$) were found in the northern part of the Olkusz Sheet in water from ponds in the Klucze village area.

## CONCLUSIONS

**1.** The content of analyzed elements indicates the significant pollution of topsoil, subsoil, sediments of various water bodies and surface water with heavy metals and other chemical elements at the Olkusz Sheet area.

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

**3.** The natural (geological) source of pollution are outcrops of Triassic carbonate deposits with zinc-lead ores.

**4.** Mining, ore processing and smelting of zinc-lead ores are the main sources of anthropogenic pollution of soils, sediments and surface water. Other important sources of pollution are connected with the related activities (e.g., mine dumps and disposal of saline mine waters into surface waters).

**5.** Up to now the exploitation of zinc-lead ores has been main industrial activity in the area, but during next several years the zinc-lead ore mines will be closed down. Reducing this activity will result in lower pollution of natural environment, but the abandoned industrial areas and non-recultivated waste dumps could be menace themselves.

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