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INTRODUCTION

The 1:25,000 geochemical mapping in the Zabrze map sheet M-34-62-B-a is a continuation of the detailed mapping project that commenced in 1996–1999 with the pilot map sheet of Sławków of the Detailed Geochemical Map of Upper Silesia (Lis, Pasieczna, 1999). By 2016, 17 map sheets had been developed. The work was financed by the National Fund for Environmental Protection and Water Management.

The map sheet area is located in the central part of the Silesian Voivodeship in the western portion of the Upper Silesian Industrial Region, which is the most heavily industrialized and urbanized area of Poland. The map sheet area spans parts of the cities of Zabrze and Ruda Śląska.

The main factor affecting the changes in natural environment is the current and historical mining of hard coal. The coal mining activity, which has been developing most intensely since the mid-19th century, coal processing (coking plants, power and thermal stations), and the ore-processing industries (zinc and iron) are responsible for the formation of geological-anthropogenic anomalies of a number of chemical elements in soils, sediments in inland reservoirs, and surface water (Lis, Pasieczna, 1995a, b, 1997). Underground mining excavations have resulted in the formation of depressions on the earth's surface (Pszonka, 2007), giving rise to changes in the hydrographic network. In contrast, numerous slag heaps have appeared due to the accumulation of waste on the ground surface.

The results of geochemical studies, presented on the maps with a comprehensive explanatory text and data tables, show the current quality of soils, sediments in inland reservoirs and surface water against the natural regional background and in relation to the legal regulations.

The information provided in this report can be useful in assessing local land use plans, making decisions concerning environmental constraints, giving water-legal permits, assessing groundwater hazards, and discharging duties imposed upon district governors by the Environmental Protection Law, i.e. conducting regular soil quality tests within the framework of state monitoring system.

The digital version of the atlas is available at http://www.mapgeochem.pgi.gov.pl The following specialists participated in the preparation of this report:

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- A. Pasieczna statistical calculations;
- T. Kołecki, W. Markowski, A. Pasieczna construction of geochemical maps;
- W. Ogrodowczyk geological map compilation.

CHARACTERISTICS OF THE MAP AREA

Geographical and administrative setting. The study area is part of the Katowice Upland which is the central area of the Silesian Upland (Kondracki, 2009). In administrative terms the map sheet area is located in the central part of Silesian Voivodeship. It spans the central and south-western quarters of Zabrze city (Mikulczyce, Centrum, Guido, Zaborze, Biskupice, Pawłów, Kończyce, Zandka and Makoszowy) and the north-western quarters of Ruda Śląska city (Ruda, Nowy Bytom, Bielszowice and Wirek). A small area in the northeast is situated within the borders of Bytom city, an area located near the western boundary of the map sheet – within the borders of Gliwice city, and that in the southwest – within the borders of the Gliwice district.

Relief and geomorphology. The geological basement of the study area is composed of Carboniferous, Triassic and Neogene deposits covered by Quaternary glacial tills (Wyczółkowski, 1957; Machowski, 2010).

The landscape of this area is relatively flat with a general trend of descending westward. Gentle hills and heights (up to 308 m a.s.l.) are marked in the eastern part of the map sheet in Ruda Śląska. The lowest elevations (about 220 m a.s.l.) are found in the west, in the Kłodnica River and Potok Bielszowicki Stream (Kochłówka) valleys.

The area is affected by anthropogenic impact and sprinkled with depressions filled with water bodies, which have formed as a result of mining activity and extraction of common mineral deposits (sand, gravel). There are also mine and post-industrial heaps and piles.

Land use. The land use structure is as follows: 30% – urban built-up areas (Pl. 2), 10% – industrial areas (smelters, coking plants, mines, settling ponds, waste piles and heaps), and <1% – rural areas.

Non-built areas include lawns and roadside green belts (23%), and forests (22%). Urban parks, allotment gardens and wasteland account for approximately 2% each, arable land -4%, and meadows -3% (Pl. 3). A small fraction of the study area is occupied by water reservoirs and railway premises.

Urban green squares, lawns, parks and allotments are distributed irregularly between the areas of industrial and housing development. In the west of the map sheet area (north of the Sośnica-Makoszowy mine) there is a large park (Park Powstańców Śląskich), woody in nature (Aktualizacja..., 2014). The southern area of the map sheet is crossed by the A4 motorway, whereas its central part – by the Central Rail Line (E-30) of international and domestic significance, and by the central highway connecting the cities of the Upper Silesian agglomeration (Studium..., 2014). The forests, playing a protective role in the zone of industrial impact within the Upper Silesian Industrial Region, cover the south-western part of the map sheet (Aktualizacja..., 2011, 2014).

Urban built-up areas include low and high residential housing and service housing areas (educational institutions with adjacent areas of sports fields, hospitals and shopping centres). Industrial zones and their infrastructure include areas of hard coal mine facilities, steel mills, coking plants and power plants, as well as sewage treatment plants and railway sidings.

The economy of the study area is associated predominantly with hard coal mining in the following mines: Sośnica-Makoszowy, Bielszowice, Pokój and Halemba-Wirek, whose mining areas are located in the southern and eastern part of the map sheet (Kompania...).

The Sośnica-Makoszowy mine was established in 2005 as a result of merger of the independent mines of Sośnica and Makoszowy into a single mining unit. Shaft sinking in the Makoszowy mine took place in 1900, and the first coal was extracted in 1906. The Sośnica mine started its activity in 1917.

The Bielszowice mine was built in 1896–1904. Its name and mining areas have changed many times. Currently, it conducts mining operations in Ruda Śląska.

The Pokój mine is among the oldest mines with its beginnings dated back to 1752. In its current form it has been active since 1995, when it was merged with the Wawel mine (Kompania...). This mine runs a modern enrichment processing plant and produces power coal.

At the south-eastern boundary of the map sheet, some mining fields of the Halemba-Wirek mine are located.

Part of the mining area of the Zakład Górniczy Siltech mine is located in the northern part of the map sheet. The mine was established in 2000 and extracts the remnants of coal deposits of the former Pstrowski mine (Zakłady...).

In the Guido quarter of Zabrze there was a coal mine founded in 1855. Currently, it is a monument being an example of reclamation of industrial areas and their use for educational and tourist purposes. The Guido mining open-air museum is open to the public and listed in the register of monuments as the Guido Monument Mine (Zabytkowa...).

The metallurgical sector in the map sheet area is represented by the Pokój Steelworks in Ruda Śląska and the Zabrze Steelworks in Zabrze.

Zabrze also hosts one of the largest producers of coke in Poland in the Jadwiga coking plant that has operated since 1884 under different names. It is located near the Zabrze power station. In the period 1990–2000 the coking plant became a modern factory producing highest-quality coke, concurrently maintaining appropriate standards of environmental protection, and therefore, in 2003, it was deleted from the list of plants most harmful to the environment in the Silesian Voivodeship (Koksownia...).

A significant industry sector is the production of machinery and equipment for the mining industry, represented by the Zabrzańskie Zakłady Mechaniczne machinery manufacturer, Kopex Machinery Group, Carbomech and Powen-Wafapomp Group.

In the study area there are also municipal boiler houses, Zespół Ciepłowni Przemysłowych Carbo-Energia thermal power plants, and a number of facilities of renovation-construction and transport sectors. In recent years, commercial and service activities have developed widely, which replace the restructured heavy industry.

GEOLOGY AND MINERAL DEPOSITS

The Zabrze map sheet area covers the northern part of the Upper Silesian Coal Basin (USCB), a borderland of a few structural units: Zabrze Dome, Concordia Trough and the southern slope of the Main Saddle. It is a part of the Palaeozoic Variscan structure cut by numerous faults. Its geological structure has been very well explored by a great number of boreholes and mining operations. The stratigraphic section is represented by the Carboniferous, Triassic, Neogene and Quaternary systems (Buła, Kotas, ed., 1994).

Carboniferous rocks occur on the surface and under a thin cover of Quaternary deposits in the central and eastern parts of the map sheet (Pl. 1). In the remaining area they are found at greater depths and under a cover of Pleistocene glacial tills, as well glaciofluvial and glacial sands and gravels, locally Triassic limestones and dolomites, and shallow-marine Miocene deposits. Their top is at the greatest depth in the Kłodnica valley, about 350 m b.g.l. The oldest known deposits are represented by the Brzeżne Beds of the Upper Carboniferous Paralic Series (Namurian A). They are overlain by limnic deposits referred to as the Upper Silesian Sandstone Series of the Upper Namurian (Namurian B and C), and the Lower Westphalian Mudstone Series (Westphalian A and B). The total thickness of these series in the map sheet area is about 2000 m (Jureczka et al., 2005).

A characteristic feature of the Paralic Series is its sedimentary cyclicity. The coal seams are usually overlain by claystones passing into mudstones, overlain in turn by coarseclastic sediments: fine-grained sandstones, occasionally medium- and coarse-grained. The sandstone again grade into mudstones and claystones which are overlain by the next coal seam. The entire series contains numerous coal seams and sediments with marine, brackish and freshwater fauna. The thickness of the Paralic Series in the study area is estimated at approx. 800 m (*op.cit.*). In the area of Zaborze (a quarter of Zabrze), its upper member is exposed on the surface – the Poręba Beds. The lowest members of the Paralic Series occur directly under Triassic rocks in the north-western part of the map sheet.

The Upper Silesian Sandstone Series (Jejkowice Beds, Saddle Beds and Ruda Beds) is represented by grey fine- and medium-grained sandstones, locally coarse-grained sandstones and conglomerates attaining a thickness of 350–400 m (Wilanowski *et al.*, 2009). The interbeds of claystones and mudstones are commonly up to several metres in thickness. The characteristic feature is the relatively frequent occurrence of coal seams with a thickness of 5 m, locally more than 10 m. The Saddle Beds host the USCB's thickest coal seam 510,

currently almost completely mined out. Deposits of this series usually occur on the surface, forming fairly extensive outcrops in the east of the map sheet area.

The Mudstone Series is represented by the Załęże Beds corresponding to the Westphalian A, and in the uppermost part also by the Orzesze Beds of the Lower Westphalian B. This series is very monotonous in terms of lithology with dominant mudstones and claystones containing fine-grained sandstone interbeds that usually attain several metres in thickness. The whole series, attaining the thickness of 200-250 m, typically shows the prevalence of aleuritic-pelitic sediments over coarse-clastic ones. It also includes a significant number of coal cyclothems, most of them containing coal seams (*op.cit*.). These deposits, which are gently folded and erosionally truncated, subcrop at the sub-Miocene and sub-Quaternary surface in the south of the map sheet. On the surface they outcrop in the south-western margin of the map sheet.

The Lower and Middle **Triassic** deposits unconformably overlie Upper Carboniferous rocks in the north and the north-western part of the map sheet, attaining a thickness of 130 m in the Zabrze-Mikulczyce area. They form the southern limb of the Triassic Bytom Trough. The Triassic lithological section is represented by sands, sandstones, clays, claystones and mudstones of the Świerklaniec Beds, roethian dolomites, marls and limestones, Gogolin limestones and vitriolic clays (Horzemski, 1978), ore-bearing dolomites as equivalents of the Górażdże, Terebratula and Karchowice beds, and locally also top members of the Gogolin Beds (Gruszczyk, 1956; Gałkiewicz, Śliwiński, 1985).

They are overlain by Quaternary sands and eluvial loams, as well as by Miocene marine clays in the northwest. On the surface there are only limestones of the Karchowice Beds, exposed in a small outcrop at Mikulczyce (Wyczółkowski, 1957).

Neogene deposits are represented by Miocene marine clays, muds, sands, gravels, marls, limestones, sandstones, gypsum, anhydrites, rock salt and tuffites occurring at the sub-Quaternary surface across much of the map sheet area. The contact with the underlying Carboniferous and Triassic deposits is erosional. They fill Triassic depressions, attaining a thickness of 50 m, or occur at shallow depths under Quaternary deposits. The maximum thickness of the Miocene deposits is found in the Kłodnica Graben (up to 200 m in the Zabrze-Makoszowy area).

Quaternary deposits cover about 80% of the map sheet area with a layer of highly variable thickness ranging from a few metres in upland areas to more than 100 m in the Kłodnica fossil valley in the south-western part of the map sheet. Outside the Kłodnica valley, in topographic depressions, the thickness of the Quaternary cover is commonly between 30

and 60 m. In addition to fluvial deposits, these are also predominantly glacial tills and glaciofluvial sands and gravels. The Holocene is represented by fluvial and swamp deposits of modern river valleys. These are fine-grained sands grading upward into swamp muds. They attain a thickness of 3 m and fill depressions, oxbow lake basins and river channels.

Large areas are covered by anthropogenic grounds that have formed as a result of long-lasting hard coal mining operations. Clusters of mine heaps and settling tanks occupy considerable areas (up to 2 km²). Over vast areas of urban agglomerations there is a few-metres-thick layer of anthropogenic grounds (embankments).

Mineral deposits. Eight multi-seam **hard coal** deposits have been documented in the map sheet area (Szuflicki *et al.*, ed., 2014). These are: Centrum-Szombierki, Bobrek-Miechowice, Sośnica, Halemba, Pokój, Makoszowy, Zabrze-Bielszowice and Jadwiga 2, lying partly or totally within the limits of the map sheet.

The largest economic resources of hard coal, up to 400–500 million tonnes, have been documented in the Sośnica, Makoszowy and Zabrze-Bielszowice deposits. In the Halemba deposit, hard coal resources have been documented to a depth of 1050–1100 m, and in the Zabrze-Makoszowy deposit – partly to a depth of 1200–1250 m.

The economic resources are represented by coal seams of the Orzesze Beds (group 300), Ruda Beds (group 400) and Saddle Beds (group 500), and in the northern part of the study area, also by the Poręba Beds. The coal types in this area include power coal (type 32–33) and coking coal (type 34–35). Coking coal occur generally in the lower portions of the deposits from the central, south-western and southern parts of the map sheet (Makoszowy, Halemba and Zabrze-Bielszowice deposits). The thickness of the individual economic coal seams is variable, ranging between 1 and 10 m. The quality parameters of the coal are highly diverse. Its calorific value varies from 16,500 to 35,000 kJ/kg, the ash content is in the range of 2–44%, and the sulphur content is from 0.08% to 2.5%. The best quality coal comes from the Saddle Beds. It contains the lowest amounts of ash (up to 10%) and sulphur (almost 1%), and its calorific value is 35,000 kJ/kg. Coal seams of these beds are characterised by considerable thicknesses and a relatively small number of gangue intergrowths. Coal from the Ruda and Orzesze beds contains more sulphur and ash (from several to 40%) due to numerous gangue intergrowths.

Most of the mining areas are threatened by highly ranked natural risks, including methane, dust, fire and rock bursts.

Hard coal mining in the study area has a long history dating back to the 18th century. The Pokój mine is one of the oldest mines in the USCB (Historia...). The first licence for coal mining was issued in 1752 for the Brandenburg mine (later renamed to Wawel). Since 1791, coal has been mined in the present-day Zabrze-Bielszowice mine (formerly Królowa Luiza mine).

Currently, hard coal mining is carried out by four mines of the Kompania Węglowa holding, and by the private-owned Siltech mine that has extracted coal from the Jadwiga 2 deposit since 2002. Extraction is carried out using the high-wall mining system, sporadically with the hydraulic filling. The hard coal production rates are variable, ranging from 0.16 million tonnes from the Jadwiga 2 deposit to approximately 2 million tonnes from the Zabrze-Bielszowice deposit. Coal extraction from the Centrum-Szombierki and Bobrek-Miechowice deposits was carried out from the 19th century to the 1990s.

Hard coal deposits are accompanied by **methane** that occurs in a sorbed form which means that it is bound physicochemically with hard coal and dispersed coal particles, and its content in coal increases with depth. In the study area, methane is documented down to a depth of about 1100–1250 m as an accompanying mineral deposit in the Sośnica, Halemba and Zabrze-Bielszowice deposits. It is extracted together with coal and partly used for heating. The total economic methane resources in these deposits are about 3,242.22 million m³ (Szuflicki *et al.*, ed., 2014).

The study area abounds in **clays for building ceramics**. Four deposits of Upper Carboniferous weathering loams, clays and clay shales have been documented: Bielszowice-Ruda Śląska, Ruda, Pawłów and Bielszowice II, and the Zabrze deposit of Quaternary tills (*op.cit.*).

Weathering loams of the Upper Carboniferous clay shales are exposed on the surface or occur under a thin, 1-m-thick cover of Quaternary deposits in the Ruda Śląska and Pawłów areas. These are bedded deposits with a simple geological structure, locally, in the lower part, with coal and sandstone interbeds. The thickness of the mineral deposit is considerable (up to 17 m) and its quality is good. Clay raw materials were extracted in the study area already in the 19th century, but all of the deposits are currently abandoned. The clays and loams were used by numerous brickyards for the production of brick and other ceramic products.

The Quaternary tills of the Zabrze deposit have been extracted since the 1930s and used in the production of solid brick.

Working pits that have formed due to the extraction of the clays, clay shales and loams are commonly used as landfills of industrial and municipal wastes owing to very good sealing conditions of these rocks, and are ultimately subjected to land reclamation. Reserves that have remained in the deposits are unrecoverable and most of them should be deleted from the national registry of mineral deposits.

In the southern part of the map sheet area there is a small portion of the Borowa Wieś **filling sand deposit**. Due to the parameters of the sands (about 99% of the grain size <2 mm) they have been used over decades as a filling material in the nearby coal mines. Currently, much of the deposit area is occupied by a reclaimed and active landfill of the Zabrze-Bielszowice mine. The land use type entails the necessity of deleting the remaining resources of this deposit from the national registry of mineral deposits.

HUMAN IMPACT

Natural environment in the study area has undergone transformation predominantly as a result of hard coal mining, and the metallurgical, coking and thermal power industries. The relief has been modified by numerous deformational events (continuous deformation in the form of troughs and depressions, and discontinuous deformation – sinkholes). The relief changes gave rise, in turn, to modification in the hydrographic network. Additionally, the natural environment is adversely affected by mine waste gathered on piles, as well as coal muds deposited in settling tanks of coal mines. Activities of the other industries, of the trade and service sector, and of the raw materials transport sector contribute to the contamination of land surface, waters and atmospheric air.

Atmospheric air. The quality of atmospheric air is affected by particulate matter and gas emission of industrial provenance, low emission from individual household sources, linear emission from transportation sources, and trans-border emission (Aktualizacja..., 2014).

The greatest amounts of contaminants are emitted to the air by the following industrial companies: Zabrze thermal power station, Zespół Ciepłowni Przemysłowych Carbo-Energia thermal power stations, Pokój Steelworks (galvanizing manufacturer), coal mines and local boiler houses (Aktualizacja..., 2011, 2014; Raport.., 2013). Individual household sources (affecting low emission) are located mainly in the Zaborze, Pawłów and Makoszowy quarters of Zabrze (PONE..., 2013). Low emission is the result of combustion of low-quality fuels in household heating systems used in housing units, and is more intense in winter seasons. As a result of heavy car traffic, emission of exhaust gases also steadily increases.

Results of studies carried out within the framework of national environmental monitoring indicate that the study area is contaminated by high amounts of particulate matter PM10 and PM2,5, and benzo(a)pyrene (Informacja WIOŚ...).

Surface water and groundwater. The map sheet area is located within the right side of the drainage basin of the Kłodnica River and is drained by its tributaries: Potok Bielszowicki Stream (Kochłówka), Czarniawka River and Bytomka River. These watercourses show high natural gradients that facilitate effective rainwater removal. Additional elements of the hydrographic network are water reservoirs that form predominantly as a result of land subsidence due to mining activity, and are characterised by high variations in their areal extent over years (Machowski, 2010).

The Bytomka River channel is partly engineered, and in the Zabrze area, some river sections are covered (Studium..., 2014). The river receives sewage from the Miechowice, Bobrek and Rozbark sewage treatment plants.

The Kłodnica River, flowing across the south-western part of the study area, is engineered along this river reach (Nocoń *et al.*, 2006).

The Potok Bielszowicki Stream channel is also engineered and, in its near-mouth section, the channel has been modified (reshaped and raised) to enable gravity flow of water, which was blocked by terrain subsidence due to coal mining. The actual flow rate of the stream water is enhanced by the influx of foreign water – municipal and industrial sewage and mine water (Studium..., 2014).

The Czarniawka River headwaters are located near a cross-cut of the former sand railway in Ruda Śląska. In the area of Zabrze the river flows in a deep valley of steep slopes (*op.cit.*). It is recharged mainly by atmospheric precipitation and, in its upper reach, by a few minor watercourses.

The results of national environmental monitoring prove that these rivers and streams carry poor quality water, as evidenced by the classes of biological and physico-chemical contamination (Ocena...). The poor water quality is due to the discharges of municipal and industrial sewage as well as mining water from hard coal mines (Studium..., 2011). They are contaminated by suspension, solutes (mainly chlorides and sulphates introduced by mine water), and bacteriological contaminants and biogenic substances (supplied as a result of unsustainable wastewater management). The water quality is also affected by leachate from mine heaps and mining waste piles.

Studies of the water from anthropogenic lakes that formed as a result of mining activity (so-called Stawy Makoszowskie ponds) show the presence of small amounts of phosphates, nitrates and chlorides as well as contamination by heavy metals (Machowski, 2010).

In the map sheet area there are three Major Groundwater Reservoirs (MGR) that do not have protection zones established, and the groundwater quality is variable (Kleczkowski ed., 1990; Aktualizacja..., 2014).

As a result of intense and prolonged drainage by coal mines and numerous water intakes, vast cones of depression have developed and their recharge system has changed. They are recharged directly through the outcrops along the contact of the Triassic aquifer with the ground surface, or indirectly through a layer of Quaternary (permeable or semi-permeable) deposits. The groundwater quality is influenced primarily by pollution outbreaks on the ground surface (Studium..., 2011).

Soils. Soils of many areas of the map sheet have been heavily altered by the current and historical activity of industry (including deposition of mine waste on heaps and piles, changes in the water regime, and formation of post-mining lakes in depressions), development of urban functions and infrastructure, and particulate matter fallout. Soil degradation includes draining, acidification, waterlogging and contamination by heavy metals and other toxic compounds (Aktualizacja..., 2011, 2014; Jechna ed., 2012).

The soil quality is also affected by chemical composition of atmospheric precipitation. Monitoring of the chemistry of precipitation and the infiltration of contaminants into the bedrock has shown that 65% of precipitation in the study area is acidic with pH <5.6 (Liana *et al.*, 2014). The bedrock receives great amounts of sulphates (19.92 kg/ha), total nitrogen (11.18 kg/ha) and chlorides (9.61 kg/ha), and much smaller amounts of heavy metals: zinc (0.443 kg/ha), copper (0.0305 kg/ha), lead (0.0503 kg/ha), cadmium (0.00399 kg/ha), nickel (0.071 kg/ha) and total chromium (0.0018 kg/ha).

Contamination by heavy metals (cadmium, zinc and lead) is found predominantly in the eastern part of the map sheet. The highest cadmium concentration (>10 mg/kg) was measured in soils of the floodplain of the Bytomka River. Areas of elevated concentrations of zinc and lead occur along the border with Bytom (Aktualizacja..., 2014).

Heaps. Gangue, separated from coal during mechanical processing of rock, and tailings are partly used in mines as an additive in hydraulic filling. The remaining part is deposited in piles on the ground surface.

Areas around smelters and steelworks abound in heaps of tailings and fragments of furnace casing. This is primarily metallurgical slag, but also molding materials, refractory debris, sludge and other industrial sediments. Smelting waste is partly used as road aggregate.

MATERIALS AND METHODS

Research conducted in the years 2013–2016 included a study of published and archival materials, location of soil sampling sites on 1:10,000 topographic maps, sample collection, and measurements of geographic coordinates at sampling sites, chemical analysis of samples, development of field and laboratory databases, development of vector topographical base map, statistical calculations, compilation of geological map and construction of geochemical maps, and interpretation of study results. The sequence of workflow steps is illustrated in the attached diagram (Fig. 1).

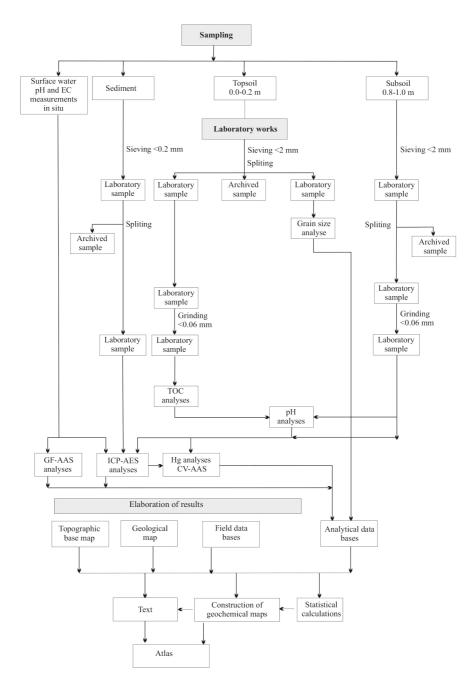


Fig. 1. The study procedure

FIELD WORKS

Soil samples were collected on a basis of a regular grid of 250x250 m (16 samples per km²). The total number of soil sampling sites was 1,365. At every site, the samples were collected from two depths of 0.0–0.3 and 0.8–1.0 m (or from a smaller depth if the parent rock was found at a shallower 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 sediments in inland reservoirs and surface water (344 and 315 samples respectively) were collected from rivers, streams, melioration ditches, canals and ponds. The distance between sampling sites along watercourses was about 250 m. Sediment samples weighing about 500 g (as fine-grained as possible) were taken from the water reservoir shores using a scoop. They were subsequently placed in 500-ml plastic containers, each labelled with a number.

Surface water samples were collected from the same sites as sediment samples. Electrolytic conductivity (EC) and acidity (pH) of water were measured on site. Conductivity was measured using an conductivity meter with automated temperature compensation, assuming the reference temperature of 25°C. Water samples were filtered in situ using 0.45- μ m 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 as well as on lithologies). The geographic coordinates were taken with an accuracy of $\pm 2 - 10$ 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 safety reasons, all the field data were also recorded on special sampling cards (Fig. 2).

| | | Shee | ι | | | | Date Sampler | |
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| Distr | ict | .Community | | Plac | ə | | | |
| | | | | | | Samp | | |
| Land d | levelopment | | | and use | . 1 . 1 | | 2 Type o | of soil |
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| 2 | village development | | 2 | | | 2 | sand-c | |
| 3 | urban areas with low | - | 3 | <u> </u> | | 3 | clay-sa | and |
| 4 | urban areas with high | development | 4 | | 1 14110 | 4 | clay till | |
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Fig. 2. Sampling cards of soils (A) as well as sediments as surface water (B)

LABORATORY WORKS

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

Sediment samples were air-dried and then sieved through a 2-mm nylon sieve to a grain size <0.2 mm. After quartering, the <0.2 mm fraction was divided into two portions: one of them was used for chemical analysis, and the other one was archived (Fig. 1).

All the archived samples are stored at the Polish Geological Institute – National Research Institute (PGI-NRI) in Warsaw.

Chemical analyses. Soil and sediment samples were *aqua regia*-digested (1 g of sample to final volume of 50 ml) for 1 hour at the temperature of 95°C in a thermostat aluminium block.

The contents of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in soils and sediments were determined by the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. Determination of Hg in soil and sediment samples was performed using the cold vapour-atomic absorption (CV-AAS) method with the FIAS-100 with flow injection system. Soil pH was measured in water extractions using a pH-meter. Organic carbon content was measured using the coulometric method (with the detection limit 0.16%), high-temperature combustion and detection with thermal conductivity TCD, and high-temperature combustion with infrared spectrometric detection (with the detection limit 0.01–0.02%).

The contents of B, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, P, SiO₂, SO₄, Sr, Ti and Zn in surface waters were determined by the ICP-AES method, and the contents of Ag, Al, As, Be, Cd, Co, Cu, Li, Mo, Ni, Pb, Sb, Se, Tl, U and V were analysed using the ICP-MS method.

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

The quality control of the determinations was performed through analysis of duplicate samples (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). Purity of reagents and vessels was controlled with "reagent blank samples" and "procedural blank samples". The expanded uncertainty of results (with the assumed probability level of 95% and coverage factor k = 2) for water, soil and sediment samples does not exceed 25%.

Grain-size analysis of topsoil samples (0.0–0.3 m) was carried out at the PGI-NRI Laboratory in Warsaw, combining the sieve analysis with the laser particle size measurement method. The grain-size analysis was conducted using unconventional methods (not in accordance with the relevant standards in soil science). Their results cannot therefore be used to classify the soils according to the soil science criteria. However, they are very helpful when interpreting the results of geochemical research.

The samples were sieved through a set of 2 mm, 1 mm and 0.5 mm sieves. Samples of some loamy soils were crumbled in a porcelain mortar before sieving. The obtained fractions of 2-1 mm, 1.0-0.5 mm and <0.5 mm were weighted. Measurements of grains from the <0.5-mm fraction were performed with use of a laser particle size analyser.

The results of grain-size analyses (recalculated to percentage ranges) are presented in the maps with respect 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 (Pls. 4-6).

DATABASES AND GEOCHEMICAL MAPS CONSTRUCTION

Base topographic map. The 1:25,000 geochemical maps were constructed based on 1:50,000-scale topographic base map in the *1992* coordinate systems, Zabrze M-34-62-B map sheet (vector map VMap L2). The topographic map contains the following vector information layers: relief, hydrography (including categorisation into rivers, streams, ditches and stagnant water reservoirs), road communication network (with road classes indicated), railway network, land development (including subdivision into rural, urban and industrial development), forests, industrial areas (industrial facilities, mine excavations, mine heaps, and tailing ponds).

Geological map. To illustrate the geological structure of the study area, the Zabrze M-34-62-B map sheet of the 1:50,000-scale Detailed Geological Map of Poland was used (Wyczółkowski, 1957). Individual elements of the geological map were digitized to create their vector images that were subsequently combined with the topographic base, producing a geological map at the scale of 1:25,000 (Pl. 1).

Databases. Separate databases were prepared for: topsoil (0.0–0.3 m), subsoil (0.8–1.0 m), sediments and surface waters.

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

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

Statistical calculations. The results gathered in 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 and urban soils, in sediments, and in the waters of individual water bodies, as well as for geochemical map construction. Statistical calculations were made for both whole datasets and subsets created for soils, sediments and surface waters. 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, and minimum and maximum values were calculated. These data specified for individual elements and indices are shown in Tables 2–5 and presented in the geochemical maps.

Median values were the most commonly used parameter to interpret the results, as a measure of the average contents of each element. The median is a statistical parameter that better characterises the average contents than the arithmetic mean, because it is less affected by extreme values. Other statistical parameters (variance, standard deviation) are not suitable for the characteristics of the population with unspecified distribution.

Maps construction. The following maps were produced for the Zabrze Sheet (Pls. 2–63): land development, land use, contents of organic carbon, and sand, silt and clay fractions in topsoil (0.0–0.3 m depth), pH of topsoil and subsoil (0.0–0.3 and 0.8–1.0 m depth), 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 and subsoil and in sediments, pH, electrolytic conductivity and contents of Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, SO₄, Sb, Se, SiO₂, Sr, Ti, Tl, U, V and Zn in surface water, classification of topsoil (0.0–0.3 m), indicating

its appropriate use (including subdivision into soil use groups based on the Regulation of the Ministry of the Environment (Rozporządzenie..., 2002).

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

To show the distribution of grain-size classes (Pls. 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 using geometric progression.

Soil pH (Pls. 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 Zabrze Sheet and the adjoining 1:25,000-scale sheets to avoid any discrepancies at the sheet boundaries. The Zabrze Sheet was then extracted from mono-element maps and combined with the topographic base map.

The geochemical maps of sediments and surface water were compiled separately for the Zabrze Sheet. 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 (Pl. 63), indicating appropriate soil use, the results of geochemical analyses were referred to the permissible concentrations of metals, defined in the Regulation of the Ministry of the Environment. According to the recommendation: "soil or land is considered polluted if the concentration of at least one substance exceeds the permissible limit value" (Rozporządzenie..., 2002).

Based on the concentrations of individual elements analysed (specified in 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 (based on guideline values for arsenic, barium and cobalt in Rozporządzenie..., 2002), the soil was categorized into class A, which is more beneficial for the soil user and enables multifunctional land use.

For publication purposes, the geochemical maps were constructed by combining the maps into pairs: i.e. the topsoil map is presented on the same Plate together with the sediments map, and the subsoil map is shown together with the surface water map on another Plate. This method of presentation provides the possibility of direct comparison of geochemical images of various environments.

To facilitate easy use of the atlas, the maps (with a bar scale shown) have been printed out in a slightly smaller format (A3). This operation does not result in missing any important details of the maps.

RESULTS SOILS

The map sheet area is dominated by pseudopodzols developed on sands and tills; river valleys are filled with alluvial muds (Aktualizacja..., 2011, 2014). Most of the soils have been heavily altered. Degradation processes are observed mainly in areas of new residential development, along transportation routes, around industrial facilities and near landfills. The factors affecting soil degradation include waterlogging, drainage and contamination by toxic compounds.

Grain size. The percentage of particles of specified sizes in the soil is called mechanical composition, grain-size composition, granulometric composition or grain-size distribution (Mocek *et al.*, 2000; Ryżak *et al.*, 2004, 2009). Under natural conditions, the soil grain-size composition changes insignificantly (excluding saline soils, in which peptization of soil colloids can occur), being one of the main features affecting soil's physical, chemical and biological properties.

For the purpose of this report, the classification of particles into grain-size groups follows the standard BN-78/9180-11, which has been valid since 2008, because this is a continuation of a serial publication performed over a long period in accordance with the instruction to the 1:25,000-scale geochemical map. The results of grain-size analysis are presented for the following grain-size groups: 1.0–0.1 mm sand fraction, 0.1–0.02 mm silt fraction, <0.02 mm clay fraction (Pls. 4–6). The change in the grain-size ranges in accordance with the guidelines of the Polish Society of Soil Science (PTG) (Klasyfikacja..., 2008) would make it impossible to compare the grain-size composition with data from previously compiled map sheets.

The study of soil's particle size was made in view of its relationship with the content of elements. Soil's grain-size composition determines significantly its resistance to degradation and has an essential effect on the content of chemical elements. Soils that contain a high proportion of clay and silt fractions are usually characterised by increased contents of elements and their lower mobility in hypergenic conditions. Compared to sandy soils they are more resistant to the removal of plant nutrients and can retain a greater amount of toxic components (including heavy metals) without harming the environment. For soils with a considerable proportion of the clay fraction, also referred to as fine particles (<0.02 mm), and the silt fraction (0.1–0.02 mm), higher levels of concentration limits are commonly allowed when developing recommendations for their use (Kabata-Pendias *et al.*, 1995). This approach stems from the fact of higher contents of elements and lower ability of their migration in these soils.

The variability in grain-size composition of soils in the map sheet area is clearly related to the lithology of parent rocks. Pleistocene glaciofluvial sands and gravels are the basic rocks for the development of sandy soils containing 40–80% of the 1.0–0.1 mm grain-size fraction. Their typical feature is the content of <20% of the silt fraction and <10% of the clay fraction. These soils cover predominantly the south-western part of the map sheet area.

Soils that developed on outcrops of glacial tills contain mainly the silt fraction (0.1-0.02 mm), commonly in excess of 40%. It is accompanied by the clay fraction (<0.02 mm) usually accounting for 10–15%. Soils that are rich in the silt and clay fractions prevail in the central and north-eastern parts of the map sheet.

Acidity. Alkaline and neutral soils predominate in the topsoil. Alkaline soils (pH >7.4) predominate in the central quarters of Zabrze and Ruda Śląska, which is probably associated with a considerable amount of alkalising materials in anthropogenic embankments and deposition of volatile ashes due to coal burning.

In industrial and post-industrial areas (near the Zabrze and Pokój steelworks, in the former Zabrze-Bielszowice mine and near the Pokój mine) the pH values often exceed 8. Among the reasons for such a high alkalinisation of the topsoil is the long-term accumulation of dust from coal combustion, in which the CaO content may reach 10% (Zapotoczna-Sytek *et al.*, 2013). Additional alkalising factors include the agents used to snow removal from streets, and the scattering of material from the heaps of mining, metallurgical and furnace waste. The material from heaps contains not only metal ores, but also auxiliary materials, including fluxes (in the form of ore-bearing dolomite), refractory linings, alloying additives, binding materials and fuel.

The prevalence of alkaline soils at a depth of 0.8–1.0 m can be associated with a higher amount of alkalising materials (building and industrial waste) in deeper parts of anthropogenic soil profiles.

In forests of the south-western part of the map sheet, the soils are acidic (pH <6.3), and even highly acidic in the near-surface layer (pH <5).

Comparison of average pH values of the topsoil in areas of different land uses (Tab. 2) indicates a clear relationship of alkalinisation with the fallout of dust from fuel combustion and industrial processes. In non-built areas the median pH value is 6.9, increasing to 7.9 in urban areas and to 8.0 in industrial areas.

Geochemistry. The spatial distributions of the chemical elements in soils of the map sheet area indicate that they originate from both the parent rocks (which is best marked in the subsoil layer from a depth of 0.8–1.0 m) and anthropogenic factors related to various industrial activities (better manifested in the topsoil).

The natural distribution of most elements in the topsoil of industrial and urban areas has been disturbed. Their average contents (expressed as median values) significantly exceed the geochemical background value of the Silesian-Cracow region. In the case of barium, magnesium, nickel, sulphur and strontium there is a two-fold increase of the contents as compared to the regional background (Tab. 2). Still higher values are recorded for elements that are emitted into the environment from metal smelters and other industrial plants. Almost three times higher contents are found as regards zinc and copper, and twice greater in the case of arsenic, cadmium, chromium and lead.

At both soil depth intervals the variability of contents of elements (aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, strontium, titanium and vanadium) that originate from the parent rocks is significant. Soils that developed on Quaternary tills (covering most of the map sheet area) are richer in these elements than the soils from the extreme south-western areas, where glaciofluvial sands predominate. The topsoil is additionally enriched in barium, calcium, magnesium and strontium due to human impact.

In the south of the map sheet there are soils that developed on outcrops of sandy deposits and contain typically 0.20–0.40% of aluminium at both soil depth intervals. In the northern region, covered predominantly by glacial tills, the aluminium content is 0.40–0.80%.

The distribution of calcium, magnesium, barium and strontium contents indicates different accumulation sources. The magnesium content is related mainly to natural sources and is very similar at both soil depth intervals (<0.12% in the southwest, and 0.12-0.50% across the remaining area). At both soil depth intervals the calcium content is >0.50% throughout most of the area. Soils with these values occupy larger areas at a depth of 0.0-0.3 m, indicating its anthropogenic provenance in dusts from coal burning, metallurgical fluxes and burnt lime used in the steel smelting process (Konieczyński, ed., 2010). Strontium-rich soils (>40 mg/kg) are more common at a depth of 0.0-0.3 m, particularly in industrial areas,

indicating waste heaps and mine water discharges as the sources of this element. The sources of barium are dusts from coal combustion (Różkowska, Ptak, 1995a, b), waste heaps, and mine water discharges. The topsoil contains >120 mg/kg of barium, and its content decreases with depth.

The organic carbon content in the topsoil commonly varies between 3 and 6%. The greatest amounts (>6%) are found in alluvial soils of river valleys, near mine heaps and in areas of coking plants.

The average phosphorus content in the topsoil is 0.037%, and the most common values range from 0.030 to 0.060%. The area of elevated phosphorus content (>0.060%) is more extensive as regards the topsoil than the subsoil. The main source of this element is municipal sewage discharges. Their effect on the chemical composition of soils is well illustrated by the phosphorus content in the subsoil in the Czarniawka River valley downstream of the Ruda Południowa sewage treatment plant.

The sulphur content in soils rarely exceeds 0.080%, but the soils near mine heaps and mine shafts locally contain >0.160% of sulphur.

Soil contamination by arsenic, cadmium, zinc, lead, mercury and copper is observed in both the topsoil and subsoil, although it is better manifested at a depth of 0.0–0.3 m. The major source of these elements is the remnants of Zn-Pb ore piles and tailings heaps of some historical zinc smelters.

Already in the 19th century there was a zinc smelter in the Bobrek quarter of Bytom (near Stara Cynkownia Street; currently a stadium area) (Bobrek...). In the close neighbourhood, a tailings heap of this smelter was located in the Bytomka River valley. In the Godula quarter of Ruda, the Godullahütte zinc smelter was active in 1854–1919, and there are smelter waste heaps of the Hugo, Franciszek and Liege-Hoffnung smelters and the Rozamunda zinc-processing plant still observed in the Nowy Bytom and Wirek quarters (near the streets of 1 Maja, Nowary and Nadurnego). Near the Pokój Steelworks, there are dumps of waste disposed of by this plant (Rudzkie...).

The soils which are most contaminated by arsenic, cadmium, zinc, lead, mercury and copper form a continuous belt in the eastern part of the map sheet (in the above-mentioned quarters of Ruda Śląska and in the Bobrek quarter of Bytom). The arsenic concentration exceeds 20 mg/kg in this area, attaining 300 mg/kg in the central parts of small anomalies. The area of soils with the cadmium concentration >4 mg/kg is greater as regards the topsoil layer. The maximum cadmium concentration (199 mg/kg) was found in alluvial soils in a stream valley on the western side of the Pod Brzozami residential area in Bytom and within

an anomaly in Ruda Śląska (>64 mg/kg). In a belt of contaminated soils, extending along the eastern boundary of the map sheet, the lead concentration is in excess of 250 mg/kg, and the zinc concentration is more than 1,000 mg/kg. Near the Pokój Steelworks there are also elevated concentrations of chromium (>40 mg/kg), iron (>2%), mercury (>0.80 mg/kg) and manganese (>1,600 mg/kg).

In other regions of the map sheet area, the mercury concentration is >0.20 mg/kg. These are industrial areas of the Zabrze Steelworks, Sośnica-Makoszowy mine and the former Wawel mine, neighbourhoods of a zinc waste heap in Bobrek, areas of a coking plant, and point anomalies in river valleys and near railway tracks. The maximum mercury concentration (17.16 mg/kg) was measured in the topsoil of the former Walenty coking plant in Ruda Śląska. The mercury originates from various sources. The contamination of soils in the eastern part of the map sheet is probably due to its presence in sulphates of iron, which are also an admixture in Zn-Pb ores. Anomalies found around coking and power plants have developed as a result of the dispersion of mercury bound in mineral matter of coal, during its combustion (Bojakowska, Sokołowska 2001, Aleksa et al., 2007; Kabata-Pendias, Mukherjee, 2007; Hławiczka, 2008). The presence of mercury in soils along railway tracks is probably due to the use of its compounds in wood protection chemicals (railway sleeper protection), whereas in allotment gardens the mercury anomalies may be the result of excessive use of insecticides. In many cases, the mercury comes from fluorescent lamps, Zn-HgO batteries, and from an equipment formerly used by many industries in measuring and control devices, and electrical devices used by plants producing chlorine and sodium (Szpadt ed., 1994; Paulo, Strzelska-Smakowska, 2000).

Local anthropogenic contamination by arsenic and metals has been found in soils of allotment gardens along the railway track and near the M. Skłodowska-Curie residential area in Zabrze: 781 mg/kg of arsenic, >500 mg/kg lead, and >1,000 mg/kg zinc. There are also elevated amounts of silver, cadmium, chromium and copper in the topsoil of these areas. In the subsoil the amount of these elements decreases. This anomaly can be associated with the use of contaminated materials for hardening of alleys in gardens, and with the use of herbicides on railway tracks and fungicidal preparations for impregnating railway sleepers.

Strong contamination by metals in the topsoil is observed in the area of the Zabrze Steelworks. In the middle of this anomaly the concentration of cadmium is 50.3 mg/kg, mercury 0.83 mg/kg, lead 1,885 mg/kg, and zinc 6,886 mg/kg.

The proportion of soils contaminated to various degrees by cadmium, lead and zinc is presented in Table 6. Over much of the map sheet area (20.96%) the topsoil contains >4

mg/kg of cadmium. The concentration of lead >100 mg/kg is observed in 45.59% of soils, and the concentration of zinc >500 mg/kg – in 29.53%.

The estimation of the degree of pollution by metals was carried out for soils from a depth of 0.0-0.3 m, classifying them into the soil use groups A, B and C, based on permissible limit values (Tab. 7). The soil classification indicates how the given area should be used in accordance with the guidelines of Rozporządzenie...(2002). While using the summary classification, we used the principle that the soil is categorised into a given group if the concentration of at least one element exceeds the permissible limit value. With respect to the concentration of arsenic and metals, 9.82% of the soils have been categorised into group A. Group B is represented by 30.33% of soil samples, and group C – by 59.85%. The criteria required for soil's multifunctional use are met by the soils assigned to groups A and B. Soils classified into group C occur in urban and industrial areas (Pl. 63). In many cases, the current land use is inappropriate and requires at least monitoring and even remediation. The concentrations of metals in most of the soils are so high that the areas should be reclaimed or used only for industrial purposes.

SEDIMENTS

The chemical composition of sediments in inland reservoirs of surface water is constrained by many natural and anthropogenic factors. It depends primarily on the geological structure of the drainage basin, geomorphology, and climatic conditions, which determine the processes of weathering of rocks, and the mobilization, migration and accumulation of elements (Bojakowska, Gliwicz, 2003).

Anthropogenic contamination of the study area, which originates from the discharge of industrial and household sewage, affects the composition of sediments more strongly than natural factors. Most of the watercourses flow through built-up residential or industrial areas. As a result of mining activities, long sections of river valleys are rebuilt, and the rivers flow in concrete-walled deep channels. Frequent river engineering operations and land drainage have led to the waning of floodplains and wetlands in many areas which are gradually replaced by housing development (Działoszyńska-Wawrzkiewicz, 2007). A special feature of most of the sediments is high content of very fine coal particles that is characterised by a sorption capacity leading to binding of metals and their easy precipitation (Nocoń, Kostecki, 2005).

Bytomka River and its catchment. The Bytomka River drainage basin area is composed mainly of glacial tills (Pl. 1). The river valley deposits are represented by glaciofluvial sands and alluvial muds. The river is engineered along nearly the entire course. It starts in Bytom, and flows across the map sheet area through the northern quarters of Ruda Śląska and the city centre of Zabrze. Its natural headwaters disappeared due to human impact,

and the Rów Karbowski ditch is considered the initial river reach. It carries municipal and industrial wastewater from Bytom (Nocoń, 2009). The Bytomka River drainage basin is characterised by a poorly developed river system. It is recharged mainly by mine water, sewage discharges from industrial plants, municipal wastewater, and by rainwater (Czaja, 1999; Nocoń, Kostecki, 2005). In its upper reach it receives treated wastewater from the Miechowice, Bobrek and Rozbark sewage treatment plants.

The content of elements (expressed as their median values) determined in sediments of the Bytomka River and its tributaries is greater than both the median values of sediments in the whole Zabrze map sheet, and the geochemical background in the Silesian-Cracow region (Tab. 4). It applies to both lithogenic elements (aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, phosphorus, strontium, titanium and vanadium) and anthropogenic elements (silver, arsenic, cadmium, copper, mercury, nickel, sulphur, lead and zinc). Part of material supplied to the Bytomka River is transported via the Rów Miechowicki ditch from the area of Bytom city. In the upper reach of the Bytomka River (beyond the eastern boundary of the map sheet), long-term discharges of industrial wastewater and leachate from a tailings heap of the former Orzeł Biały zinc smelter in Bytom city (currently Zakłady Górniczo-Hutnicze Orzeł Biały – a producer of refined lead from used batteries) are probably one of the sources of this metal.

The greatest amounts of contaminants in sediments of the Bytomka River were found along the border of Bytom and Ruda Śląska cities. They are polluted by silver (up to 14 mg/kg), arsenic (up to 186 mg/kg), cadmium (up to 150 mg/kg), chromium (up to 438 mg/kg), copper (up to 438 mg/kg), mercury (up to 2.07 mg/kg), lead (up to 10,859 mg/kg), and zinc (up to 60,264 mg/kg). They also retain considerable amounts of iron (6–10%), manganese (up to 14,420 mg/kg) and phosphorus (0.200–0.350%). High concentrations of cadmium (10–20 mg/kg), lead (300–1,000 mg/kg) and zinc (2,500–4,000 mg/kg) persist along the entire river section within the map sheet area. The major source of metals is the drainage of the area of a historical zinc smelter and its tailings heap in Bobrek. The contamination can also be associated with sewage from the Stal-Odlew plant (formerly the Zygmunt iron smelter; initially a zinc-processing plant that operated from 1857) located in the neighbouring map sheet of Chorzów, and with the influx of contaminated water and sediments transported by an unnamed stream from Świętochłowice. The stream drains the area in which a zinc smelter was established as early as 1823 (Dawid Steelworks, renamed to Guidotto). In the 1930s, the smelter ended its activities; however a part of its tailings heap (the Kopyto heap)

has survived until the present times in Lipiny of Świętochłowice. It contaminates the sediments and water of nearby water bodies after almost a hundred years.

In the lower reach of the river, another source of metals is leachate from a tailings heap of the Zabrze Steelworks, causing a clear increase in the concentrations of silver, arsenic, cadmium, copper, lead, sulphur and zinc in sediments of the Bytomka River.

Lithogenic elements show different concentrations in sediments of the Bytomka River and watercourses of its drainage basin. The median aluminium concentration in the Bytomka River sediments (0.58%) is lower than in the watercourses of its catchment (0.67% of aluminium), which drain glacial tills. In turn, concentrations of other elements are better marked in sediments of the Bytomka River, as compared to those in its drainage basin. The values are as follows: 26 mg/kg and 14 mg/kg of arsenic, 1.73% and 1.05% of calcium and 95 mg/kg and 63 mg/kg of strontium (Tab. 4). Cobalt, magnesium, nickel, titanium and vanadium show insignificant variations across the entire drainage basin.

Czarniawka River and its catchment. In its upper and middle reaches the river drains areas composed of glacial tills, and the lower part of its drainage basin is covered by glaciofluvial sands. There is only a small area with outcrops of Carboniferous sandstones and claystones. The Czarniawka River drainage basin is mostly an industrial area. The river receives wastewater from municipal sewage treatment plants in Ruda Śląska and Zabrze, and from industrial plants. Mine water is also discharged into the river.

Median values of the analysed elements in sediments of the river and in sediments of watercourses and water reservoirs of its drainage basin are much higher than the geochemical baseline values in the Silesian-Cracow region (Tab. 4).

The distribution of elements concentrations distinctly changes in sediments of the upper, middle and lower parts of the drainage basin, indicating their different origins and different possibilities for accumulation of the individual elements. The smallest concentrations are characteristic of the middle reach of the river, most likely due to its fast flow in a deep valley with steep banks, where the sediments are subjected to displacement and washing-out. A good example illustrating the concentration changes in different sections of the river is the barium concentration. In the uppermost reach of the Czarniawka River, the barium concentration is 150–250 mg/kg, in the middle reach 40–90 mg/kg, and close to the western boundary of the map sheet, near a mine heap of the Sośnica-Makoszowy coal mine, it is up to 1,629 mg/kg. In the last-mentioned river reach, the high barium concentration is probably due to coal enrichment processes with the use of barite as an additive to heavy liquids.

A similar variability is also observed in the concentrations of aluminium, iron, mercury, manganese, nickel, lead, sulphur, strontium, vanadium and zinc. In the upper part of the Czarniawka River the contamination of sediments can be associated with the concentration of industry in this area, including the Pokój Steelworks and metallurgical and renovation companies, as well as with the long-term activity of the Wawel and Bielszowice hard coal mines, including the impact of their mine heaps and sewage discharges. The following concentrations have been measured in the sediments: cadmium up to 8 mg/kg, chromium and copper up to 100 mg/kg, mercury up to 0.66 mg/kg, manganese up to 2,000 mg/kg, nickel up to 35 mg/kg, lead up to 470 mg/kg, and zinc up to 2,500 mg/kg. Previously, sediments of the Czarniawka River contained lower amounts of these metals (Nocoń, 2009). The quoted concentrations point to increasing contamination of sediments in spite of modern technologies and changes in the industrial production profiles within the drainage basin.

The greatest contamination of sediments by metals and sulphur is observed in the watercourses and stagnant water bodies near a mine heap of the Sośnica-Makoszowy mine, where the coking plant was additionally active for a few decades. The Czarniawka River valley, filled with alluvial muds, is very wide in places and covered with wetlands, which results in slower water flows and facilitates easy precipitation of constituents transported in the water and in suspension. The main pollution source is probably the drainage of the heap located in this valley. The concentrations of metals indicate that not only mining waste but also tailings and waste of the metallurgical industry were likely deposited in this area. The highest concentrations of elements in sediments are found in ditches draining areas of ventilation shafts of the Sośnica-Makoszowy mine, and in a settling tank near the heap. These deposits are represented by organic slurry. The following concentrations have been measured: cadmium up to 395.2 mg/kg, cobalt 502 mg/kg, mercury 2.03 mg/kg, nickel 192 mg/kg, lead 1,580 mg/kg, vanadium 156 mg/kg, and zinc 8,076 mg/kg. The sediments are also abundant in calcium (up to 23.45%), iron (up to 22%), manganese (up to 115,540 mg/kg) and sulphur (up to 14.90%).

The right-hand tributary of the Czarniawka River is the Potok Sośnicki (Guido) Stream. The concentrations of most of the analysed elements fall within the range of geochemical background values. In the initial reach of this watercourse there is a small enrichment in chromium, copper, mercury, lead and zinc.

Potok Bielszowicki (Kochłówka) Stream and its catchment. The drainage basin of this stream is composed mainly of glaciofluvial sands. The headwaters area of this watercourse that flows in an engineered channel is located beyond the eastern boundary of the

map sheet, at the border of Zabrze and Ruda Śląska cities. Much of the drainage basin area is covered by forests, crosscut by numerous watercourses and with a few water reservoirs. The largest ones are the Bagier and Staw Makoszowski ponds that formed as a result of land deformation due to mining activity (Działoszyńska-Wawrzkiewicz, 2007).

Periodic floods in the Potok Bielszowicki Stream valley are caused by water transfer from other drainage basins to supply the residents and industry with water, and due to pumping out of mine water. The chemical composition of water and sediments is affected mostly by the discharges of mine water from the Pokój, Halemba-Wirek and Bielszowice mines, as well as of household wastewater (Cudak *et al.*, 2009).

The chemical composition of sediments of the Potok Bielszowicki Stream is clearly different in its upper reach, above the Bielszowice mine, than further on downstream of that place. Sediments of the upper section are abundant in cadmium (up to 21 mg/kg), chromium (up to 42 mg/kg), copper (up to 42 mg/kg), mercury (up to 0.70 mg/kg), phosphorus (up to 0.333%), lead (up to 400 mg/kg), sulphur (up to 2.550%), and zinc (up to 5,760 mg/kg). The major source of these metals is probably the long-term discharge of sewage from the former Batory smelter (located beyond the eastern boundary of the map sheet). The upper part of the drainage basin was successively contaminated for over 100 years by deposition of raw materials, waste and wastewater from the smelter. Under the name of Bismarckhütte the smelter was active from 1873, producing steel, pipes and sheet metal. In the years 1912–1915, ammunition, ship boilers and armor plates were produced. In following years the smelter produced steel, sheet metal and mining tools (Huta...). Production redeployment required the use of many raw materials, which influenced the nature of the wastewater. The sources of contamination were also leachate from a heap of the Halemba-Wirek mine as well as industrial sewage discharged by the mine.

The ability of accumulation of metals in sediments of the lower reach may be controlled by the shape of the valley that widens in the area of mine heaps located on the eastern side of the Bielszowice mine, causing a decrease in the transport rate, easier sediment deposition, and sorption of metals by clay minerals and organic matter.

Downstream of the Bielszowice mine, mineralized mine water is discharged into the stream. Dilution the stream water results in a change in the chemical composition of the sediments. The concentrations of some metals in the sediments of this stream course are clearly lower than in the upper reach. The sediments easily accumulate elements that originate from mine water: barium (up to 800 mg/kg) and strontium (up to 370 mg/kg), while the zinc concentration is at a continuously high level (up to 900 mg/kg).

Klodnica River. Within the map sheet limits there is a small part of the Kłodnica River valley. Its sediments in this area are characterised by lower contents of the analysed elements as compared to the sediments of the Bytomka River and Potok Bielszowicki Stream. Noteworthy is their contamination by barium (up to 460 mg/kg), mercury (up to 0.34 mg/kg) and zinc (up to 1,284 mg/kg).

The chemical composition of sediments from minor watercourses draining the area extending along the southern boundary of the map sheet (tributaries of the Kłodnica River) reflects the chemistry of basement rocks in this part of the drainage basin. The contents of the analysed elements can be considered the regional geochemical background values. The sediments are conspicuous by the abundance of aluminium (3–5%). In some watercourses and stagnant water bodies there are elevated concentrations of cadmium (up to 46 mg/kg). In some others, nickel (up to 100 mg/kg), lead (up to 550 mg/kg), sulphur (up to 6.500%) and zinc (up to 1,500 mg/kg) are found.

Sediments of the watercourses flowing on the western side of the Kłodnica River valley frequently contain 0.800–0.900% of phosphorus. It can originate from the discharge of water from pump stations located in this area, and its accumulation ability is enhanced by wetland vegetation.

SURFACE WATER

The studies have shown strong contamination of water in all the watercourses by compounds characteristic of coal mine water (suspended particles, chlorides and sulphates) and municipal sewage.

Bytomka River and its catchment. Using a system of ditches and collectors, mine water and household and industrial sewage are discharged into the Bytomka River. They account for up to 85% of its mean flow rate (Cempiel *et al.*, 2014). The river is actually a sewage ditch, and its water do not meet any criteria or standards for water quality applied to surface water. Monitoring of the Bytomka River water shows elevated values of most physical–chemical indicators, especially as regards ammonium nitrogen, phosphorus compounds, total suspended solids and chloride ions, as well as very low levels of dissolved oxygen (Ocena...).

Noteworthy is the high electrolytic conductivity of the Bytomka River water (EC 6.19–10.30 mS/cm) as it is an important factor indicating their chemical composition. The high values are due to considerable salinity of mine water discharged into the river from the

area located north of the map sheet, where the Bobrek mine is active. High water contamination is evidenced already by EC values in excess of 1 mS/cm (Witczak, Adamczyk, 1994; Rozporządzenie..., 2011). Low mineralization is observed only in the water of stagnant water reservoirs occurring close to the northern boundary of the study area (EC 0.20–0.40 mS/cm), which are probably recharged also by atmospheric precipitation.

The pH values of the water are fairly uniform across the drainage basin, range from 7.9 to 8.2, and are slightly higher than those measured by the Regional Inspectorate of Environmental Protection (pH 7.1–7.8; Wyniki..., 2012).

The discharge of mine water causes severe pollution by elements derived from mines, including boron, potassium, lithium, magnesium, sodium, sulphate and strontium. Along the whole reach of the Bytomka River, analysed for the study, the contents of these elements in its water is uniform, and the lower content was recorded only in a few stagnant water reservoirs within its drainage basin. The median boron concentration in the Bytomka River is 1.55 mg/dm^3 , and in its drainage basin – 0.89 mg/dm^3 . A similar trend is observed in the case of potassium and lithium. The median potassium concentrations in the Bytomka River and in stagnant water bodies (not contaminated by mine water) of its drainage basin are 48.4 mg/dm³ and 7 mg/dm³, respectively, and the median lithium concentrations are 205.3 µg/dm³ and 10 µg/dm³, respectively.

The discharges of mine water are associated with very high concentrations of sodium and sulphates in the Bytomka River (median values: 1,225 mg/dm³ and 10,800 mg/dm³, respectively). There is especially high concentrations of sulphates in relation to the values measured in 2011 at the point where the Bytomka River joins the Kłodnica River – 705.5 mg/dm³ (Wyniki..., 2012). The increase in the concentrations is related likely to the discharge of more saline mine water from active and closed–down coal mines.

Along the whole reach of the river, analysed in this study, the barium concentration is constant (0.050 mg/dm³). In some closed reservoirs, the barium concentration is 0.010–0.020 mg/dm³, but there is one water body where the value is 1.060 mg/dm³. The median calcium and magnesium concentrations are 232.6 mg/dm³ and 138.1 mg/dm³, respectively, and the concentrations of these elements are uniform along the entire river reach. They can be derived from mine water, sewage and surface runoff. The concentrations of metals in the Bytomka River measured within this study are lower than those from earlier ones (Wyniki..., 2012).

It is advantageous that the study area water contain small amounts of metals toxic to living organisms. The concentration of chromium is below 0.003 mg/dm³, of copper 1 μ g/dm³, and of cadmium 0.05 μ g/dm³. The median concentration of lead is 0.44 μ g/dm³, and

of zinc 0.010 mg/dm³, and the values do not exceed the boundary limits for these elements in the water included in quality class I. The median concentrations of antimony (0.56 μ g/dm³), selenium (5 μ g/dm³) and thallium (<0.05 μ g/dm³) do not exceed the boundary limits for water quality I, either. An elevated thallium concentration (0.10–0.20 μ g/dm³) was found in the water of a small left–hand tributary the Bytomka River.

In the Bytomka River water the iron concentration varies from 0.02 to 0.12 mg/dm³, and there are only two stagnant water reservoirs in the drainage basin with the values of up to 2–3 mg/dm³. The distribution of manganese concentration is variable. In the upper course of the river its water contain more manganese (0.250–0.500 mg/dm³) as compared to the lower reach 0.200 mg/dm³, while the water reservoirs of the drainage basin show its elevated amounts attaining 1.870 mg/dm³.

The average concentration of nickel in the water is 3.3 μ g/dm³, and the contamination by this metal (up to 37.42 μ g/dm³) is observed only in a watercourse near a landfill.

As regards the phosphorus concentration (median 0.23 mg/dm³) the water of the Bytomka River can be categorised into quality class II. Compared to the previous results (0.48 mg/dm³) their quality has significantly improved (Wyniki..., 2012).

Czarniawka River and its catchment. The river receives wastewater from small local sewage treatment plants and from coal mines and coking plants. Wastewater accounts for a significant part, and the river is recharged naturally only to a small extent.

The pH in the river water varies from 7.5 to 8.4, and the median value is 8.0. The EC vary within a wide range from 2.09 to 17.78 mS/cm (Tab. 5). In the upper reach of the Czarniawka River the EC values are commonly 2–3 mS/cm. They increase in the lower reach, while in the ditches and near settling tanks of the Sośnica–Makoszowy mine the values are >40 mS/cm. The strong mineralization is due to discharges of mine water; there are elevated concentrations of sodium, lithium, potassium, calcium and magnesium. Like with the case of EC, the greatest concentrations of these elements in surface waters were found in the watercourses downstream of the coal mine area. The sodium concentration is 3,500–7,800 mg/dm³, and in the upper part of the Czarniawka River 200–300 mg/dm³. A similar distribution is observed in the case of lithium: 100–200 μ g/dm³ and >500 μ g/dm³, potassium: 30–40 mg/dm³ and 60–70 mg/dm³, and magnesium: 100 mg/dm³ and >200 mg/dm³, respectively.

Sulphates contaminate the water across the whole drainage basin, and their concentrations are of the order of a few to several thousand mg/dm³. Water abounding in sulphate ions are poor in barium (0.034–0.450 mg/dm³) and show variable concentrations of

strontium and uranium. In the upper part of the drainage basin, the uranium concentration is $2-5 \ \mu g/dm^3$, and after the influx of mine water from the Sośnica–Makoszowy mine it decreases to $1 \ \mu g/dm^3$. According to the classification of the USCB water that contain radioactive elements, it can be supposed that the water also contain radium (Smoliński, 2006; Olkuski, Stala–Szlugaj, 2009).

Mine water is also probably the source of antimony and selenium. In the upper reach of the Czarniawka River and in the water of the Guido Stream the antimony concentration is 0.20–50 μ g/dm³, but downstream of the coal mine it is 2–3 μ g/dm³. In the case of selenium the values are <2 μ g/dm³ and 5 μ g/dm³, respectively.

Given the small amount of other elements it can be inferred that their effect on living organisms is insignificant. The concentrations of cadmium, chromium, lead, thallium and vanadium are below the detection limit. The most frequent concentration of cobalt and copper is 1 μ g/dm³, and of nickel 3–4 μ g/dm³. The amount of calcium is uniform across the whole area (approx. 220 mg/dm³).

The amount of phosphorus in the upper reach of the Czarniawka River does not exceed 0.05 mg/dm³, and after receiving wastewater from the sewage treatment plant in Ruda Południowa the amount increases to 0.50 mg/dm³, exceeding the boundary limit for water quality class II. Still greater contamination by phosphorus (1.00–1.60 mg/dm³) is observed in an unnamed watercourse draining the residential area in Zabrze city.

Potok Bielszowicki (Kochlówka) Stream and its catchment. The stream receives wastewater from local sewage treatment plants in Ruda Śląska as well as wastewater and mine water from the Wirek and Bielszowice mines.

The pH of the water in the stream and its tributaries is 6.5-8.7 (Tab. 5). The EC in the upper section of the stream is 1-9 mS/cm, and downstream of the Bielszowice mine facilities it increases to 13-20 mS/cm (up to 21.60 mS/cm).

The constituents that contribute to water quality degradation are sulphates, boron, sodium, potassium, lithium, iron, manganese and barium, derived from saline mine water. These elements attain the following concentrations: boron $0.90-1.75 \text{ mg/dm}^3$, potassium 40– 90 mg/dm³, lithium 200–900 µg/dm³, sodium 800–3,800 mg/dm³, sulphates 7,000–11,000 mg/dm³, and strontium 4–7 mg/dm³.

In the upper course of the stream the presence of phosphorus (0.80–1.20 mg/dm³) is probably related to the discharge of sewage from the Barbara treatment plant in Ruda Śląska (outside the map sheet area). Downstream of the Bielszowice mine and after the dilution of stream water by mine water the phosphorus concentration decreases to 0.20–0.50 mg/dm³.

Influx of mine water is also evidenced by the distribution of barium concentrations, which are 0.040 and 0.160 mg/dm^3 respectively in the upper and lower reach of the stream.

The concentrations of metals (cadmium, cobalt, chromium, copper, nickel, lead and zinc), antimony and selenium do not exceed the boundary limits for water quality class I (Tab. 5).

Kłodnica River. The water in this part of the drainage basin is characterised by neutral pH. There are only a few cases of alkaline pH (>8.0). The EC varies within a wide range from 0.22 to 9.75 mS/cm (Tab. 5). The high values of EC and concentrations of many elements are due to the discharges of industrial wastewater and mine water.

Acidic water (pH 4.5–5) of an unnamed watercourse that drains a forested area around a heap near the southern boundary of the map sheet are conspicuous by high concentrations of aluminium – 3,285.4 μ g/dm³ and beryllium – 1.31 μ g/dm³. The aluminium concentrations in the river water range from 2 to 1,000 μ g/dm³; averaging 64 μ g/dm³, and the beryllium concentrations are <0.008–0.6 μ g/dm³ (Kabata–Pendias, Pendias, 1999; Kabata–Pendias, Mukherjee, 2007). The highest water solubility of both elements is observed in strongly acidic environments. Particularly harmful is the presence of aluminium that shows a toxic effect on living organisms. The water contaminated by aluminium and beryllium also contain cadmium (10–21 μ g/dm³), cobalt (4–9 μ g/dm³), iron (4–10 mg/dm³), nickel (7–13 μ g/dm³), lead (12 μ g/dm³), silica (25–27 mg/dm³), thallium (0.40–0.69 μ g/dm³) and zinc (1.700–1.881 mg/dm³). The likely source of the contamination is the drainage of the heap and the discharge of sewage from the area of ventilation shaft in the Makoszowy mine.

CONCLUSIONS

- Anthropogenic pollution sources in the natural environment of the study area include: hard coal mining, emissions of particulate matter and gases from coking plants, the impact of mine and furnace waste heaps and tailings ponds, historical smelting of zinc and iron, metallurgy, and transport.
- 2. Lithology of the parent rocks of soils is reflected in their geochemistry and grain-size composition. Soils that developed on glaciofluvial and fluvial sandy deposits are abundant in the sand fraction. They contain low amounts of aluminium, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, phosphorus, strontium, titanium and vanadium. This applies to both soils from the depth interval of

0.0–0.3 m (topsoil) and 0.8–1.0 m (subsoil). Soils that developed on outcrops of Quaternary tills are richer in these elements and in the silt and clay fractions.

- 3. As a result of anthropogenic factors the topsoil is enriched in barium, calcium, magnesium and strontium as compared to the subsoil.
- 4. Acidity of the soils is variable and largely depends on the land use. The soils of urban and industrial areas are commonly alkaline and neutral, whereas those in forests are acidic.
- 5. The contamination of sediments of inland water reservoirs and surface water is anthropogenic in nature. It originates from the discharge of mine water of active and inactive coal mines, and industrial and municipal sewage, as well as from the drainage of waste heaps.
- 6. The sediments are contaminated by elements derived from contemporary and historical metallurgy of metals (chromium, zinc, cadmium, cobalt, copper, nickel, lead, silver and iron), from coking plants (mercury, arsenic), and from the discharges of municipal sewage (phosphorus).
- 7. The water of the study area is characterized by high variability in terms of the content of chemical elements, pH and EC. Salinity of most watercourses is associated with the discharges of mineralized mine water. The water discharged from coal mines cause pollution of the watercourses by barium, boron, chlorine, potassium, lithium, molybdenum, sodium, strontium, sulphates, rubidium, thallium and antimony. The most polluted watercourses are those flowing in the vicinity of mining waste dumps.

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