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INTRODUCTION

The 1:25,000 geochemical mapping in the Mikołów map sheet M-34-62-B-d is a continuation of the detailed mapping project that commenced in 1996–1999 with the pilot map sheet of Sławków M-34-63-B-b 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. Its north-eastern portion is in the range 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 Mikołów, Ruda Śląska and Katowice. Small areas at its northern boundary and in the south-eastern part belong to Chorzów and Tychy cities, respectively.

The main factor affecting the changes in natural environment of the map sheet area is the current and historical mining of hard coal. The mining activity, which has been developing most intensely since the 1970s, is responsible for the formation of geological-anthropogenic anomalies of a number of chemical elements in soils, sediments, and surface water (Lis, Pasieczna, 1995a, b, 1997).

The results of geochemical studies, presented on the maps with a comprehensive explanatory text and data tables, show the current quality of soils, sediments and surface water. They were compared with the values of natural regional background and related to the legal regulations. The results 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 and land 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. According to the physico-geographical subdivision of Poland 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 parts of a number of cities Katowice, Ruda Śląska, Chorzów and Mikołów. The area of Mikołów city occupies the southwestern part of the map sheet (residential areas: of Piłsudskiego, Mickiewicza and Norwida in the town centre, as well as Gniotek, Janina and Reta on its outskirts). In the eastern part of the map sheet there are the south-western quarters of Katowice (Załęska Hałda, Ligota, Panewniki-Ochojec, Zarzecze, Kostuchna and Podlesie). The north-western part spans the quarters of Kochłowice and Kłodnica in Ruda Śląska. A small area in the north belongs to Chorzów.

Relief and geomorphology. The basement rocks of the study area are represented by Carboniferous coal-bearing deposits cut by numerous faults manifested in the surface relief. In the south and north there are fault-bounded plateaus, ridges and hills, composed of

Carboniferous sandstones. At the top parts of the hills (exceeding 300 m a.s.l. in elevation) the Carboniferous deposits occur on the surface. At lower levels, they are covered by weathering mantles and Quaternary sediments. In the eastern part of the map sheet the more prominent hills are composed of Triassic limestones and marls. The hills are separated from each other by tectonic depressions filled with Neogene and Quaternary deposits (Pl. 1).

To the west of the Ligota-Tychy line there is an axis of a Palaeogene fossil valley, about 1 km wide. Its bottom is filled with Miocene clays interbedded by sands covered with Pleistocene deposits (predominantly glaciofluvial and glacial sands and gravels with a total thickness of approx. 50 m). It is cut by the Holocene valley of the Mleczna River, about 250 m in width. The valleys of its tributaries, poorly incised into the basement of Pleistocene deposits, are 50–70 m wide.

The Holocene valleys of the Kłodnica and Ślepotka rivers are narrow. They have plane-bed channels, are well marked in the relief, and their slopes are 3–6 m in height.

The map sheet area is crossed by the Odra-Vistula first-order watershed. The Kłodnica drainage basin is part of the left side of the Odra River system. The Kłodnica River flows nearly longitudinally from east to west, and its headwaters are located to the east of the map sheet area. In the study area the river channel is engineered and its sediments are heavily altered due to human impact (Nocoń *et al.*, 2006). The Jamna Stream is engineered in its upper reach (in the built-up area of Mikołów), but along the remaining course the river channel is natural. To protect the landscape, the valley area (190.45 ha) is under legal protection as the Jamna Valley Landscape-Nature Protected Complex (Aktualizacja..., 2013). In the middle reach of the Jamna Stream there is a mining waste landfill of Panewniki, owned by the Halemba-Wirek hard coal mine, which poses a negative effect on the valley (Kowalska, Pierwoła, 2010; Studium..., 2013). The rock material gathered on the dumping ground (mainly sandstones and mudstones) is currently being extracted to acquire coal and qualified aggregates. Within the facilities and its surroundings, monitoring of surface water and groundwater, terrain subsidence, and slope stability is carried out (Kledzik, 2012).

The south-eastern area of the map sheet is situated in the left side of the Vistula River drainage basin. It is the Mleczna River drainage basin with its tributaries, whose headwaters are located in this region.

Within the map sheet area there are small drainless lakes that developed as a result of mining operations, artificial water reservoirs (settling ponds, water reservoirs for fire fighting, and recreational lakes), as well as flow-through lakes, e.g. Starganiec and Czarny Staw (Program..., 2014).

Land use. Residential, service and industrial (coal mine infrastructure, transport bases, services and trade) areas occupy the eastern and southern parts of the map sheet (Pl. 2). Among built-up areas, low-rise housing in urban areas is dominant (27%). High-rise housing areas account for 6% of the territory, industrial facilities (mines, landfills and dumps) 5%, and rural housing 2%. Green urban areas of city centers are represented by greenery and allotment gardens.

Unbuilt areas cover 60% of the study area (44% of the map sheet is represented by forests, 7% by arable land, and 5% by meadows) – Pl. 3. Other unbuilt areas include roadside green belts, allotment gardens, and railway areas. The forests are included into the protective forest belt of the Upper Silesian Industrial Region (Program..., 2014) and cover the northwestern part, extending from the Panewniki and Ligota quarters of Katowice city to the western boundary of the map sheet (Studium..., 2013; Program..., 2014).

Legally protected areas include the landscape-nature protected complexes of the Jamna Stream Valley and Wzgórze Kamionka hill in Mikołów (elevation 327.3 m a.s.l.), established in order to conserve the landscape view values (Aktualizacja..., 2013).

Economy in the map sheet area is strictly linked with the mining of hard coal deposits. The beginnings of mining activities in the area of Załęska Hałda in Katowice date back to 1788, but it is considered that the Wujek mine was established only in 1801. Modern industrial mining commenced early in the 20th century, using steam engines, generators, electric motors, pneumatic machinery and gas machines (KWK Wujek...). Further development of the mine took place in the 1960–1970s, and currently it is expected to stop the operation soon because of too great depths to coal deposits.

In the southeast of the map sheet there is also part of the mining area of the Murcki-Staszic mine, established in 2010 by merging two mines. The first notes on open-cast mining of hard coal in the so-called Wzgórze Murckowskie hill date back to 1657 (KWK Murcki-Staszic...). Intense development of coal mining accelerated after the construction of a railway track in the 19th century, and the greatest output of this mine took place in the second half of the 20th century.

Mining areas of the Halemba I and Halemba II mines, located in the north of the map sheet, belong to the Halemba-Wirek mine established by merging the Halemba and Polska-Wirek mines in 2007 (Kompania...). As a result of the exhaustion of resources and technical infrastructure depreciation, the Polska-Wirek mine has formally been closed down since the end of 2014.

In the south-western area of the map sheet there is a part of the Łaziska II mining area that belongs to the Bolesław Śmiały mine.

Mikołów hosts the Experimental Mine Barbara, which is a research institute. The mine has an underground testing area enabling research in real-mine conditions. The main goal of its activity is to study safety systems and to combat hazard related to gas and dust bursts (Kopalnia...).

Despite the reduction in coal production the mining industry still plays a significant role in the study area. Moreover, the production of machines and equipment for the mining industry (Mifama, Zakłady Mechaniczne Wiromet mechanical manufacturer, Famur), transformers (Schneider Electric Energy Poland) and plastic components (Geo Glob Polska) has been lately developing in Mikołów city. There are also numerous facilities of the renovation and construction industry and the transport sector. Service and trade activities are carried out as well.

GEOLOGY AND MINERAL DEPOSITS

The Mikołów map sheet area is located within the northern limb of the Main Trough of the Upper Silesian Coal Basin (USCB). It is part of the Palaeozoic Variscan structure cut by numerous faults. Locally, it is covered by horizontal strata of Triassic, Neogene and Quaternary deposits (Wyczółkowski, 1957; Buła, Kotas, ed., 1994). The geological structure of this region is very well explored owing to numerous boreholes and mining operations.

In the southern and northern parts of the map sheet, **Carboniferous** rocks occur on the surface or under a thin cover of Quaternary deposits. In its central and western parts, they occur at greater depths under the overburden of Pleistocene glaciofluvial sands and gravels, and, locally, Triassic limestones and dolomites (Pl. 1).

The oldest rocks in this area are the Upper Carboniferous Paralic Series – the Marginal Beds (Namurian A). These are clastic deposits showing sedimentary cyclicity and containing coal seams. They also host marine, brackish and freshwater fauna.

Upper in the section there are limnic deposits of the Upper Silesian Sandstone Series of the Upper Namurian (Namurian B and C), Mudstone Series of the Lower Westphalian (Westphalian A and B), and the Cracow Sandstone Series corresponding to the upper part of the Westphalian B and Upper Westphalian. The total thickness of these series in the map sheet area is approximately 3,000 m (Jureczka *et al.*, 2005).

The Upper Silesian Sandstone Series (Jejkowice, Saddle and Ruda beds) consists of fine- and medium-grained sandstones, occasionally coarse-grained, and conglomerates (Wilanowski *et al.*, 2009). Interbeds of claystones and mudstones attain a thickness of several metres. A characteristic feature of these deposits is the frequent occurrence of coal seams, up to 5 m thick, but locally more than 10 m. The Saddle Beds host the USCB's thickest coal seam 510, currently almost completely mined out.

The Mudstone Series is represented by the Załęże Beds corresponding to the Westphalian A, and by the Orzesze Beds of the Lower Westphalian B in the uppermost part. These deposits are lithologically very monotonous. The dominant lithologies are mudstones and claystones with fine-grained sandstone interbeds usually attaining several metres in thickness. The whole series typically shows the predominance of aleuritic-pelitic sediments over coarse-clatic ones, as well as a significant number of coal cyclothems, most of them containing hard coal seams (*op.cit.*). These deposits outcrop on the surface in the northern and southern parts of the map sheet area (Pl. 1).

The Cracow Sandstone Series is represented by coarse-grained sandstones and conglomerates, passing upward into medium-grained sandstones with mudstone and claystone interbeds and coal seams. Within the map sheet area there is only the basal portion of this series (about 15 m in thickness), which does not contain significant coal seams.

The **Triassic** deposits uncomfortably overlie Upper Carboniferous rocks and are preserved only in erosional outliers. Their thickness is highly variable (commonly 40–80 m). The Triassic section is represented by sands, sandstones, clays, claystones and mudstones, dolomites, marls and limestones, ore-bearing dolomites and dolomitized limestones.

The **Neogene** is represented by Miocene marine deposits— clays, muds, sands and gravels, marls, limestones, sandstone, gypsum, anhydrites, rock salt and tuffites. They occupy much of the sub-Quaternary surface in the map sheet. In the north-western part of the map sheet (Kłodnica River valley) the Miocene deposits exceed 150 m in thickness. Of Neogene age are also freshwater sands and clays exposed on the surface in the Reta residential area in Mikołów (Pl. 1).

The **Quaternary** deposits cover about 60% of the map sheet area with a layer of variable thickness ranging from a few metres on glacial uplands to more than 100 m in the Kłodnica fossil valley. Outside the Kłodnica River valley the thickness of the Quaternary series in depressions is commonly in the range of 30–60 m. In addition to alluvial sediments of fossil valleys the Quaternary cover is represented predominantly by glacial tills and glacial and glaciofluvial sands and gravels. The Holocene is represented by fluvial deposits of

modern valleys. These are fine-grained sands grading upward into swamp muds. These deposits (up to 3 m thick) fill depressions, oxbow lake basins, and river channels. Locally, aaeolian dune sands occur in some areas.

Mineral deposits. There are 12 documented multi-level **hard coal** deposits occurring wholly or in part within the map sheet area (Siata *et al.*, 2011; Szuflicki *et al.*, ed., 2014): Murcki, Staszic, Wujek, Bolesław Śmiały, Śląsk, Halemba, Wujek-part Stara Ligota, Wujek-southern part, Halemba II, Śląsk-Pole Panewnickie, Mikołów and Śmiłowice. The greatest economic resources of hard coal, up to 500–600 million tonnes, have been documented in the Staszic, Śmiłowice and Murcki deposits.

Coal resources of the Halemba II and Śmiłowice deposits are documented to a depth of 1,250–1,300 m, and in the remaining deposits to a depth of about 1,000 m. The coalbearing series is represented by coal seams of the Orzesze Beds (group 300), Ruda Beds (group 400) and Saddle Beds (group 500). The deposits provide power coal (types 31–34) and coking coal (type 35, sporadically semi-coking coal type 37). Coking coal is generally found in the southern and western parts of the map sheet in the lower portions of the following deposits: Halemba, Halemba II, Wujek-southern part, Murcki, Mikołów, Śmiłowice and Śląsk. The best quality coal comes from the Saddle Beds whose coal seams attain a thickness of 10 m and have a relatively small number of gangue intergrowths. The coal contains low amounts of ash (up to 10%) and sulphur (up to 1%). Its calorific value varies from 23,000 to 35,000 kJ/kg. The lowest quality coal seams are those from the Łaziska Beds and top parts of the Orzesze Beds. They show small and variable thicknesses (1–2 m, sporadically up to 3 m), and contain numerous intergrowths of gangue rocks. This coal typically contains much ash (up to 40%) and sulphur (locally >2%) so its calorific value is low (16,500–27,600 kJ/kg).

Currently, hard coal mining is carried out by the Halemba-Wirek, Wujek and Murcki-Staszic mines from eight coal deposits. These mines were formed as a result of merger of independent mines in the 1990s. Extraction is carried out using the high-wall mining system, sporadically with the hydraulic filling. The coal output is variable – from 0.19 million tonnes/year from the Halemba II deposit, up to 2.34 million tonnes/year from the Staszic deposit.

Still undeveloped deposits include the Wujek-southern part, Mikołów and Śmiłowice deposits. The Bolesław Śmiały deposit has been abandoned.

The hard coal deposits are accompanied by **methane** that occurs in a sorbed form, i.e. it is physicochemically bound to hard coal and dispersed coal particles, and its content in the coal increases with depth. Coalbed methane is considered the main or accompanying mineral

deposit. In the Mikołów map sheet there are three methane deposits categorised as main mineral deposit (Szuflicki *et al.*, ed., 2014). These are the undeveloped deposits of Paniowy-Mikołów-Panewniki, Murcki (deep) and Halemba II, documented below the base of hard coal deposits. The total economic resources are 8,534.8 million m³.

As an accompanying mineral deposit, methane is documented down to a depth of 1,000 m, sporadically to 1,250 m. It is mined together with hard coal and partly used in the heating sector. The total economic resources of methane in these deposits are 5,123.64 million m³. In the Mikołów and Śmiłowice deposits, methane is documented outside the areas of coal mining down to a depth of 1,000 and 1,300 m, respectively. The total economic resources are 3,988 million m³.

The map sheet area is rich in **clays for building ceramics**, which have been mined since the early 19th century. Clays and loams were used by numerous brickyards in the production of bricks and other products. Old working pits are utilised as landfills for industrial and municipal waste, and subsequently they are usually subject to reclamation.

Within the map sheet limits, four deposits of Upper Carboniferous weathering loams, clays and clay shales have been documented: Ligota-Katowice, Sitko-Mikołów, Mikołów-Emma and Kochłowice II (*op.cit.*). The Sitko-Mikołów and Mikołów-Emma deposits are currently abandoned, and the Kochłowice II and Ligota-Katowice deposits remain undeveloped. The bedded deposits of clays and claystones, with a simple geological structure, locally contain coal and sandstone interbeds at the bottom. The thickness of the good quality clay mineral deposit is 27–29 m.

A filling sand deposit called Panewniki and a sharp sand deposit of the same name have also been documented in the study area (*op.cit.*). The filling sand deposit is a several-metres-thick bedded deposit of good quality sands occurring under a thin overburden. The sand had been extracted over a few decades (until the early 1990s), and was used as a filling material in the nearby coal mines. In the period 1985–1993, a separate sand deposit was isolated in the southern part of the filling sand deposit, which was exploited for the needs of the construction sector.

HUMAN IMPACT

Natural environment in the study area has undergone transformation predominantly as a result of hard coal mining carried out over centuries. The relief has been modified by deformational events (continuous deformation in the form of troughs and depressions, and discontinuous deformation – sinkholes). The relief changes give rise, in turn, to the

modification in the hydrographic network. Additionally, the natural environment has been adversely affected by mine waste gathered on piles and heaps. Activities of the other industries and the trade and service sector contribute to the contamination of land surface, water and atmospheric air.

Atmospheric air. The quality of atmospheric air is dependent on many factors. In the study are it is affected by particulate matter and gas emissions from the industrial and service sector sources, low emission from individual household sources, linear emission from transportation sources, and emission from neighbouring areas, mainly from industrial facilities located in the municipality of Łaziska Górne and the city of Tychy (PONE 2012; Program..., 2014).

The main pollution hot spots are represented by low emissions and those from transport sources (Program..., 2014). Currently, the power plants have been using efficient exhaust gas cleaning systems for some time. Obsolete individual heating systems (coal-fired) used in residential and public buildings, as well as dusting caused by the ever-increasing vehicular traffic are the important sources of air pollution by particulate matter. Among the largest sources of air pollution are heating plants.

Results of the environmental monitoring shows that the permissible limits for the concentrations of benzene, lead, arsenic, cadmium, nickel and carbon monoxide are not exceeded, but the concentrations of particulate matter PM10, PM2.5 and benzo(a)pyrene are above the permissible levels (Ocena..., 2013).

Surface water and groundwater. Industrial activities and local economy have an impact on the aquatic environment. Only a few short sections of river channels, mainly of those flowing through forested areas, are close to natural. Rivers flowing through urban areas are generally strongly transformed by human impact. River channels are mostly artificial – straighter than their original courses, often deepened, and locally lined with concrete slabs.

Contamination of surface waters is caused by improperly treated municipal wastewater, sewage discharging from industrial plants, saline mine water, and surface runoff. The contamination level of river water is predominantly the result of both the discharges of mine water rich in sulphates and chlorides, and unsustainable wastewater management.

According to analyses of the Regional Inspectorate of Environmental Protection in Katowice, the water covered by the monitoring network require undertaking activities in order to improve its quality. Loss of a significant part of biological populations has been proven in these waters. They are not suitable for public use, and cannot be subject to any treatment.

The environmental monitoring results show that the Kłodnica and Mleczna rivers and the Jamna Stream convey poor quality water (*op.cit*.). The ecological status of the water of the Kłodnica River and Jamna Stream is assessed as unsatisfactory, while those of the Mleczna River as poor. The decisive factor is their biological and physico-chemical status.

The Kłodnica River is contaminated predominantly by the influx of sewage from the Ligota, Ochojec and Panewniki quarters in Katowice city and from Mikołów city, which are discharged either directly into the river. The Kłodnica River receives treated wastewater from the Panewniki sewage treatment plant in Katowice, which treats sewage from the Ligota, Panewniki and Brynów quarters and from some area of the Ochojec quarter. The Panewniki sewage treatment plant is a mechanical-biological-chemical unit with enhanced removal of nitrogen and phosphorus compounds (Program..., 2014).

The Mleczna River receives sewage from the Podlesie mechanical-biological-chemical sewage treatment plant in Katowice.

The Jamna Stream takes sewage from the area of Mikołów, and has been contaminated by organic compounds for several years now. Because there is no impermeable barrier at the base, the quality of its water is also negatively affected by a mine heap of the Halemba-Wirek mine, located in the middle reach of this stream (Studium..., 2013).

The groundwater of the southern and eastern parts of the map sheet is of satisfactory quality (Wyniki..., 2013). The north-western portion of the map sheet is situated within the range of the Major Groundwater Reservoir No. 331 – fossil valley of the upper Kłodnica River (Kleczkowski ed., 1990). It is a confined Quaternary reservoir with neither maximum protection (ONO) nor high protection (OWO) areas established (Nowicki ed., 2007). Because of both the presence of point pollution sources and the draining effect of dewatering operations in coal mines, the quality and resources of the reservoir (on a regional scale) show negative changes (Prognoza..., 2009).

Soils. Some soils of the study area have undergone transformation due to anthropogenic processes, mainly exploitation of hard coal deposits and dispose of mine waste, development of the housing sector, urban functions and infrastructure, as well as fallout of particulate matter and contaminated atmospheric precipitation. Precipitation monitoring shows that 65% of rainwater is acidic (pH below 5.6), and the pH values vary from 3.45 to 6.78 (Liana *et al.*, 2014).

Because of contamination by heavy metals, soils of the Piotrowice, Podlesie, Kostuchna and Zarzecze quartes in Katowice city are not suitable for agricultural use, and the area around a PKN ORLEN fuel base is contaminated by petroleum compounds. This area is currently under reclamation (Program..., 2014).

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).

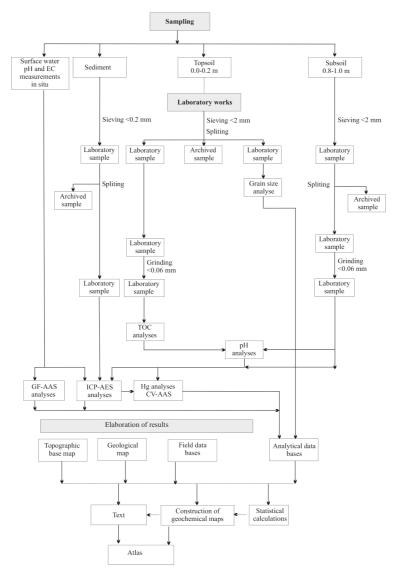


Fig. 1. The study procedure

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 1,367. 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 (342 and 309 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-µm Millipore filters and acidized with nitric acid in 30-ml bottles. The bottles were also labelled with numbers.

All the sampling sites were indicated in topographic maps at a scale of 1:10,000 and numbered

Locations of the sampling sites were defined with GPS, using a device equipped with an external antenna and a computer which can record not only coordinates but also additional information (pH and EC of water samples, data on land development and land use 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).

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Sample nu	inber			, ,	0.0-0.3	m			imates			
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2	village	develo	oment				forest		2			d-clay
3	1	-	th low dev	elopment		-	meadow		3		- '	y-sand
4	urban ar	eas wit	th high dev	elopment		4	barren la	and	4		cla	у
5 industrial areas						5	lawn		5		till	
						6	park		6		silt	
						7 :	allotmen	nt	7		pea	t
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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 water 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 topsoils (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: topsoils (0.0–0.3 m), subsoils (0.8–1.0 m), sediments and surface water.

Soils 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 water of individual water bodies, as well as for geochemical map construction. Statistical calculations were made for both whole datasets and subsets created for soils, sediments and surface water. In the case of some elements with the content lower than the detection limit value for the given analytical method, half of the detection limit value was taken. The arithmetic and geometric means, median, 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 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 Mikołów 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 Mikołów Sheet and the adjoining 1:25,000-scale sheets to avoid any discrepancies at the sheet boundaries. The Mikołów 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 Mikołów 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 parent rocks of soils in the map sheet area are variable in terms of lithology and age (Pl. 1). They gave rise to different soil types that typically reflect the chemical composition of the bedrock. Podzols and pseudopodzols have developed from the Carboniferous sandstones and Quaternary glaciofluvial and glacial sandy sediments. The parent rocks for cambisols are glacial tills. In the Kłodnica River valley, muddy-swampy soils are predominant, whereas industrial areas are covered with anthropogenic soils with disturbed soil profiles, transformed as a result of human activities (Program..., 2014). Podzols, the least abundant in nutrients, occur in forest areas, while the more fertile soils are utilised for arable land and meadows.

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.

Grain-size composition of the soil largely determines its resistance to degradation and has a significant effect on the content of chemical elements. Soils that contain a high proportion of clay and silt fractions are usually characterised by high contents of elements and their reduced 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.

In the topsoil of the map sheet area the original grain-size composition has been significantly obscured by earthmoving and construction works (especially in industrial and urban areas). However, its variability is strictly related to the lithology of parent rocks. The most common soil type is sandy soils (slightly loamy sands) containing 40–80% of the 1.0–0.1 mm fraction (Pl. 4), which developed on Carboniferous sandstones, Pleistocene glacial and glaciofluvial deposits, and fluvial sediments (Pl. 1). These soils contain <20% of the silt fraction (0.1–0.02 mm) and <10 % of the clay fraction (<0.02 mm).

Soils that contain a considerable amount of the silt and clay fractions occur commonly in areas of outcropping Carboniferous rocks in the northern and southern part of the map sheet. The silt content in these rocks is locally in excess of 20% (Pl. 5), and the clay fraction content ranges from 10 to 20% (Pl. 6).

Acidity. Soil pH is constrained by the mineral composition of parent rocks, soil use, and anthropogenic factors.

In the topsoil layer, acidic soils are prevalent (52%), and at a depth of 0.8–1.0 m the most common group (45%) are neutral soils (Pls. 7 and 8). Strongly acidic pH (<5) are sandy soils in forested areas of the middle and western part of the map sheet (Pl. 7).

Alkaline soils (pH >7.4), locally strongly alkaline (pH >8), are found in residential and industrial quarters of Katowice city and in residential areas of Mikołów city. A natural factor affecting soil pH in these areas is the high concentration of calcium which is present in the Quaternary glacial tills and Carboniferous claystones. The soil alkalinisation is also due to the fallout of alkaline dusts, use of chemicals for snow removal from streets, as well as due to the presence of rubble containing fragments of sand-lime mortar as evidenced by the study of soils in many cities (Greinert, 2000; Gąsiorek, Niemyska-Łukaszuk, 2004; Tomassi-Morawiec ed., 2016).

As regards the subsoils, alkaline areas are larger than in the topsoils. This is probably due to the migration of industrial dust into the soil profiles (predominantly dust from industrial combustion of coal), which are rich in magnesium and calcium compounds (Różkowska, Ptak, 1995a, b).

Neutral soils (pH 6.3–7.4) occupy small areas in the south-eastern and northern parts of the map sheet.

Geochemistry. The content of major and trace elements in soils depends on the chemical composition of basement rocks, types of weathering processes, soil-forming

processes, and human impact. In the study area, soil-forming processes have led to some changes in the chemical composition of soils in relation to the parent rocks, but the contents of most elements do not deviate from the geochemical background value in the Silesian-Cracow region (Lis, Pasieczna, 1995b). The degree of human impact is manifested by the increase in concentration of heavy metals, and the areas of anomalies represent zones of potential risk, which should undergo reclamation processes.

The contents of silver, arsenic, cadmium, iron, mercury, magnesium, nickel, phosphorus, strontium, vanadium and zinc in topsoils (expressed by median values) are close to the geochemical background values for these elements in the Silesian-Cracow region (Tab. 2). Slightly higher values are found for barium, cobalt, copper, manganese, lead and sulphur. In the case of calcium, chromium and titanium, the measured concentrations are about twice greater than the geochemical background.

The lowest contents of lithogenic elements – aluminium, barium, calcium, cobalt, chromium, iron, manganese, nickel, phosphorus, strontium and vanadium – are observed in both soil depth intervals in forest soils that developed on Pleistocene glaciofluvial sands covering the western part of the map sheet. This is due to the poor chemical composition of bedrock and its acidic pH, which favours leaching of elements. Soils that developed on outcrops of various Carboniferous rocks and Quaternary glacial tills show higher contents of these elements.

Sandy soils of the north-western part of the map sheet contain below 0.40% of aluminium. In other regions the content is in the range of 0.40–0.80%. The aluminium-richest soils (>0.80%) develop on glacial tills and Carboniferous claystones. The higher aluminium content is related to the occurrence of aluminium-rich constituents (feldspars, micas and clay minerals) in these fine-grained rocks.

The arsenic content in the soils is natural and invariable. In most of soils that developed on sandy rocks, it does not exceed 10 mg/kg, and in soils developed on glacial tills and older deposits, it is up to 10–20 mg/kg. The arsenic enrichments (20–80 mg/kg) are of natural origin and have been detected in meadow soils that show features of iron bog sediments. The concentration of >100 mg/kg of arsenic in the topsoil was measured in some samples from industrial areas, which indicates its anthropogenic source.

The spatial distribution of barium content is associated with both the presence of this element in soil's parent rocks and its dispersion in dusts from industrial combustion of coal. Among Carboniferous rocks, clay shales, which are the parent rocks of some soils, show the highest ability of retaining barium (Čurlík, Šefčík, 1999; Kabata-Pendias, Pendias, 1999).

Barium is also a natural component of hard coal, in which its concentration can be up to 330 mg/kg (Różkowska, Ptak, 1995a; Kabata-Pendias, Mukherjee, 2007). The distribution of barium in the soil samples is similar in both depth intervals. Larger areas of soils rich in this element (>120 mg/kg) are observed in the topsoils, which indicates its immission from anthropogenic sources. The barium content in sandy soils of forest areas of the western part of the map sheet rarely exceeds 60 mg/kg. It increases to 120 mg/kg in the remaining area, and a clear anomaly (>240 mg/kg) is marked in soils around the facilities of the Wujek mine and the former chemical plants in the Ligota quarter of Katowice.

The content of calcium and magnesium (0.25–1.00% and >0.12%, respectively) is greater in soils of built-up areas of Katowice and Mikołów in both depth intervals compared to forest areas and arable land of the central and western parts of the map sheet (0.01–0.25% calcium and 0.01–0.12% magnesium). Locally, the concentrations of calcium are >2%, and of magnesium >0.50%. The highest calcium concentration is found in the anthropogenic soils (median 0.43%) and in urban lawns (median 0.46%). The main reason for the calcium enrichment is probably emission of dust from coal combustion, plus an admixture of lime debris (concrete, plaster, mortar) in the grounds.

The organic carbon content in the topsoils is commonly in the range of 1.5–3% (median 1.9%). Soils that are more abundant in organic carbon (>3%) are found in forest areas of the northern and western part of the map sheet, while those of arable land contain 0.5–3.4% of this constituent. They are more abundant in organic carbon than those with the most common contents of this constituent (0.4–2.1%) in soils of arable land of Poland (Pasieczna, Markowski, 2014). Near the waste heap located in the Jamna Stream valley the organic carbon content locally exceeds 12%, which is due to the presence of hard coal pieces in soil.

The phosphorus content is dependent mainly on the chemical composition of parent rocks. Soils that developed on Quaternary glacial tills and Carboniferous rocks are richer in this element (0.038%) compared to those in areas of sandy deposits (0.021%). The phosphorus content in the topsoil of the study area varies from <0.002 to 0.690%, and in the subsoil from <0.002 to 0.143%. Comparison of the median phosphorus contents in both soil depth intervals (0.027% in the topsoil, and 0.007% in the subsoil) indicates a contribution of anthropogenic sources to the accumulation of this element. The lowest amounts of phosphorus are found in sandy soils of forest areas (median 0.015%), while the highest contents are known from urban areas (0.040%).

The sulphur content in soils from both depth intervals ranges most commonly between <0.003 and 0.080%, only locally exceeding 0.320%.

The spatial distributions of some elements (especially heavy metals) are determined not only by lithogenic sources but also significantly by anthropogenic factors.

Among the regions with soils significantly contaminated by metals due to industrial activity is the area near Ligocka Street in Katowice. In the topsoil the concentrations are as follows: >80 mg/kg of arsenic, >16 mg/kg of cadmium, >250 mg/kg of lead, and >1,000 mg/kg of zinc. The soil contamination is probably related to the activity of chemical industry plants. As early as before World War I, the Górnośląska Fabryka Farb paint manufacturer operated in this area. It was one of Upper Silesia's largest chemical industry plants (active until the 1960s) producing Glauber's salt and hydrochloric acid. Other historical industrial plants of the region include an oil refinery company, a mine wood preservatives manufacturer, a brickyard, and an acetylene plant (Ligota.info...)

Contaminations by metals are found at a depth of 0.0–0.3 m in lawn soils of residential areas in Hierowskiego Street in the Piotrowice quarter of Katowice. The concentrations are as follows: 4.7 mg/kg silver, 399 mg/kg arsenic, 606 mg/kg copper, 5,318 mg/kg lead, and 16,200 mg/kg zinc. The soil pollution is probably a result of mixing natural soils with foreign material that originated in old reclaimed slag heaps.

Of similar origin is also the local contamination by metals found in the topsoil near Sasanek Street in Katowice-Podlesie. It can be supposed that the metals come from slag heap material once used for levelling the area during construction works. The following metals have been found: cobalt (up to 74 mg/kg), chromium (up to 267 mg/kg), copper (up to 3,134 mg/kg), nickel (up to 393 mg/kg), lead (up to 730 mg/kg) and titanium (up to 1,404 mg/kg).

The quarters of Załęska Hałda, Katowicka Hałda, Brynów, Kokociniec and Ligota in Katowice represent a massive area where, predominantly, the topsoils are contaminated by lead (>100 mg/kg) and zinc (>250 mg/kg). Similar contamination levels by these metals in soils developed on various lithologies (Carboniferous claystones and sandstones, glacial tills, and glacial and glaciofluvial sandy deposits) allows inferring that the metals originate from anthropogenic sources (probably from fallout of industrial dust, and from historical slag heaps of zinc smelters). In the settlement of Katowicka Hałda there was the Henrietta zinc smelter and the Beate hard coal mine active already in the early 18th century. In the area of Załęska Hałda, the Johanna and Victor zinc smelters also operated (Degenhardt, 1870). An additional source of zinc and lead could be the transport of industrial dust from beyond the northern boundary of the map sheet, where a forge and, subsequently, the Baildon iron smelter

operated from the 15th century on. In the inter-war years this smelter produced various types of sheet metal, electrodes, carbides and magnets, during World War II also materials for the military industry, and, after the war, various grade steel (Huta Baildon...).

In the middle reach of the Jamna Stream the chemical composition of soils is affected by a pile of waste and scrap of the Halemba-Wirek mine. Elevated concentrations of some elements have been detected in this area. The organic carbon content locally attains a level of 6.0–12.0%. There is also the presence of cobalt (>8 mg/kg), copper (>20 mg/kg), nickel (>10 mg/kg), sulphur (>0.080%) and vanadium (>10 mg/kg).

The topsoil layer shows a number of local anomalies of silver concentration at 1–2 mg/kg, while the natural concentrations in soils are merely 0.06–0.4 mg/kg (Kabata-Pendias, Mukherjee, 2007). Silver from anthropogenic sources is presumably related to sulphur or organic matter. It is evidenced by both the locally elevated sulphur contents at sites of silver anomalies and the concentrations of silver in meadow and swampy soils rich in organic carbon.

In the topsoil the mercury concentration does not typically exceed 0.10 mg/kg. In areas composed of Carboniferous rocks and glacial tills the concentration is 0.10–0.20 mg/kg. Anthropogenic sources of mercury (up to 4.49 mg/kg) are probably responsible for its elevated contents in the topsoil of lawns in the Brynów quarter of Katowice (near Kępowa Street) and near the railway station in Mikołów (up to 2.13 mg/kg), where the subsoil is not contaminated.

The proportion of soils contaminated to various degrees by cadmium, lead and zinc is presented in Table 6. The compilation shows that the cadmium contamination (>4 mg/kg) is observed in 7.6% of the topsoil area. The lead concentration >100 mg/kg was found in 21.95% of soils, and the zinc concentration >500 mg/kg in 6.88% of soils. In the 0.8–1.0 m layer the percentages of soils contaminated by these metals are much lower.

The topsoil (0.0–0.3 m depth) was analysed for the degree of pollution by metals, classifying them into the soil use groups A, B and C (Tab. 7), based on permissible limit values (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 content of arsenic and metals, 40.60% of the soils have been categorised into group A (purity meeting the requirements for protected areas and special use land). Group B (soils useful for agricultural and forest cultivation) is represented by 45.06% of the samples analysed, and group C (soils useful for industrial and transportation purposes only) is represented by 14.34% of the samples. The

criteria required for soil's multifunctional use are met by the soils assigned to groups A and B. The soils classified into group C occur in urban-industrial areas (Pl. 63). The discussed soil classification indicates how the given area should be used in accordance with the guidelines of the Ministry of the Environment (Regulation ..., 2002). In many cases, the current land use is inappropriate and requires monitoring and, locally, remediation. Areas of high concentrations of metals should be reclaimed or used only as industrial areas.

SEDIMENTS

Sediments of watercourses and reservoirs of surface water are deposited from mineral and organic suspension derived from erosional processes, as well as constituents that precipitate from the water. Their chemical composition is determined by many natural and anthropogenic factors. It depends mainly on the lithology of the drainage basin, geomorphology and climatic conditions. All of them determine the processes of weathering of rocks, as well as the mobilisation, migration and accumulation of elements (Bojakowska, Gliwicz, 2003).

In industrial, urban and agricultural areas, sediments are penetrated by potentially harmful trace elements and organic compounds carried by the leachate from waste dumps, as well as those contained both in industrial and municipal sewage discharged to surface water, and in runoff water (Ciszewski, 1997, 2002, 2005; Matschullat *et al.*, 1997; Miller 1997; Bojakowska *et al.*, 2006; Harnischmacher, 2007; Kozieł, Zgłobicki 2010; Lagauzère *et al.*, 2011; Govil *et al.*, 2012; Cempiel *et al.*, 2014).

In the study area, anthropogenic contaminants that originate from the discharge of industrial and household sewage affect the chemical composition of sediments more strongly than natural factors do. Considerable parts of the valleys have been engineered, so that the rivers flow in high-walled, concrete-lined channels. Frequent engineering operations and land drainage have resulted in the disappearance of wetland and floodplains in many places, which are now commonly replaced by housing development areas (Działoszyńska-Wawrzkiewicz, 2007). The peculiar feature of most of the sediments is the high content of very fine coal particles that shows sorption properties enabling binding of metals and their easy precipitation (Nocoń, Kostecki, 2005).

Contaminants in sediments may be toxic to fish and other aquatic organisms, especially predators, posing health risk to humans and animals consuming fish or shellfish that feed at polluted sites (Šmejkalová *et al.*, 2003; Liu *et al.*, 2005; Vink, 2009). Harmful constituents of the sediments may be re-mobilized into the water following various biological,

chemical and physical processes. Contaminated sediments that are displaced into floodplains also cause an increase in the concentration of heavy metals in soils (Bojakowska, Sokołowska, 1995; Bojakowska *et al.*, 1996, 2011; Gabler, Schneider, 2000; Weng, Chen, 2000; Middelkoop, 2000; Gocht *et al.*, 2001; Miller *et al.*, 2004).

In the Mikołów map sheet area, sediments were analysed in watercourses and water reservoirs located in the drainage basin of the upper Kłodnica River and its tributaries – Ślepotka Stream and Jamna Stream, and in the drainage basin of the upper Mleczna River. The ranges of concentrations and statistical parameters of the analysed elements in the individual drainage basins are given in Table 4.

In the map sheet area, the greatest aluminium content (2–4%) is observed in ditches, minor watercourses and small unnamed lakes located mostly in forested areas. The calcium content is much lower than the geochemical background value in the Silesian-Cracow region. The iron content varies within a wide range (0.06–19.85%), and the highest contents are found in sediments of lakes and watercourses in forests and uncultivated areas in the Kłodnica River drainage basin. The content of phosphorus in the sediments is up to 0.600%; its content above 0.300% is found in watercourses draining urban areas. The content of sulphur is much greater than the regional geochemical background value, and its maximum level (5.140%) was found in sediments of a small stagnant water body in a depression near Okrężna Street in Katowice.

The silver concentration in most of the samples does not exceed the detection limit (1 mg/kg). Almost half of the samples show the arsenic concentrations close to the regional geochemical background value (6 mg/kg). It is worth noting that about 75% of the sediments contain <10 mg/kg of arsenic, i.e. the amount below which its negative effect on aquatic organisms is not observed. However, at the concentration of >33 mg/kg, harmful effects of arsenic on aquatic organisms can occur (MacDonald et al., 2000). Such amounts of arsenic have been found in several samples (including all from a stream flowing near Kokociniec settlement). The sediments that contain considerable amounts of arsenic are also characterised by high contents of iron (>1%). The presence of iron hydroxides or sulphates in sediments favours the accumulation and mobilisation of arsenic.

The maximum concentration of cadmium is 201.6 mg/kg, and its levels above 5 mg/kg have been found in 30% of samples analysed. The median cadmium concentration (2.9 mg/kg) is slightly greater than the regional geochemical background value (2.5 mg/kg). Extremely high cadmium concentrations have been detected in sediments of a stream draining the Kokociniec and Ligota settlements.

Copper concentration >200 mg/kg has been detected in sediments of the Mleczna River in the area of allotment gardens in Katowice, in a ditch meeting the Jamna Stream in Mikołów, and in a stagnant water body near the northern boundary of the map sheet.

Mercury content below the detection limit was observed in 36.3% of samples, and the concentration above 1 mg/kg was found in 6 samples. The highest mercury concentration is found in sediments of the Ślepotka Stream and in its tributary flowing through Katowice, at three localities in sediments of the Kłodnica River, and in sediments of the stream flowing from Kokociniec and Ligota settlements.

The average nickel content in sediments of the study area is very close to the geochemical background value in the Silesian-Cracow region. An extremely high nickel concentration (>100 mg/kg) has been recorded in a ditch meeting the Kłodnica River in a forested area in Katowice.

The maximum lead concentration in the sediments is up to 923 mg/kg, and the concentration of zinc >1,000 mg/kg is observed in 13.16% of them. Especially high zinc concentrations are found in the stream flowing from Kokociniec and Ligota settlements.

Kłodnica River and its catchment. The study area hosts only the upper reach of this river. Its headwaters are located to the east outside the map sheet area. The Kłodnica River valley preserves much of its natural character; the river strongly meanders, and there are oxbow lakes in many places. Along the entire length of its valley there are small lakes, meadows and reedlands (Działoszyńska-Wawrzkiewicz, 2007).

To the west of the map sheet the Kłodnica River flows across forested areas (Kochłowickie Forests), and in the upper part of its drainage basin there are residential areas of Katowice (Kokociniec, Ligota, Brynów), also with metallurgical plants, repair workshops and transport bases which can contaminate sediments by wastewater discharges. Earlier geochemical studies showed that the contents of heavy metals in the sediments do not deviate from the average for the Silesian Voivodeship (Nocoń, 2006).

The contents of major elements (calcium, iron, manganese and phosphorus) in the Kłodnica River is lower than the regional geochemical background values, however, the contents of some trace elements are higher.

In the upper reach, sediments contain locally 10–40 mg/kg of arsenic, whereas in forested areas of the lower course of the river the concentrations are <3–5 mg/kg. The silver content is locally 2 mg/kg in the upper reach, and <1 mg/kg in the lower course. The highest contamination of sediments in the upper reach of the Kłodnica River is related to the material supplied by its right-hand tributary flowing from the Ligota and Kokociniec settlments, which

drains an area of the former chemical plants with highly contaminated soils (Ligota.info...). Upstream of this tributary, sediments of the Kłodnica River contain 80–200 mg/kg of barium, and downstream of it 200–350 mg/kg. Still more clearly marked are the cadmium concentrations, which are 4–5 mg/kg and 100–200 mg/kg, respectively. The sediments also contain considerable amounts of chromium (up to 58 mg/kg), copper (up to 116 mg/kg), mercury (up to 1.63 mg/kg), phosphorus (up to 0.560%), lead (up to 540 mg/kg), strontium (up to 90 mg/kg) and zinc (up to 9,614 mg/kg).

Like with the case of soils, the contamination of sediments is likely caused by the activities of the Górnośląska Fabryka Farb paint manufacturer in the Ligota quarter of Katowice (Ligota.info...) and by the activities of historical industrial plants in Kokociniec settlment. Kokociniec settlment was established on the basis of a forge built in 1650. In the 19th century, the settlement was developing around a smelter and a metallurgical manufacturer processing pig iron to produce steel. In 1845–1846, two large coal-fired furnaces, an iron foundry were built here (Kokociniec...).

In its lower part the Kłodnica River drainage basin is recharged by streams and ditches draining the area of mine heap of the Halemba hard coal mine, which is probably the source of contamination. Sediments of these streams are characterized by considerable amounts of aluminium (up to 4.09%), iron (up to 12%), manganese (up to 93,972 mg/kg), cobalt (up to 703 mg/kg), nickel (up to 547 mg/kg), strontium (up to 585 mg/kg) and zinc (up to 7,240 mg/kg).

Jamna Stream and its catchment. The headwaters of the stream are located in the area of Mikołów. In its upper reach the stream flows mostly in a concrete-lined channel across urban areas. Below the centre of Mikołów, actually downstream to the Kłodnica, the stream flows in a natural valley.

The Jamna Stream had carried pristine water until the 1950s, but the stream and its tributaries were gradually receiving more and more local sewages. Currently, the Jamna Stream receives wastewater from the Centrum and Śmiłowice sewage treatment plants. In its middle reach there is the mine heap of the Halemba mine, whose leachate contaminates the sediments of the nearby tributaries of the Kłodnica.

Sediments of the Jamna Stream and its tributaries are characterised by a relatively low amount of the major and trace elements analysed for this study. Their average contents (expressed in medians) are lower than the regional geochemical background values, but are closer to the geochemical background values for Poland. The content of chromium, copper,

mercury and sulphur in sediments of the Jamna Stream drainage basin is the same as the background values in the Silesian-Cracow region.

Sediments of the drainage basin are characterised by low content of aluminium (0.29%), calcium (0.14%), iron (0.50%), phosphorus (0.035%) and sulphur (0.059%).

The content of trace elements in sediments of the Jamna Stream drainage basin is lower as compared to these of the Kłodnica River, Ślepotka Stream and Mleczna River. Locally, the sediments are contaminated by some elements. In sediments of the Jamna Stream in the Goj quarter, the concentration of arsenic is up to 114 mg/kg, cadmium up to 13.1 mg/kg, copper up to 325 mg/kg, and zinc up to 2,089 mg/kg. The likely source of the metals and arsenic is surface runoff water contaminated due to industrial activity in Mikołów. In the 19th century, the small iron smelters of Maria-Ludwika, Manna-Mikołów and Walter, as well as a number of coking plants operated in this area (Kantyka, Targ, 1972; Mikołów...).

Ślepotka Stream and its catchment. The stream begins its flow in Katowice, on the border of the Ochojec and Murcki quarters. It flows across the quarters of Ochojec, Ligota and Panewniki where it meets the Kłodnica River. In the 1960s and 1980s, the watercourse was engineered and its channel was lined with concrete slabs. In the past the stream was significantly contaminated by sewage illegally discharged by residents of the nearby city quarters. Currently, the sources of contamination are the rain and melt water, primarily from urban areas, workshops and industrial plants.

Sediments of the stream are characterised by lower contents of calcium, magnesium, iron, manganese and phosphorus in relation to the geochemical background values in the Silesian-Cracow region. Compared to sediments of the Mleczna River and Jamna Stream, those of the Ślepotka also contain smaller amounts of aluminium, and slightly higher amounts of calcium, magnesium and phosphorus, and especially of sulphur.

The maximum concentrations of toxic trace elements detected in sediments of the stream are as follows: silver 6 mg/kg, cadmium 14.1 mg/kg, mercury 19.00 mg/kg, lead 282 mg/kg, and zinc 3,138 mg/kg.

Along its entire length, sediments of the stream are contaminated by cadmium (3–7 mg/kg), and in its upper reach by chromium (20–40 mg/kg) and copper (30–50 mg/kg).

In the upper reach of the Ślepotka Stream (near a hospital), sediments of its small tributary contain 19 mg/kg of mercury. Its concentration in the watercourse draining also the premises of a former hospital (between Śląska Street and the Ślepotka valley) is 6 mg/kg. The likely source of mercury is hospital waste that migrates into the sediments.

In the Ślepotka Stream drainage basin, contamination by heavy metals (239 mg/kg of arsenic, 364 mg/kg barium, 54.5 mg/kg cadmium, 636 mg/kg lead, 141 mg/kg vanadium, and 1,680 mg/kg zinc) has been detected in sediments of its left-hand tributary that carries water from the area of warehouses and a railway transport base. These sediments are also characterised by high contents of iron (4.27%), phosphorus (0.185%) and sulphur (0.676%) – the elements whose compounds (phosphates, sulphides and hydroxides) can retain heavy metals.

The Mleczna River and its catchment. The river begins its flow in the Odrodzenie quarter in Katowice. Near the southern boundary of the map sheet it receives wastewater from the Podlesie mechanical-biological treatment plant that takes sewage from the Piotrowice, Podlesie, Kostuchna and Murcki quarters of Katowice.

The content of calcium, iron, manganese and phosphorus in sediments of the Mleczna River is lower than the regional geochemical background value, while the sulphur content is twice as much. Sediments most contaminated by metals have been found in the Piotrowice quarter of Katowice. The maximum concentration of barium in this area is up to 428 mg/kg, chromium up to 119 mg/kg, copper up to 551 mg/kg, lead up to 182 mg/kg, and zinc up to 1,359 mg/kg.

Metals in these sediments may come from illegal sewage discharges and surface runoff from allotment gardens, which contain compounds of these metals in plant protection chemicals.

Sediments of stagnant water reservoirs show clearly elevated concentrations of calcium and sulphur, and are depleted in phosphorus as compared to sediments of watercourses in the study area. Most of them are not contaminated by metals.

High amounts of metals are found in sediments of a small water reservoir of a sinkhole in a forest near the northern boundary of the map sheet: 427 mg/kg of barium, 452 mg/kg chromium, 205 mg/kg copper, 0.11 mg/kg mercury, 519 mg/kg lead, and 1,806 mg/kg zinc.

In sediments of a small water reservoir near the railway track west of the Wujek mine the concentrations are as follows: 22.9 mg/kg of cadmium, 393 mg/kg lead, and 4,780 mg/kg zinc.

Sediments of Starganiec Duży and Starganiec Mały lakes, located in a forest on the border of Katowice and Mikołów, contain up to 7.9 mg/kg of cadmium, 0.19 mg/kg mercury, 147 mg/kg lead, and 881 mg/kg zinc. The possibility of release of these metals to the water is certainly a threat for residents using them for recreational purposes.

SURFACE WATER

Human impact on water resources has a quantitative (a change in hydrologic regime), qualitative (water pollution, changes in chemical composition) and morphological (transformation of watercourse channels and lake basins) significance. Unfavourable changes result in ecological effects involving the disturbance of habitat conditions, regression of certain species, and reduction in biodiversity (Bańkowska...).

The studies conducted in the Jamna Stream, Mleczna River, Kłodnica River and Ślepotka Stream catchments were focused only on their chemical composition. In order to compare and easier evaluation of the quality of the analysed water, provided are the contents of their individual components and the results of calculated statistical parameters along with the threshold values of the surface water quality indices used in Poland (Rozporządzenie..., 2011), and the indices for mineral and drinking water in accordance with UE recommendations (EU Directive, 1998/83/EC; 2009/54/EC) – Table 5.

The pH values of the water in watercourses and stagnant water reservoirs in the map sheet area do not exceed normative recommendations. Their mineralization, indicated by EC values, frequently exceeds 1.5 mS/cm, which is approved as a boundary limit for good quality water (Witczak, Adamczyk, 1994; Rozporządzenie..., 2011). Unsatisfactory water quality is due to discharges of municipal sewage and industrial wastewater.

Klodnica River and its catchment. The water of the river, whose pH is in the range of 6.8–8.4, meet the criteria for water quality classes I and II, while in the water of its drainage basin the pH varies from 4.1 to 8.4. The water of the Kłodnica River are characterised by electrolytic conductivity values varying within a wide range from 0.72 to 11.85 mS/dm³, and in its drainage basin – within a much wider range (0.10–15.63 mS/dm³). The maximum EC values have been recorded in the Kłodnica River downstream of the Panewniki sewage treatment plant, while in its tributaries – downstream of the mine heap of the Halemba mine.

The poor water quality in the Kłodnica River and the watercourses in its catchment results predominantly from high sulphate concentrations, even several ten times as much as the admissible limit for water quality class II. The water of the river contain up to 4,170 mg/dm³ of sulphates, and the water of some tributaries even up to 33,520 mg/dm³. The extremely high sulphate concentrations are found in the tributaries flowing from the mine heap.

The water in the drainage basin is poor also due to high iron concentrations. Over 40% of the samples reveal higher iron concentrations than the limit value for water quality class II

(0.3 mg/dm³). The iron concentration in the water of the Kłodnica River is up to 0.73 mg/dm³, and of its tributaries up to 141.65 mg/dm³. High amounts of iron are also found in forest streams (a stream flowing through Starganiec lake, and a stream flowing through Czarny Staw pond) and in the tributaries flowing from the mine heap.

The aluminium content in the water of the Kłodnica River is low $-<50~\mu g/dm^3$. Much greater concentrations (up to 2,261.1 $\mu g/dm^3$) have been recorded in forest streams of its drainage basin.

The calcium content in the water of the Kłodnica River varies most commonly from 70 to 200 mg/dm³ and does not exceed the boundary limit for water quality class II. Higher calcium concentrations (up to 560.6 mg/dm³) are found in the water of the streams draining the mine heap area.

The distributions of magnesium, potassium and sodium are clearly affected by the sewage discharge from the Panewniki sewage treatment plant. Upstream of the discharge site the magnesium concentration is 15–20 mg/dm³, and downstream from the site it increases to 100–150 mg/dm³. Similar distribution patterns are observed for potassium and sodium concentrations, with the values of 8–10 mg/dm³ and 45–50 mg/dm³ for potassium, and 50–80 mg/dm³ and 1,500–2,000 mg/dm³ for sodium, respectively.

The median manganese concentration in the water of the Kłodnica is 0.127 mg/dm³, but the maximum value in its drainage basin is 12.140 mg/dm³. Especially high concentrations of this element have been recorded in a watercourse in the Kokociniec settlement. Like in the case with soils and sediments, this contamination is probably caused by the Górnośląska Fabryka Farb paint manufacturer in the Ligota quarter of Katowice (Ligota.info...) and by the activities of historical industrial plants of Kokociniec settlement (a smelter and an iron foundry) (Kokociniec...).

The phosphorus concentration in many water samples from the Kłodnica River drainage basin exceeds the boundary limit for water quality class II (0.4 mg/dm³).

Trace elements in the water of the Kłodnica drainage basin are present most commonly at low content, corresponding to water quality classes I and II. Elevated contents of cadmium, zinc, lead, antimony, selenium, beryllium, nickel and molybdenum have been recorded only in a few samples. The most contaminated water occur in a stream draining industrial areas of Kokociniec settlement. It contain significant loads of these elements, resulting in increased concentrations also in the water of the Kłodnica River.

The elevated concentrations of manganese, silver, beryllium, cadmium, cobalt and nickel in minor tributaries flowing through forest areas are probably the result of acidic pH of soils in that area, leading to the leaching of these elements and their migration into the water.

Jamna Stream and its catchment. The water of the Jamna Stream is alkaline, varying within a narrow pH range (7.4–8.2) that falls in the interval of water quality class I. Higher pH variability is observed in the water of its drainage basin, with the pH values ranging from 4.4 to 8.8. The lowest pH was detected in a few unnamed streams flowing across forested areas north of Mikołów. Strongly alkaline water occur in two ditches in this town.

The electrolytic conductivity of the water of the Jamna Stream varies from 0.70 to 2.72 mS/cm, and the most common level is 1.20–1.30 mS/cm. Higher EC values have been recorded in the lower reach of the stream, downstream of a waste pile, and in its upper reach along the highway in Mikołów. In the water of the Jamna drainage basin the EC values range from 0.16 to 2.91 mS/dm³.

The aluminium concentration in the Jamna Stream water is most commonly $10-20 \,\mu g/dm^3$. Much higher concentrations (up to 2,955.5 $\mu g/dm^3$) are observed in the water of its two small tributaries flowing through a forested area north of Mikołów, composed of Quaternary glacial tills.

The poor water quality of the Jamna Stream and the tributaries in its drainage basin is mostly due to high sulphate concentrations, even several times greater than 250 mg/dm³ (boundary limit for water quality class II), and due to iron concentrations (>0.3 mg/dm³), especially in the western part of the drainage basin.

Another factor deteriorating the water quality is the high concentration of phosphorus in the Jamna Stream (0.5–2.0 mg/dm³), probably due to the discharge of municipal sewage. In the watercourses flowing in the Goj residential area, its concentration is up to 15.83 mg/dm³.

Along the entire length of the stream there is a variable concentration of potassium (10–30 mg/dm³) and a highly variable concentration of sodium (50–300 mg/dm³). The greatest amounts of sodium have been found in the water downstream of the mine heap of the Halemba mine, suggesting its origin from leaching of pore water from the heap.

As regards the calcium (up to 182.3 mg/dm³) and magnesium (up to 90.7 mg/dm³) contents, the water of the Jamna Stream catchment represent quality classes I and II.

The waters of the Jamna Stream and its drainage basin are characterised by small amounts of trace elements, with the exception of cadmium. The cadmium concentration (up to $7.74 \, \mu g/dm^3$) is much greater than the boundary value for water quality class II ($1 \, \mu g/dm^3$) in

the water of a left-hand tributary of the Jamna Stream, draining the area extending along the highway. The cadmium comes probably in runoff from road surfaces. Most of the drainage basin is also characterised by elevated silver concentrations (0.05–0.10 $\mu g/dm^3$) due sewage discharges.

Ślepotka Stream and its catchment. The water of the stream show neutral or slightly alkaline pH values (6.8–8.2). Acidic pH has been measured only in the water of the left-hand tributaries flowing through forest areas. The water of the Ślepotka Stream and its tributaries are characterised by low EC values (0.15–0.91mS/dm³).

Throughout the drainage basin there are high concentrations of sulphates (median 840 mg/dm³), so the water do not meet the criteria for quality class II.

The iron concentration exceeds the boundary limit for water quality class I. In the water of the Ślepotka Stream it is 1.22 mg/dm³, and in its tributaries it attains 6.70 mg/dm³.

The phosphorus content in most of the samples is low (<0.05 mg/dm³). Higher values of 0.20–1.32 mg/dm³ have been recorded locally in the premises of metallurgical and machinery manufacturers in the Ligota quarter of Katowice.

The contents of calcium, magnesium, manganese, potassium and sodium are relatively low. The water is also characterised by low content of aluminium (up to 47.3 mg/dm³) that is found at greater amounts only in the water of some tributaries in forest areas (up to 2,691.2 mg/dm³).

The water of the Ślepotka Stream and its drainage basin generally show low contents of trace elements, corresponding to water quality classes I and II. There are only a few water samples from forest streams in the left-hand part of the drainage basin, which show elevated concentrations of cadmium, zinc, lead, nickel and thallium.

Mleczna River and its catchment. Based on the pH and EC values, the water of the Mleczna River can be categorised into quality classes I or II. In the water of river pH varies in the range of 7.5–8.4, and the pH of the water of its drainage basin is 6.8–8.7. Electrolytic conductivity of the water in the drainage basin is low (EC 0.21–1.11 mS/dm³).

The crucial parameter for classifying the water of the drainage basin of the Mleczna River into a poor quality class is the sulphate concentration that most commonly exceeds many times the permissible limit for water quality class II. The median sulphate concentration in the drainage basin is 1,190 mg/dm³.

The content of iron in the water of the Mleczna River is relatively low (0.05–0.20 mg/dm³), and it locally attains 1–4 mg/dm³ in its tributaries. The greatest amounts of iron are found in forest streams.

The aluminium and phosphorus concentrations in most of the area meet the criteria for surface water quality classes I or II. There are also relatively low contents of calcium (up to 107.0 mg/dm³), magnesium (up to 25.1 mg/dm³), potassium (up to 39.1 mg/dm³) and sodium (up to 149.1 mg/dm³), which allow classifying most of the water into quality class I.

Trace elements have been detected most frequently at low contents, sometimes below the limit of detection. The contents of most of the elements correspond to water quality classes I and II. There are also some samples with elevated contents of beryllium, nickel and zinc. The cadmium concentration is locally up to $22.36 \,\mu\text{g/dm}^3$ (due to runoff from the highway surface).

CONCLUSIONS

- 1. Lithology of the parent rocks of soils is reflected in their geochemistry and grain size composition. Soils that developed on Pleistocene sandy deposits are poor in all elements analysed in this study. Carboniferous rocks and Quaternary glacial tills are the parent rocks for soils enriched in the silt and clay fractions as well as in aluminium, barium, cobalt, chromium, iron and nickel.
- 2. Acidity of the soils is variable and largely depends on the land use. The soils of urban and industrial areas in the eastern part of the map sheet are alkaline, whereas forest soils of its western part are acidic.
- 3. The arsenic, cadmium, lead and zinc anomalies that are found in soils of both depth intervals in the north-eastern part of the map sheet are associated with the historical activity of chemical industry and zinc metallurgy.
- 4. The silver, mercury and copper anomalies found in the topsoil show small areal extents and are caused by anthropogenic factors.
- 5. The contamination of sediments of inland water reservoirs and surface water are the result of discharge of mine water and industrial and municipal sewage, drainage of the mine heap, and surface runoff.
- 6. Sediments are contaminated by metals (silver, barium, chromium, copper, mercury, nickel, lead and zinc) derived from industrial sewage, as well as by phosphorus coming from the discharge of municipal sewage. Enrichments in cadmium, lead and zinc found in some sediments can be related to the nearby zinc metallurgy area.
- 7. Surface water of the study area is characterised by high variations in pH and electrolytic conductivity values. The strong contamination of water by sulphates is due

to the discharges of mine water. The elevated concentrations of phosphorus and metals result from the discharges of municipal and industrial sewage. The abundance of iron is probably associated with the natural drainage the catchment surface.

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