

## INTRODUCTION

The Nowa Góra Sheet M-34-64-A-c area is located in the southern part of the Silesia-Cracow Upland.

At the Nowa Góra Sheet area the main source of geologic-anthropogenic anomalies are ore-bearing dolomites which hosts zinc-lead ores, and their historical exploitation and treatment. One of the oldest centre of zinc-lead ores mining and metallurgy on the European Continent was located there. Preserved traces of mining activity, which became the source of hazard for natural environment, are visible until today. Occurrence of the numerous old mine waste dumps does not affect much the forested post-mining areas but in the agricultural areas, they are a significant source of soil contamination. In the past the poor oxidized zinc ores were stored not only at the mine waste dumps but they were also scattered over the fields (Górecki, Szwed, 2005, 2006) making the additional source of soil pollution.

The extraction and treatment of Pb–Zn ore around the Silesia-Cracow region have caused environmental pollution similar to that found in other regions of Europe where mining for non-ferrous metal ores, e.g. Plovdiv region in Bulgaria (Atanassov, Angelova, 1995; Velitchkova *et al.*, 2003), Příbram in Czech Republic (Rieuwerts, Farago, 1996), Smolnik region in Slovakia (Cicmanova, 1996), Plombiers–La Calamin district in Belgium (Swennen *et al.*, 1994; Cappuyens *et al.*, 2005), Derbyshire area in central England (Cotter-Howells, Thornton, 1991; Thornton, 1994), the Harz Mountains in Germany (Gäbler, Schneider, 2000) or polymetallic mineralization e.g. on the border between the Czech Republic and Germany (De Vos *et al.*, 2005) is common.

The Nowa Góra Sheet area is famous for its exceptional natural and tourist values. Majority of the area is covered with forests and is known as Dolinki Krakowskie Park. There is also a tourist route called the Old Mining Route.

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

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## CHARACTERISTICS OF THE MAP AREA

**Geographical and administrative setting.** The area of the Nowa Góra Sheet is located in the northwestern part of Małopolska voivodeship; in terms of the administrative

setting it belongs to Chrzanów, Olkusz and Cracow poviats. Its northern part comprises Olkusz commune area, middle – Trzebinia commune and southeastern one – Krzeszowice commune.

As far as the division on physic-geographic units, the area belongs to the Silesia-Cracow Upland and majority of the area belongs to a lower unit – the Cracow-Częstochowa Upland (Kondracki, 2000).

In the southern part there are springs of the following streams: Czernka, Miękinka, Filipówka and Dulówka flowing into Rudawa River, and in the western part there are springs of two left-bank tributaries of Przemsza River – Kozi Bród Stream and Sztoła River.

**Relief and geomorphology.** Nowa Góra Sheet area is a plateau built of Triassic and Upper Jurassic rocks (Kurek, Preidl, 1993). The terrain surface is slightly wavy, in the south it is covered with loess, and cut by deep valleys of Czernka, Miękinka, Filipówka and Dulówka streams. Between the valleys and northwards of their springs altitude is usually 350–460 m a.s.l. The highest elevation (462 m a.s.l.) is in Płoki village area. Almost the whole area is characterized by water deficit.

**Land use.** In the past an intense exploitation of Zn–Pb ores was carried out at the Nowa Góra Sheet area.

Nowadays essential role in the land use is played by forests covering 50% of the area. Due to the natural values the forests are under preservation. The biggest forest is Puszcza Dulowska forest, rich in natural habitats. Part of the forest was degraded due to the environmental changes caused by historical exploitation of Zn–Pb ores.

Agricultural soils are mostly fertile but difficult for farming due to very diversified relief. Dominant group of soils are *Rendzinas* but *Cambisols*, *Podsols* and *Histosols* are also frequent (Nieć *et al.*, 2001).

Within the Sheet boundaries there are areas of protected landscape, soil and forests (Kawulak, 1997). Essential part of the protected area makes Park Krajobrazowy Dolinki Krakowskie – landscape park preserving landscape of Jurassic carbonate rocks. A nature-landscape protection area of the Sztoła River valley is going to be established there as well.

## GEOLOGY AND MINERAL DEPOSITS

The area of the Nowa Góra Sheet is located at the eastern edge of the Upper Silesia Coal Basin. Four structural units can be distinguished here (Kurek, Preidl, 1992, 1993), and three of them crop out: Early Paleozoic (Carboniferous), Permian–Mesozoic (Permian, Triassic and Jurassic) and Cenozoic (Quaternary). Old Paleozoic formation (Cambrian and Silurian deposits) is known from boreholes only.

**Carboniferous** deposits crop out fragmentary in the southeastern part of the sheet area in Czernka Stream valley. These are claystones, mudstones and sandstones of the Namurian/Visean (Malinowice beds) and Visean limestones (Plate 1).

**Permian** deposits exposure are represented by carbonate Myślachowice conglomerates as well as volcanic Filipowice tuffs and Karniowice travertines.

**Triassic** rocks crop out in the western part of the area under study. These are mainly Middle Triassic carbonate deposits: Gogolin beds – limestones and marls, diplopore dolomites and Zn–Pb ore-bearing dolomites hosting oxidized zinc ores and galena.

In some areas deposits of Roethian – dolomites, cavernous limestones and marls as well as Keuper clays occur. Several-meter thick packages of sandy-clayey lower Buntsandstein deposits were found in drillings.

The **Jurassic** comprises Middle and Upper Jurassic rocks. The Middle Jurassic contains conglomerates, sandstones and oolitic limestones about 10 m thick. They are

overlaid by Upper Jurassic limestones and marls several tens of meters thick. Jurassic carbonate rocks crop out mainly in the northern part of the Nowa Góra Sheet area.

The **Quaternary** deposits are diversified genetically and lithologically. Pleistocene deposits hold glaciofluvial sands, colluvial clay deposits, and loesses (covering southern and southeastern part of the sheet area). In the north of the Nowa Góra Sheet large area is occupied by sands and colluvial clay deposits as well as eolian sands. Holocene silts, clays and sands fill in the bottoms of stream valleys.

**Mineral deposits.** Currently exploited mineral deposits include: limestones, dolomites and sands.

Some deposits (Triassic diplopore dolomites in Niesułowice–Lgota deposit and Carboniferous limestones documented in the Kamienice deposit) cannot be exploited because of their location within the landscape park area.

Mining of the **Zn–Pb ores** has long traditions in the Nowa Góra Sheet area although their exploitation was abandoned long time ago. Most of the ore bodies were exploited from 15th to 19th century. Up to date there are still traces of old Zn–Pb ores mining (Górecki, Szwed, 2005), which are partly effaced by agricultural activities. They can be found in the Ostrężnica and Płoki villages mainly.

The village name Płoki, where exploitation of Zn–Pb ores was conducted, was noted in documents as early as in the 30's of the 14th century. After year 1400 very poor and dispersed ores were exploited and the exploitation reached water-bearing horizon. Existence of the mines until the 16th century is confirmed by historical notes. In the middle of the 15th century Zn–Pb ores mining developed in the village Psary. Some information on mines in Lgota from the turn of the 15th and 16th centuries has been found as well.

Poor resources of the Zn–Pb ores decided about short-term mining activities but small mine waste dumps are still visible, mainly in the vicinity of Galman, Lgota, Nowa Góra and Czerna villages.

The Mining and Metallurgy Company in Siersza was established in 1854. The Company gathered zinc-lead ore mines, coal mine and zinc smelter. The Zn–Pb ore mine in the Ostrężnica–Lgota area named Katarzyna, located in the Galman village area operated until 1912. It is known from archived mining maps that the mine area covered about 5 km<sup>2</sup>. The Katarzyna mine adjoined some areas of different Zn–Pb ore mines of total area of about 3.5 km<sup>2</sup>.

The zinc-lead mining activities growing in the 19th century is evidenced by the old waste dumps of mines near Nowa Góra and Czerna. The historical mines exploited both the sulfide and oxidized ores. In the forests around Płoki, Lgota and Nowa Góra villages there are numerous preserved shafts, adits and mine waste dumps. More than 400 post-exploitation open pits covering area of 8 km<sup>2</sup> were found in the Lgota area. Diameter of some pits is up to 20 m with up to 7 m depth.

## HUMAN IMPACT

**Atmospheric air.** Atmospheric air at the Nowa Góra Sheet area is slightly polluted (Ocena..., 2005; Raport..., 2005). The area is mainly covered with forests, and built-up area is limited to several small villages only. Local sources of pollution are house-heating and local roads emissions. Some of the pollution comes from the emissions of industrial plants localized westwards of the sheet boundaries in Chrzanów and Trzebinia towns.

**Surface water and groundwater.** The main source of water quality declining are surface and point pollutions. Surface sources of pollution are difficult to estimate and control. They are the result of intensive fertilization of agricultural soil, applying plant protection

products and old Zn–Pb ores mining. The point pollution sources are mainly the sites of community and industrial sewage discharge, illegal dumps, septic tanks and petrol stations.

An unfavourable phenomenon for groundwater is occurring mine depression cone which is related to the zinc-lead ore mining in the Olkusz Sheet area draining Triassic and Jurassic water-bearing horizons.

Groundwater in the area of the Nowa Góra Sheet occurs abundantly in the Triassic and Jurassic carbonate rocks making two groundwater reservoirs. Water in the southern part of the Nowa Góra Sheet is in danger due to mineral fertilizers spread over the arable fields, historical Zn–Pb ore mining dumps and the lack of the sewage system net. Within the Nowa Góra Sheet boundaries there is no communal dump, however, many illegal dumps which are dangerous for surface water and groundwater can be found there.

**Soils.** Soil transformation results from both natural and anthropogenic factors. The main natural factors are water and wind erosion and mass movements. On the other hand, anthropogenic factors are historical open-pit and underground mining activity, ground levelling for construction and economic activity leading to activate natural processes in the environment.

Traces of historical Zn–Pb ore mining influence soil pollution. Plenty of old dumps, stockpiles and tailings, containing mixed material from the mining, processing and smelting, create a significant problem. In the forested post-mining areas such hazard is practically not important but close to the villages, in the woodless, agricultural areas, old mine waste dumps can be the source of excessive soil contamination. It is known from the Mining Authority archives that oxidized poor zinc-lead ores were scattered not only over the mine waste dumps but also over the fields.

Earlier studies show that soils in the neighbourhood of Lgota, Ostrężnica, Czerna and Nowa Góra contain heavy metals (such as zinc, lead, cadmium, arsenic and thallium) exceeding permissible limit values accepted in Poland for agricultural soils (Sass-Gustkiewicz *et al.*, 2001). In the historic mining areas topsoil contains up to 5.5% zinc, 300 mg/kg of arsenic and >250 mg/kg of cadmium. In the subsoil concentration of heavy metals is also high especially in the areas of the oldest mining and metallurgy activity.

## MATERIALS AND METHODS

Studies done in years 2003–2005 comprised study of published and archival materials, choosing sampling sites at topographic maps at a scale of 1:10 000, samples collection, laboratory works, set up of field and laboratory databases, elaboration of a vector topographic base map, 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<sup>2</sup>). The total number of soil sampling sites was 1330. At every site were collected two samples from depths: 0.0–0.3 m (topsoil) and 0.8–1.0 m (subsoil). In case of shallow deposited parent rocks the subsoil sample was collected from shallower depth. Soil samples (of about 500 g) were collected by means of a hand probe and were initially dried at the field storage.

Samples of aqueous sediments and surface water were collected from various bodies of water – streams, melioration ditches, canals and pools. 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  $\mu\text{m}$ ) and acidized with nitric acid.

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

## LABORATORY WORKS

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

**Sample preparation.** 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.

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

The determination of Al, B, Ca, Fe, K, Li, Mg, Na, P,  $\text{SiO}_2$ , 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,  $\text{SO}_4$ , 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  $\pm 10\text{--}15\%$ , based on duplicate samples. For the surface water samples, analytical precision is about  $\pm 10\text{--}20\%$  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, ditches, pools), road communication net (with division into classes of roads), land development (with division into village development and 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: number of samples, sampling coordinates, a site description (land development, land use, district, commune, town), soil texture, date of collection, sampler name and analytical data.

Aqueous sediment and surface water databases contain: number of samples, sampling coordinates, a site description (land development, land use, district, commune, town), type of water body (stream, ditch, pool) 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, e.g.: concentrations of elements in soils under cultivation, forest soils and elements content in sediments and water of particular bodies of water.

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

**Geochemical maps production.** The following maps were made for the Nowa Góra 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<sub>2</sub>, SO<sub>4</sub>, 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 Nowa Góra Sheet. Colour surface maps were constructed for several neighbouring sheets to avoid disagreement of element distribution at the sheet borders. The data was interpolated to generate a regular grid using Inverse Distance to a Power method. A multi-grade colour scale was selected to present the elements distribution. The 1:25 000-scale map sheet of interest was then cut out from several neighbouring sheets after

interpolation. The colour surface maps were produced using arbitrarily chosen colour classes (most often using geometric progression).

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

For publication reasons, geochemical maps were made by presenting the following pairs in one plate: topsoils and aqueous sediments as well as subsoils and surface 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

**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 (0.1–0.02 mm) fractions are usually characterised by high content of many elements and their low mobility in hypergenic conditions. In the standards and recommendations defining permissible concentrations of metals in soils this feature is usually included accepting high permissible limits for soils with high contribution of clay fraction and low concentrations for soils of high content of sand fractions (Kabata-Pendias *et al.*, 1995).

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

Sandy and strongly sandy soils occur in the predominant part of Nowa Góra Sheet area. Strongly sandy soils containing >90% of 1.0–0.1 mm fraction occur as a wide belt from the northwestern edge of the map sheet to the Gorenice village (Plate 4). Small lobes of these soils were also noted in the western part of the sheet. Parent rocks of these soils are mainly sands and colluvial tills as well as eolian and glaciofluvial sands (Plate 1).

Soils developed on the Jurassic and Triassic rocks with dominant silt or clay fractions prevail in the southern and southeastern part of the Nowa Góra Sheet. Contribution of silt and clay fractions of the soils is high, reaching even >30% of silt fraction (Plate 5) and >15% of clay fraction (Plate 6).

Soils developed from the Pleistocene loesses which occur southeastwards of the Psary–Ostrężnica–Gorenice belt are characterised by a very specific grain size composition. Contribution of sand fraction rarely exceeds 10%, and dominant are silt (0.1–0.02 mm) and clay fractions (<0.02 mm).

**Acidity.** Topsoil of acidic (pH 5.0–6.3) or neutral reactions (pH 6.3–7.4) is dominant in the area, respectively 38.5% and 38.7%. Contribution of strongly acidic soils (pH <5.0) is 16.9% and alkaline – 5.9%. Subsoils are mostly neutral (54.2%) and alkaline reactions (15.9%). Amount of acidic subsoil is 26.6% and strongly acidic – 3.4%.

In many cases soil reaction is weakly differentiated and related to their use. At the arable fields and forest areas average reaction is the same – 6.7 (Table 4). The topsoil of forests is more acidic – median pH 5.4.

Alkalization of topsoil is brought by human activity. It is proved by high values of pH of soils in the village areas (median pH 7.1) related to the emission of suspended dust of hard coal combustion for house-heating.

A direct relationship of acidity and chemical composition of bedrock is observed for subsoil. Soils developed from the Middle Triassic limestones and dolomites in the western

part of the sheet area as well as from the Upper Jurassic limestones in the northern part are characterised by alkaline reaction.

**Geochemistry.** Chemical composition of soil was, to a large extent, inherited from the parent rocks. Due to pedogenetic processes the soil composition is being more or less changed in relation to the parent rock chemistry although the most common, the main geochemical features of parent rocks are preserved.

Distribution of chemical elements in soil of the Nowa Góra Sheet area shows a strong relationship with chemical composition of parent rocks. Soils developed from Pleistocene glaciofluvial sands, eolian sands and sandy colluvial deposits (with sandy fraction content of over 90%), contain low values of aluminum, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, strontium, titanium and vanadium. It refers to both topsoil and subsoil.

Soils developed from Triassic and Jurassic carbonate rocks are characterised by particularly high content of calcium (Plates 19, 20) and enrichment in most elements studied. This phenomenon is very well observed in subsoil. Soils originated from the Middle Triassic carbonate rocks are also enriched with magnesium reaching maximum 7.18% in topsoil (Plate 36) and 10.13% in subsoil (Plate 37).

Very specific chemical composition of soils originated from Pleistocene loesses was noted in the southern and southeastern part of the Nowa Góra Sheet. They are characterised by high values of aluminum, cobalt, iron, chromium, titanium and vanadium, and an exceptional subsoil enrichment in these elements in relation to topsoil. However, these soils show low values of calcium and magnesium.

Soil use affects significantly content of many studied elements. Forest soils (mainly sandy soils) are poor in all elements studied (Tables 2, 3). They are only enriched in organic carbon – usually 1.5–6.0% (Plate 18). Agricultural soils (currently often fallows) as well as soils of gardens, allotments and lawns are slightly enriched in most of the elements. Built-up village areas are more affected by the antropogenic factors than non built-up areas (Table 2).

Elements related to Triassic zinc-lead ores formation as well as mining and smelting activities include: cadmium, zinc, lead, arsenic, mercury, magnesium and calcium. Area of the elements occurrence in topsoil is bigger than in subsoil. 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 (Plates 22, 47, 62). This regularity is the most distinct for cadmium, zinc and lead (Table 7).

High anomalies of cadmium, zinc and lead were found in the area of old Zn–Pb ores mine Katarzyna. In the area of anomaly cadmium content in topsoil exceeds 16 mg/kg (Plate 21), lead – 1000 mg/kg (Plate 46) and zinc – 5000 mg/kg (Plate 61). In this area high concentrations of arsenic (Plates 14, 15) and mercury (Plates 32, 33) in topsoil and subsoil can be observed too. Maximum concentrations in the topsoil and subsoil were found: arsenic 375 mg/kg and 329 mg/kg; mercury 0.48 mg/kg and 1.39 mg/kg respectively.

Less significant anomalies of cadmium, lead and zinc were noted in the spring areas of Miękinka, Czernka and Filipówka streams, where ore-bearing dolomites crop out. In the past oxidized zinc ores were exploited there (Cygorijni, 1970; Górecki, Szwed, 2006).

Similar high values of cadmium, lead and zinc in soils were noted by Sass-Gustkiewicz and others (2001). It was shown that topsoil in the Lgota, Ostrężnica, Czerna and Nowa Góra areas contains up to 5.5% of zinc, up to 300 mg/kg of arsenic and >250 mg/kg of cadmium. These authors reported that high concentrations of heavy metals occur also in the deeper soil layer, especially in the areas of the oldest mining and smelting activity between Nowa Góra and Czerna.

The heavy metal contamination of soils is a problem for the municipal authorities and should be discussed with respect to the land use. To fit the geochemical data to local



authorities needs topsoils of the Nowa Góra Sheet area 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 content 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 effect on the ecosystem or the human health. Guideline values are applied for the three-level scale: A (protected areas), B (agricultural, forest and residential areas) and C (industrial areas); Table 8.

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, 21.73% of the topsoil samples were classified into group A, 36.32% into group B, and 41.95% into group C (Table 8).

Soils classified into the group C contain high values of arsenic, cadmium, lead and zinc. They occur in forests area of the Katarzyna mine which exploited oxidized zinc ores – between Psary, Płoki, Lgota and Ostreżnica, and in the spring areas of Miękinia, Czernka and Filipówka streams, where ore-bearing dolomites crop out and also locally in the Nowa Góra area (Plate 63).

## AQUEOUS SEDIMENTS

Table 3 lists element content in aqueous sediments in streams of the Nowa Góra Sheet.

Within the Nowa Góra Sheet there are only a few streams. In the northern part of the sheet there are springs of Sztoła River and Witeradówka Stream. Upper course of Kozi Bród Stream occurs at the western boundary of the sheet, and springs of Czernka, Miękinia, Filipówka and Dulówka Streams are located in the south of the sheet area. There are also few stagnant water reservoirs.

**Sztoła River.** Sediments of Sztoła River contain low values of many elements – average content (median) is: silver – <1 mg/kg, aluminum – 0.11%, arsenic – <5 mg/kg, barium – 15 mg/kg, calcium – 0.23%, cadmium – <1 mg/kg, cobalt – <1 mg/kg, chromium – 3 mg/kg, copper – 1 mg/kg, iron – 0.21%, mercury – <0.05 mg/kg, magnesium – 0.11%, manganese – 33 mg/kg, nickel – 1 mg/kg, phosphorus – 0.007%, sulphur – 0.009%, strontium – 3 mg/kg, titanium – 93 mg/kg and vanadium – 1 mg/kg.

High concentrations of lead (up to 361 mg/kg), cadmium (up to 9 mg/kg), manganese (up to 362 mg/kg), sulphur (up to 0.230%) and zinc (up to 670 mg/kg) noted in sediments are related to the outcrops of the Triassic ore-bearing dolomites.

**Witeradówka Stream.** Sediments of a short (c. 0.5 km), upper course of Witeradówka Stream are very poor in all elements studied.

**Kozi Bród Stream.** At the whole course of Kozi Bród Stream sediments contain low and little differentiated content of aluminum, arsenic, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, sulphur, titanium, and vanadium. Increased concentrations of lead (up to 750 mg/kg) and zinc (up to 1183 mg/kg) were observed in the area of outcrops of Triassic ore-bearing dolomites.

**Dulówka Stream and its catchment.** Sediments of the upper course of Dulówka Stream, which drains Pleistocene loesses as well as Middle Triassic dolomites and limestones are enriched in aluminum (median 0.29%), barium (median 48 mg/kg), calcium (median 1.18%), cadmium (median 5 mg/kg), copper (median 11 mg/kg), iron (median 0.59%), magnesium (median 0.38%), manganese (median 167 mg/kg), sulphur (median 0.040%), strontium (median 19 mg/kg) and titanium (median 106 mg/kg). High concentrations of lead (median 217 mg/kg), cadmium (up to 34 mg/kg), and zinc (median 821 mg/kg) are related to

the Triassic ore-bearing dolomites occurring in the upper part of the stream catchment. Sediments of numerous tributaries of Dulówka Stream area characterised by low contents of the elements studied.

**Filipówka Stream and its catchment.** Catchment area of Filipówka Stream is built mainly of Pleistocene loesses. Triassic limestones and dolomites as well as Permian Myślachowice conglomerates crop out only in the stream valleys. Chemical composition of sediments of Filipówka Stream and its tributaries is similar to the chemistry of Dulówka Stream sediments; values of cadmium, lead, and zinc are a little lower.

**Czernka Stream and its catchment.** The chemical composition of the geological structure of the catchment is similar to that of the Filipówka Stream (Plate 1) and Czernka Stream; sediments contain similar content of particular elements. Cropping out numerous Middle Triassic carbonates in the catchment makes enrichment of sediments in lead (median 201 mg/kg) and zinc (median 363 mg/kg).

**Sediments of small streams (unnamed).** In the area under study the sediments of a little unnamed watercourse occurring between the valley of Kozi Bród Stream and Płoki village are worth mentioning. The sediments are enriched in arsenic (up to 139 mg/kg), barium (up to 68 mg/kg), calcium (up to 8.06%), cadmium (up to 155 mg/kg), iron (up to 2.63%), magnesium (up to 4.04%), manganese (up to 680 mg/kg), lead (up to 29,570 mg/kg), and zinc (up to 36,230 mg/kg). The source of so high concentrations of these elements are Zn–Pb ore mine wastes of the nearby Katarzyna mine.

## SURFACE WATER

**Sztoła River.** The studied water samples show slightly alkaline reaction (pH 7.7) and electrical conductivity at 0.26–0.46 mS/cm, pointing out their low mineralization. The water is characterised by high content of barium (median 143.3  $\mu\text{g}/\text{dm}^3$ ) and low content of following elements (medians): silver ( $<0.05 \mu\text{g}/\text{dm}^3$ ), aluminum (14  $\mu\text{g}/\text{dm}^3$ ), arsenic ( $<2 \mu\text{g}/\text{dm}^3$ ), boron (21  $\mu\text{g}/\text{dm}^3$ ), calcium (66.2 mg/dm<sup>3</sup>), cadmium ( $<0.2 \mu\text{g}/\text{dm}^3$ ), chlorine (14 mg/dm<sup>3</sup>), cobalt ( $<0.2 \mu\text{g}/\text{dm}^3$ ), copper ( $<0.5 \mu\text{g}/\text{dm}^3$ ), iron ( $<0.01 \text{mg}/\text{dm}^3$ ), potassium (0.8 mg/dm<sup>3</sup>), lithium ( $<2 \mu\text{g}/\text{dm}^3$ ), magnesium (25.6 mg/dm<sup>3</sup>), manganese (0.8  $\mu\text{g}/\text{dm}^3$ ), molibdenum (0.22  $\mu\text{g}/\text{dm}^3$ ), sodium (1.7 mg/dm<sup>3</sup>), nickel (1  $\mu\text{g}/\text{dm}^3$ ), phosphorus ( $<0.05 \text{mg}/\text{dm}^3$ ), lead (0.2  $\mu\text{g}/\text{dm}^3$ ), rubidium (0.7  $\mu\text{g}/\text{dm}^3$ ), antimony ( $<0.05 \mu\text{g}/\text{dm}^3$ ), sulphates (60 mg/dm<sup>3</sup>), silica (6.0 mg/dm<sup>3</sup>), strontium (106  $\mu\text{g}/\text{dm}^3$ ), thallium (0.10  $\mu\text{g}/\text{dm}^3$ ), titanium ( $<2 \mu\text{g}/\text{dm}^3$ ), uranium (0.65  $\mu\text{g}/\text{dm}^3$ ) and zinc (29  $\mu\text{g}/\text{dm}^3$ ).

**Witeradówka Stream.** Water of Witeradówka Stream is slightly mineralized (EC within 0.40–0.41 mS/cm), slightly alkaline (pH 7.6) and contains low values of all elements studied.

**Kozi Bród Stream.** Slightly alkaline (pH 7.7) and low mineralized (median EC 0.34 mS/cm) water of Kozi Bród Stream contains low values of almost all the elements studied. High content of cadmium (up to 1.5  $\mu\text{g}/\text{dm}^3$ ), zinc (up to 137  $\mu\text{g}/\text{dm}^3$ ), and barium (up to 120.96  $\mu\text{g}/\text{dm}^3$ ) is related to the occurring of the Triassic Zn–Pb ore-bearing dolomites outcrops.

**Dulówka Stream and its catchment.** Water of Dulówka Stream catchment is slightly alkaline (pH 7.7) and characterizes with low conductivity (EC 0.46–0.51 mS/cm). It contains very low values of silver, aluminum, arsenic, cadmium, cobalt, copper, lithium, phosphorus, antimony and titanium, rarely exceeding detection limits of used analytical methods. The water is slightly enriched in boron (19–55  $\mu\text{g}/\text{dm}^3$ ), calcium (67.13–184.77 mg/dm<sup>3</sup>), chlorine (9–16 mg/dm<sup>3</sup>), iron ( $<0.01$ –0.03 mg/dm<sup>3</sup>), potassium (0.9–2.6 mg/dm<sup>3</sup>), manganese ( $<0.5$ –16.1  $\mu\text{g}/\text{dm}^3$ ), molibdenum (0.08–0.46  $\mu\text{g}/\text{dm}^3$ ), sodium (2.9–6.5 mg/dm<sup>3</sup>), nickel (1.9–3.5  $\mu\text{g}/\text{dm}^3$ ), lead ( $<0.2$ –1.4  $\mu\text{g}/\text{dm}^3$ ), rubidium (0.7–2.5  $\mu\text{g}/\text{dm}^3$ ), sulphates (59–78 mg/dm<sup>3</sup>), silica (5.5–14.6 mg/dm<sup>3</sup>), thallium ( $<0.05$ –0.28  $\mu\text{g}/\text{dm}^3$ ) and uranium (0.46–1.95

$\mu\text{g}/\text{dm}^3$ ). Elements with increased values are: barium (59.85–24.81  $\mu\text{g}/\text{dm}^3$ ), magnesium (8.6–25.7  $\text{mg}/\text{dm}^3$ ), strontium (92.8–870.8  $\mu\text{g}/\text{dm}^3$ ) and zinc (15–942  $\mu\text{g}/\text{dm}^3$ ).

**Filipówka Stream and its catchment.** Water of the Filipówka Stream and its catchment is slightly alkalic (pH 7.8) and has low conductivity (EC 0.47–0.51 mS/cm). The content of silver, aluminum, arsenic, cadmium, cobalt, copper, lithium, phosphorus, lead, antimony, titanium and thallium in studied water samples is very low. Slightly higher content can be observed for boron (<10–28  $\mu\text{g}/\text{dm}^3$ ), calcium (72.15–118.68  $\text{mg}/\text{dm}^3$ ), chlorine (7–21  $\text{mg}/\text{dm}^3$ ), iron (<0.01–0.13  $\text{mg}/\text{dm}^3$ ), potassium (0.9–2.6  $\text{mg}/\text{dm}^3$ ), manganese (0.9–94.5  $\mu\text{g}/\text{dm}^3$ ), molibdenum (<0.05–0.19  $\mu\text{g}/\text{dm}^3$ ), sodium (2.8–12.6  $\text{mg}/\text{dm}^3$ ), nickel (1.7–2.8  $\mu\text{g}/\text{dm}^3$ ), rubidium (0.9–4.1  $\mu\text{g}/\text{dm}^3$ ), sulphates (37–69  $\text{mg}/\text{dm}^3$ ), silica (8.0–26.0  $\text{mg}/\text{dm}^3$ ), uranium (0.44–1.18  $\mu\text{g}/\text{dm}^3$ ) and zinc (<3– 5  $\mu\text{g}/\text{dm}^3$ ). The water is enriched with barium (28.46–310.43  $\mu\text{g}/\text{dm}^3$ ), magnesium (14.4–33.6  $\text{mg}/\text{dm}^3$ ) and strontium (70.7–1219.5  $\mu\text{g}/\text{dm}^3$ ).

**Czernka Stream and its catchment.** Water of the Czernka Stream catchment is slightly alkalic (pH 7.6–7.7) and has low conductivity (EC 0.45–0.60 mS/cm). It contains very low values of silver, aluminum, arsenic, cadmium, cobalt, copper, iron, lithium, phosphorus, lead, antimony, and titanium. Slightly higher are contents of boron (up to 84  $\mu\text{g}/\text{dm}^3$ ), barium (18.6–35.6  $\mu\text{g}/\text{dm}^3$ ), calcium (57.65–90.49  $\text{mg}/\text{dm}^3$ ), chlorine (8–21  $\text{mg}/\text{dm}^3$ ), potassium (0.5–6.7  $\text{mg}/\text{dm}^3$ ), manganese (1.8–21.8  $\mu\text{g}/\text{dm}^3$ ), molibdenum (0.11–0.43  $\mu\text{g}/\text{dm}^3$ ), sodium (2.6–9.2  $\text{mg}/\text{dm}^3$ ), nickel (2.5–3.3  $\mu\text{g}/\text{dm}^3$ ), rubidium (0.7–2.2  $\mu\text{g}/\text{dm}^3$ ), sulphates (40–94  $\text{mg}/\text{dm}^3$ ), silica (7.4–10.4  $\text{mg}/\text{dm}^3$ ), thallium (<0.05–0.28  $\mu\text{g}/\text{dm}^3$ ), strontium (42.9–82.2  $\mu\text{g}/\text{dm}^3$ ), uranium (0.28–0.68  $\mu\text{g}/\text{dm}^3$ ) and zinc (25–78  $\mu\text{g}/\text{dm}^3$ ).

**Water of small streams (unnamed).** Water of small unnamed watercourse, localized between the valley of the Kozi Bród Stream and the Płoki village contains high concentrations of barium (up to 159.07  $\mu\text{g}/\text{dm}^3$ ), magnesium (up to 22.2  $\text{mg}/\text{dm}^3$ ), lead (up to 18.2  $\mu\text{g}/\text{dm}^3$ ) and zinc (up to 200  $\mu\text{g}/\text{dm}^3$ ). The source of these elements occurrence are probably wastes of the ancient Zn–Pb ores mine Katarzyna.

## CONCLUSIONS

1. The content of analyzed elements indicates the significant pollution of topsoil, subsoil, sediments of some water bodies and surface water with heavy metals and other chemical elements at the Nowa Góra 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. Historical mining and ore processing of zinc-lead ores are the main sources of anthropogenic pollution of the soils, sediments and surface water.

## LITERATURA REFERENCES

- ATANASSOV I., ANGELOVA I., 1995 – Profile differentiation of Pb, Zn, Cd and Cu in soils surrounding lead and zinc smelter near Plovdiv (Bulgaria). *Bulgarian Journal of Agricultural Science*, **1**: 343–348.
- ASLIBEKIAN O., MOLES R., 2003 – Environmental risk assessment of metals contaminated soils at silvermines abandonem mine site, Co Tipperary, Ireland. *Environ. Geochem. Health*, **25**: 247–266.

- CABAŁA S., 1994 – Ocena walorów przyrodniczych doliny rzeki Sztoły. Uniwersytet Śląski, Katowice.
- CAPPUYNS V., SWENNEN R., VANDAMME A., NICLAES M., 2005 – Environmental impact of the former Pb–Zn mining and smelting in East Belgium. *J. Geochem. Explor.*, **88**: 6–9.
- CICMANOVA S., 1996 – Hydrogeological and hydrogeochemical problems of the Smolnik pyrite deposit. Guide to excursion environmental geochemical baseline mapping in Europe: 12–15. Geological Survey of Slovak Republic, Spisska Nova Ves.
- COTTER-HOWELLS J., THORNTON I., 1991 – Sources and pathways of environmental lead to children in a Derbyshire mining village. *Environ. Geochem. Health*, 13: 127–135.
- CYGORIJNI K., 1970 – Hutnictwo cynku w XIX wieku w okręgu krakowskim. *Rudy Metale*, **5**: 280–283.
- DE VOS W., BATISTA M.J., DEMETRIADES A., DURIS M., LEXA J., LIS J., MARSINA K., O’CONNOR P.J., 2005 – Metallogenic mineral provinces and world class ore deposits in Europe. *W: Geochemical atlas of Europe. Part 1*: 43–49. Geological Survey of Finland, Espoo.
- GÄBLER H.E., SCHNEIDER J., 2000 – Assessment of heavy-metal contamination of floodplain soils due to mining and mineral processing in the Harz Mountains, Germany. *Environ. Geol.*, **39**: 774–782.
- GÓRECKI J., SZWED E., 2005 – Pozostałości dawnego górnictwa kruszcowego na Ziemi Krzeszowickiej. *Pr. Nauk. Inst. Gór. PWroc.*, **111**, Konferencje, 43.
- GÓRECKI J., SZWED E., 2006 – Pozostałości dawnego górnictwa kruszcowego na Ziemi Krzeszowickiej. Internet: <http://www.teberia.pl/>
- GRZECHNIK Z., 1978 – Historia dotychczasowych poszukiwań i eksploatacji. *W: Poszukiwanie rud cynku i ołowiu na obszarze śląsko-krakowskim. Pr. Inst. Geol.*, **83**: 23–42.
- ISO 11464. 1999. Soil quality – pretreatment of samples for physico-chemical analyses. International Organization for Standardization.
- ISO 11885. 1996. Water quality – determination of 33 elements by inductively coupled plasma atomic emission spectroscopy. International Organization for Standardization.
- KABATA-PENDIAS A., PIOTROWSKA M., MOTOWICKA-TERELAK T., MALISZEWSKA-KORDYBACH B., FILIPIAK K., KRAKOWIAK A., PIETRUCH C., 1995 – Podstawy oceny chemicznego zanieczyszczenia gleb. Metale ciężkie, siarka i WWA. Biblioteka Monitoringu Środowiska. Warszawa.
- KAWULAK M., 1997 – Objąsnienia do Mapy geologiczno-gospodarczej Polski 1:50 000, ark. Olkusz. Państw. Inst. Geol. Warszawa.
- KONDRACKI J., 2000 – Geografia regionalna Polski. Wyd. Nauk. PWN. Warszawa.
- KUREK S., PREIDL M., 1992 – Szczegółowa mapa geologiczna Polski 1:50 000, ark. Olkusz. Wyd. Geol. Warszawa.
- KUREK S., PREIDL M., 1993 – Objąsnienia do Szczegółowej mapy geologicznej Polski 1:50 000, ark. Olkusz. Wyd. Geol. Warszawa.
- LIS J., PASIECZNA A., 1995a – Atlas geochemiczny Polski 1:2 500 000. Państw. Inst. Geol. Warszawa.
- LIS J., PASIECZNA A., 1995b – Atlas geochemiczny Górnego Śląska 1:200 000. Państw. Inst. Geol. Warszawa.
- LIS J., PASIECZNA A., 1997 – Anomalie geochemiczne Pb–Zn–Cd w glebach na Górnym Śląsku. *Prz. Geol.*, **45**, 2: 182–189.
- LIS J., PASIECZNA A., 1999 – Szczegółowa mapa geochemiczna Górnego Śląska 1:25 000. Promocyjny arkusz Sławków. Państw. Inst. Geol. Warszawa.

- LISZKA J., ŚWIĆ E., 2000 – Zakłady Górniczo-Hutnicze „Bolesław”. Dzieje – Wydarzenia – Ludzie. Bukowno.
- MOLENDĄ D., 1960 – Górnictwo kruszców. W: Zarys dziejów górnictwa na ziemiach polskich (red. J. Pazdur). T. 1: 120–162. Wyd. Górn.-Hutn. Katowice.
- NIEĆ M., KAWULAK M., SALAMON E., 2001 – Mapa geologiczno-gospodarczo-geologiczna w skali 1:25 000 miasta i gminy Trzebinia. Inst. Gosp. Sur. Miner. i Energią, PAN. Kraków.
- OCENA jakości powietrza w województwie małopolskim w 2004 r., 2005. WIOŚ Kraków. Internet. <http://www.krakow.pios.gov.pl/>
- PAZDUR J., PIETRASZEK E., 1961 – Górnictwo rud metali nieżelaznych. W: Zarys dziejów górnictwa na ziemiach polskich (red. J. Pazdur). T. 2: 91–106. Wyd. Górn.-Hutn. Katowice.
- RAPORT o stanie środowiska naturalnego w województwie małopolskim w 2004 r., 2005. WIOŚ Kraków. Internet. <http://www.krakow.pios.gov.pl/>
- RIEUWERTS J., FARAGO M., 1996 – Heavy metal pollution in the vicinity of a secondary lead smelter in the Czech Republic. *Appl. Geochem.*, **11**: 17–23.
- ROZPORZĄDZENIE Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi. D.U. Nr 165 z dnia 4 października 2002 r., poz. 1359.
- SASS-GUSTKIEWICZ M., MAYER W., GÓRALSKI M., LEACH D.L., 2001 – Zawartość metali ciężkich w glebach na obszarach eksploatacji rud Zn–Pb w rejonach olkuskim i chrzanowskim. Warsztaty 2001 Przywracanie wartości użytkowych terenom górniczym: 189–208. PAN-IGSMiE, WUG. Kraków.
- SWENNEN R., VAN KEER I., DE VOS W., 1994 – Heavy metal contamination in overbank sediments of the Geul river (East Belgium): its relation to former Pb–Zn mining activities. *Environ. Geol.*, **24**: 12–21.
- THORNTON I., 1994 – Mining on the environmental; local, regional and global issues. *Appl. Geochem.*, **11**: 355–361.
- VELITCHKOVA N., PENTCHEVA E.N., DASKALOVA N., 2003 – ICP-AES investigation on heavy metal water and soil pollution in Plovdiv Region (Bulgaria). Scientific Publications „Ecology”, 141, Book 2.