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INTRODUCTION

The Polish Geological Institute-National Research Institute has conducted investigations in the environmental field for many years, successfully using geochemical mapping methods. These studies allow the assessment of environmental pollution in a quick, cost-effective and objective way.

The Geochemical Atlas of Poland is one of the first atlases included in the series of mapping projects performed mainly for the purpose of environmental protection. It was prepared by an experienced team geochemists, chemists and cartographers, using the most modern analytical instrumentation, enabling investigations in accordance with the world standards.

The study involved soils as well as sediments and waters of inland water bodies. In areas of agriculture and forestry, prevailing in the country, sampling was carried out in a grid of 5 × 5 km. A more detailed grid sampling (2 x 2 km) was applied in urban agglomerations (Warsaw, Łódź, Cracow, Gdańsk, Szczecin, Wrocław, Poznań and other smaller cities) and highly industrialized areas (e.g. Silesian-Cracow region commonly considered an ecological disaster area, as well as Tarnobrzeg and Legnica-Głogów regions and the Lublin Coal Basin (LCB).

The following specialists participated in the preparation of this Atlas:

J. Lis, A. Pasieczna – concept and project proposal, supervision and coordination of research, databases and geochemical map construction, interpretation of research results, editorial work on maps and text;

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The Geochemical Atlas of Poland was developed (at scale 1:500 000) and printed (at a scale of 1:2 500 000) in 1995. Information on soil pollution (and, to a lesser extent, sediments) has remained largely unchanged and deserves to be widely available on the Internet for the purpose of dissemination of information about the natural environment. A new version of the Atlas was developed in 2012 using software that allows web presentation.

GEOLOGY AND MINERAL DEPOSITS

To illustrate the geology of Poland, geological maps presented in the Geological Atlas of Poland were used (Znosko, ed., 1968) – Plates 1 and 2.

Synthetic presentation of the geology of Poland as a natural background for geochemical processes that result in a distribution pattern of elements in soils, sediments and surface waters, has been limited to those formations and structures that occur on the surface or just below and affect the surface conditions due to the water circulation system. Only those deeper-seated formations are described, which affect the ground surface environment because of extraction of mineral deposits from those formations.

Therefore, in terms of geological structure, Poland can be subdivided into two areas that differ in age and geology of individual formations: the belt of uplands and mountains in the south, and the lowland area covering the rest of the country.

The northern part of Poland (Polish Lowlands) is covered by Quaternary deposits. Older rocks outcrop only locally (Plate 1).

The region of mountains and uplands of southern Poland includes the Sudetes, Meta-Carpathian Swell (Upper Silesian Coal Basin, Cracow-Częstochowa Upland, Miechów Trough, Holy Cross Mountains and Lublin Upland), Carpathian Foredeep and Carpathian Mountains. Pre-Quaternary rocks outcrop (although discontinuously) in these areas (Plate 2). Due to the complex geological structure, the individual regions of southern Poland are presented in a more detailed way.

THE SUDETES

The Sudetes and their foreland are the marginal part of the Bohemian Massif. The Sudetes are subdivided into the Western Sudetes, being part of the Lugicum that is included in the Saxo-Thuringian Zone, and the Eastern Sudetes (Silesicum) belonging to the Moravia-Silesia Zone, whose position in the Bohemian Massif is not quite clear. Most likely, this is an equivalent of the Rhenohercynian Zone, which also includes the basement of the Fore-Sudetic Block where metamorphic-magmatic rocks are buried at greater depths.

The following structural units can be distinguished in the Sudetes: the Karkonosze-Izera Crystalline Massif with the granite Karkonosze Block, the Kaczawa Structure, the Sowie Mts. Metamorphic Block with its frame intrusions, the Orlica-Śnieżnik Crystalline Massif (including the Orlica Mts. and Bystrzyca Mts. crystalline massifs as well as the Lądek and Śnieżnik crystalline massifs) and other granitoid massifs. These units, representing the lower structural level, form structural elevations separated from each other by depressions that can also occur within the elevations. The depressions are filled with young non-metamorphosed deposits of the upper structural level. These are, among others, the Intra-Sudetic Synclinorium (Intra-Sudetic Trough) and North-Sudetic Synclinorium (North-Sudetic Trough) along with the Świerzawa Graben.

The occurrence of a number of structures in a relatively small area is reflected by a mosaic character of the geological structure of the Sudetes. Due to the small size of individual elements of this mosaic, the major rivers transect several structural units. The Bóbr River can serve as an example; its bed consecutively transects the Karkonosze-Izera Crystalline Massif, Intra-Sudetic Synclinorium, Kaczawa Structure, North-Sudetic Synclinorium, and then it runs across the Fore-Sudetic Monocline covered with Quaternary deposits.

The Karkonosze-Izera Crystalline Massif. Metamorhic rocks predominate in the geological structure of the Karkonosze Crystalline Massif. Its northern part (Izera Mts. Block) is composed of leucokratic rocks (Izera granitogneisses) that contain schist belts represented by micaceous-chloritic schists. Metamorphic rocks of the eastern part (eastern margin of the Karkonosze Block) are more differentiated. In addition to granitogneisses, there are also such rocks as amphibolites, dolomitic marbles and micaceous-chloritic schists. The central part of the Karkonosze Block is occupied by a biotite granite intrusion.

There are zones of ore mineralization in the Izera Mts. Block. As, Co, Sn, Sb, Bi, Pb, Zn and F ores are associated with biotitic-chloritic-garnet tin-bearing schist belts. Some of the ore-bearing zones were previously the subject of exploitation.

The zones of leucocratization and greisenization, which developed within granitogneisses, are the areas of As, Bi, Nb, Sn, Mo, Ni, F and B ores. Uranium ores developed at the contacts of schist belts and granitogneisses.

In the eastern part of the Karkonosze Crystalline Massif, the ores are associated with the variegated series, in which regional metamorphism has been combined with contact metamorphism.

A polymetallic mineralization of variable character in the Kowary and Miedzianka deposits has superimposed on the magnetite skarn formation; an abundant set of elements is represented in this mineralization (Ag, As, Ba, Bi, Co, Cu, F, Hg, Mo, Ni, Pb, Sb, Sn, Zn, U). Arsenopyrite (with Sb and Zn minerals) dominated in the Czarnów deposit. At Wieściszowice, pyrite (with Cu and Sb minerals) was the dominant mineral, and U-type mineralization occurred in the Podgórze deposit.

The Kaczawa Structure includes the Kaczawa Mts. and the Kaczawa Foothill. The history of this structure is complex and evidenced by several structural levels. The oldest one is the Assynthian level, which is represented by small outcrops of the Wądroże gneisses and Radzimowice greywacke phyllites, slightly folded within the structures of the younger level. The old Variscan level is of the largest extent. It is well exposed in the Sudetic part of the structure, which is separated by the Świerzawa Graben into the southern and northern legs.

This formation starts with a thick Cambrian limestone and greenstones series, overlain by Ordovician quartzites and sericitic schists, and subordinate Silurian graptolitic shales with lydites.

The intrusive young Variscan level comprises the Strzegom-Sobótka Granitoid Massif patchily exposed in the Fore-Sudetic part of the area, and the Upper Carboniferous porphyry stock at Żeleźniak, accompanied by kersantite veins. Younger porphyries and melaphyres (Permian) occur in a tectonic graben near Bolków and Świerzawa. A number of ore deposits were mined in the Kaczawa structure. The most important ore deposits include: gold-bearing quartzitic-sulphide veins in the Radzimowice-Klecza-Pilchowice area; polymetallic Radzimowice deposit (Stara Góra) associated with the Carboniferous porphyry stock (with Ag, As, Ba, Co, Cu, F, Mo, Ni, Pb, Sn, W and Zn minerals); small polymetallic deposits associated with carbonate-quartzic-barite veins (at Jeżów Sudecki, Grudno, Lipa, Męcinka, Chełmiec, Dębowa Góra and Stanisławów–Wilcza). This vein system also includes a large barite and fluorite deposit at Stanisławów, which has been mined since 1959. The deposit contains admixtures of quartz, hematite, Mn oxides and hydroxides as well as trace amounts of Pb, Zn, Cu, Ag, Sb and Bi sulphides.

The Sowie Mts. Metamorphic Block is of special importance within the Sudetic structure since this is the only one element in the marginal zone that is equivalent to the Moldanubicum of the central part of the Bohemian Massif. The triangular area of the block is divided by the Sudetic Marginal Fault into the Sudetic and Fore-Sudetic parts. In the latter, crystalline rocks are patchily exposed from under the younger formations. Oligoclase paragneisses of variable structure and texture are dominant rocks here; locally they pass into migmatites. There are also late Proterozoic amphibolites and serpentinites within the dominant rock type. Grabens are filled with preserved Lower Carboniferous clastic deposits. The gneisses contain small mineral deposits (mined in the past), among which it is possible to distinguish ore-bearing barite veins, occasionally with fluorite, quartzite and calcite, and with a small amounts of Cd, Cu, Fe, Pb, Sb and Zn sulphides. There are also quartz-calcite veins with polymetallic and uranium mineralization (Dziećmorowice; with Ag, As, Bi,Co, Cu, F, Fe, Pb, U and Zn minerals).

On each of its three sides, the Sowie Mts. Block borders on intrusions of basic rocks (gabbroes, diabases) and ultramafites (peridotites metanorphosed into serpentinites) forming the following massifs: Gogołów-Jordanów (to the north), Szklary and Brzeźnica (to the east) and Nowa Ruda-Słupiec (to the west). These massifs contain small mineral deposits of historical exploitation of Ni silicates (accompanied by magnesite and chrysoprase) at Szklary and chromite at Tąpadła, as well as other mineralization signs that are locally associated with pegmatites (e.g. B, Be, F, Nb and Sn minerals in the Jordanów–Wiry area).

The Orlica-Śnieżnik Crystalline Massif. Two metamorphic units are exposed in the Kłodzko Region: the Bystrzyca Mts. and Orlica Mts. Metamorphic Massif (to the west) and the Śnieżnik-Krowiarki- Bialskie Mts.- Złote Mts. Metamorphic Massif (to the east). The areas composed of metamorphic rocks continue to the east and west onto the territory of Czech Republic.

Crystalline formations, included in the old Assynthian structural level, are represented by two rock series. The Śnieżnik Series comprises gneisses, granitogneisses and migmatites intercalated with granulites and eclogites. The Stronie Series is composed of monotonous paragneisses in its lower part, and of variegated micaceous, graphitic and quartzitic schists with amphibolites and marbles in the upper portion. The relation between these series is not clear. In both areas (eastern and western), the Śnieżnik Series always occurs in anticlinal zones, while the Stronie Series – in synclinal zones. Mineralized zones are associated with synclines filled with variegated deposits of the Stronie Series. A weak mineralization observed in the central part of the elevation can be explained by a poor development of the Stronie Series in this area. Some deposits in the eastern part were mined in both Poland and Czech Republic. The Kletno deposit, occurring within the limestones, amphibolites and magnetite skarns of the Stronie Series, contained predominantly fluorite associated by Ag, As, Bi, Co, Cu, Fe, Hg, Pb, Se, Sn, U and Zn minerals. The Janowa Góra deposit is of similar type. The same assemblage of elements is observed in the Zalesi, Bila Voda and Horni Hośtice deposits in the Czech area. Small mineral deposits with mineralization of Pb, Cu, Fe and Zn occur in the Stronie Series at Lutynia near Lądek, Marcinków and Travna (in the Czech side). The Złoty Stok deposit is of special type; it is included in the Stronie Series with a significant portion of carbonate rocks, and contains arsenic ores with admixtures of Au Co, Cu, Fe and Zn minerals.

Granitoid massifs of the Sudetes and their foreland. There are two large and several minor granite massifs in the Sudetic area. The Karkonosze Mts., located in the central part of the Karkonosze Crystalline Massif, is a complex intrusion composed of several types of granites, accompanied by various vein rocks. A number of weak signs of mineralization (Ag, As, Au, B, Be, Bi, Cu, F, Mo, Nb, Pb, Sb, Sn, Ta, Th, U and W) were found within the well-exposed part of the massif.

The Strzegom Massif, located within the Kaczawa Structure, crops out in the Sudetic foreland area. In its western part, the massif is exposed in numerous large quarries. It is composed of various types of granites, pegmatites and hydrothermal veins. Ore minerals dispersed on the fissure planes include As, Au, B, Be, Bi, Cu, F, Fe, Mo, Pb, Sn, W, Y and Zn.

The Strzelin granitoids form a number of occurrences inherent in the metamorphic aureole. Ore mineralization is dispersed (B, Be, Bi, Cu, Fe, Mo, Nb, Pb and Zn minerals).

The other granitoid massifs at Niemcza, Kudowa, Kłodzko-Złoty Stok, Bielice, Jawornik and Żulova (the last one is only fragmentarily exposed in the territory of Poland) occupy small areas and do not show any signs of mineralization.

The Intra-Sudetic Synclinorium is the main unit of the Sudetic sedimentary cover. It continues southwards and turns into the Upper Nysa Graben filled with Cretaceous deposits. The Synclinorium is filled with Lower Carboniferous deposits, Upper Carboniferous and Lower Permian coal-bearing series and an incomplete sequence of Upper Permian and Cretaceous rocks. Due to uplifting movements of horsts within the structure during sedimentation, most of the rock series show a diastrophic nature. Only the Permian and Cretaceous formations were deposited in epicontinental seas. The contacts between the Synclinorium and the marginal units are of tectonic character. The effects of strong discontinuous tectonic movements, taking place during the entire development of the Synclinorium, were utilized by Westphalian and early Permian volcanic processes.

The Lower Carboniferous is represented by conglomerates and greywackes, locally with tuffogenic interbeds. Cobbles, containing As, Cu, Fe, Sb and Zn minerals, were found in this formation (at Leszczyniec), indicating that older formations had been washed out here. The vein mineralization at Jabłów includes quartz-fluorite-barite veins with Cu, Fe, Pb, Sb and Zn minerals; the veins at Księżno are of carbonate-quartz type with Sb minerals.

Upper Carboniferous limnic deposits are represented by sandstones, mudstones and claystones with coal seams. Ore mineralization is dispersed or occurs in veins and ore-bearing breccias near porphyries that had intruded at the turn of the Westphalian B and C. The volcanism was acidic at that time (rhyolites, alkaline rhyolites, rhyodacites). The veins contain quartz, carbonates and barite (Boguszów and Jedlinka deposits and other numerous occurrences), fluorite, and ore minerals (Ag, As, Co, Cu, Hg, Pb, U and Zn). There are conglomerates and marly and bituminous shales in the upper portions of the Permo-Carboniferous section (Stephanian-Rotliegend); they occur in both the western (Uniemyśl, Okrzeszyn) and eastern (Nowa Ruda, Ratno, Grzmiąca) flanks of the Synclinorium. Metallic concentrations are common, but scanty (Cu, U).

The North-Sudetic Synclinorium and the Fore-Sudetic Monocline. The North-Sudetic Synclinorium (including the Świerzawa Graben) is covered by Permian rocks. The mineral potential of this epoch exceeds the potential of all other units of the sedimentary cover. The Upper Carboniferous commences the stratigraphic sequence of the Synclinorium. It is overlain by the Rotliegend that contains a thick eruptive formation (Świerzawa, Bolków). Of particular importance is the lower Zechstein series of copper-bearing marly shales exposed in the flanks of the Leszczyny (Złotoryja) and Grodziec tectonic troughs. Several mines have been developed in the area between Bolesławiec and Złotoryja to exploit the copper-bearing series. The central part of the Synclinorium is filled with Triassic and Cretaceous deposits. The Legnica-Głogów Copper District is the main mining region of the Fore-Sudetic Monocline. A deeply seated ore bed (600–1200 m) is mined by several active mines (at Lubin, Polkowice, Rudna and Sieroszowice).

The ore mineralization is associated mainly with the lower Zechstein bituminous marly shales, also including the adjoining sandstones and carbonates. This is a variable assemblage of minerals and elements: Ag, As, Au, Ba, Bi, Co, Cu, F, Fe, Ge, Hg, Mo, Ni, Pd, Pb, Pt, Re, Sb, Se, U and Zn.

Some small synclinal structural units (such as the Świebodzice and Bardo structures or the Wleń and Czerwieńczyce grabens) do not contribute to the metallogenesis of the Sudetes.

The East-Sudetic Structure. The East-Sudetic Structure – called the Silesicum - is situated east of the Ramzova line. It is exposed only fragmentarily in a several-kilometres wide zone extending along the state border. It is included in the Rheno-Hercynian zone with a characteristic occurrence of Devonian metamorphosed deposits. In the Czech area, not far from the border, two mining regions are active: Zlaté Hory and Horní Benešov (with pyrite mineralization and admixtures of Ag, As, Au, Ba, Bi, Cu, Fe, Mo, Ni, Pb, Sb and Zn minerals). The streams flowing down the Zlaté Hory region belong to the drainage basin of the Odra River tributaries. The East-Sudetic Culm formation is only patchily exposed in the territory of Poland (Prudnik, Głubczyce and Toszek). Native gold is locally found in Quaternary alluvial sediments of the Głuchołazy region.

THE UPPER SILESIAN COAL BASIN

The Upper Silesian Coal Basin (USCB), situated east of the outcrops of the Moravo-Silesian zone, is one of the units composing the outermost zone of the Bohemian Massif (Sub-Hercynian zone). The Upper Carboniferous molasse coal-bearing formation is the most characteristic feature of this zone. Boundaries of the USCB coincide with the outcrops of Upper Carboniferous coal-bearing deposits. The coal basin is triangular in area and its southern side is concealed under the Carpathian overthrusts, and the corners are situated at Pyskowice, Skawina and Valašske Meziříči. The total area of the basin is approximately 7500 km^2, and the area not overthrust by the Carpathians is about 5750 km^2 (including 1700 km^2 in the Czech Republic). Mining industry developed over approximately 30% of the coal basin area; the remaining part is considered the reserve and prospective area. The greatest areal concentration of coal mining, metallurgical industry and urbanization occurs along the Main Anticline (running between Dąbrowa Górnicza and Gliwice), and in the Rybnik Coal District.

The Carboniferous coal-bearing deposits overlie the Culm formation of the Moravo-Silesian zone (in the west) or the Lower Carboniferous Limestone (in the east). The following series have been distinguished in the Carboniferous coal-bearing succession (from bottom to top): Paralic Series, Upper Silesian Sandstone Series, Siltstone Series and Cracow Sandstone Series.

The Paralic Series (of the Namurian A) with marine and fresh-water interbeds occurs mainly in the south-western part of the Upper Silesian Coal Basin. It is composed of coarse clastics with interbeds of phytogenic sediments (coal seams accounts for approximately 3% of the total thickness).

The Upper Silesian Sandstone Series (Namurian B and C) is the first limnic megacycle of the Carboniferous succession. It is characterised by the predominance of sandstones and conglomerates along with a significant proportion of phytogenic material (approximately 10% of the entire sequence) and a great thickness of coal seams.

Dominant fine-grained clastic sediments and high coal productivity (approximately 6% of the thickness) is a characteristic feature of the Siltstone Series (Westphalian A).

The Cracow Sandstone Series (Westphalian B, C and D) is the uppermost unit of the limnic succession of the Carboniferous coal-bearing sequence. It is dominated by coarse clastic sediments accompanied by subordinate phytogenic material (approximately 3% of the section).

The Upper Carboniferous succession in the eastern part of the Upper Silesian Coal Basin is completed with the Kwaczała Arkose included in the Stephanian.

The Late Carboniferous sedimentation was characterised by a shifting of the depocentre from the west to the east. The lower lithostratigraphic units in the western part of the basin are disturbed by folds and overthrusts, the mode and direction of which follows similar structures occurring within the Culm facies. In the northern part of the basin, the so-called Main Anticline is the major tectonic element where the most coal-rich beds have been uplifted to the ground surface. The central part of the basin is occupied by the Main Trough. Its dips are gentle but disjunctive tectonics is strongly marked.

The overburden of the folded coal-bearing deposits is composed of Permian, Triassic, Jurassic and Neogene rocks, overlain by patches of Quaternary sediments.

Permian conglomeratic and tuffogenic deposits, with the Rotliegend acidic and basic volcanites, occur only in the south-eastern part of the Upper Silesian Coal Basin.

Triassic deposits of the basin and its northern and eastern peripheries occur patchily. All lithostratigraphic units of the System (Buntsandstein, Muschelkalk and Keuper) are represented in this area. Of particular importance in terms of metallogenic and ore-bearing potential is the Muschelkalk limestone-dolomitic sedimentary complex. In some areas, it is represented by the Ore-Bearing Dolomite. The Muschelkalk lies upon rocks of different ages: it overlies the Culm facies in the Tarnowskie Góry area, various members of the Upper Carboniferous in the central part of the basin, and folded Devonian formations in the east. Between Tarnowskie Góry and Olkusz, dolomitization is associated by ore mineralization. Ore deposits occur in the peripheral parts of dolomite zones, in places of their transition into limestones.

Neogene (Miocene) deposits occur over a large area in the southern part of the coal basin, attaining a relatively considerable thickness. Especially important are tuffites, gypsum, salt and anhydrites (containing Na, Ca, Se, S, Sr and Cl minerals).

Devonian deposits with traces of mineralization occur in the eastern margin of the Upper Silesian Coal Basin and are overlain by Triassic rocks (Muschelkalk and Keuper) and Upper Jurassic limestones. Thus, the Devonian deposits do not affect the geochemical conditions in the surface environment of the area.

THE SILESIA-CRACOW UPLAND

This upland constitutes the north-western flank of the Upper Silesian Coal Basin. Its basement is composed of folded and partly metamorphosed rocks of the Cracow Zone, spanning the age interval from the Precambrian to the earliest Namurian. These rocks crop out in a few places only (Devonian limestones outcrop at Dębnik, Klucze, Zawiercie and Dziewki; Tournaisian and Visean limestones – near Krzeszowice).

Evidences of Permian magmatic activity are observed at the surface in the Krzeszowice region. Numerous hypabyssal intrusions have been encountered in boreholes drilled near Mrzygłód, Myszków and Pilica. They are covered by platformal formations represented at the surface by the Keuper composed of mudstones overlain by Rhaetian breccias and limestones and sand-gravelly deposits with lignite. These, in turn, are overlain by Middle Jurassic clays with siderite iron ores mined between Kłobuck and Zawiercie. A number of mine dumps are the remnants of currently inactive mines.

The characteristic features of the landscape are related to the Upper Jurassic platy and rocky limestone. The monoclinally arranged platformal series dip eastwards underneath the Cretaceous of the Miechów Trough.

THE MIECHÓW TROUGH

The Miechów Trough (NNW-SSE oriented) continues to the north in the area of Polish Lowlands, into the Łódź-Szczecin Trough. In the Meta-Carpathian uplands, it forms a depression between the Cracow-Częstochowa Upland and the uplifted Palaeozoic core of the Holy Cross Mountains. The Miechów Trough is filled with Cretaceous deposits. These are sandstones at the bottom, passing upward into marls and carbonates. The uppermost part of the Cretaceous sequence is composed of marls and gaizes with sandy-conglomeratic interbeds and sporadic phosphorites.

THE HOLY CROSS MOUNTAINS

The Palaeozoic core of the Holy Cross Mountains is the easternmost Central European Variscan massif. The mountains are also the highest culmination of the Meta-Carpathian Range. They are divided into two regions that differ with respect to the geology of Palaeozoic formations: the Kielce region (in the south) and the Łysogóry region (in the north).

An incomplete sequence of Lower Cambrian to Upper Carboniferous rocks crops out in the Kielce region. The section is dominated by Cambrian and Devonian deposits. Ordovician, Silurian and Cambrian rocks are poorly exposed. The Cambrian clastics are represented by claystones, mudstones and sandstones with conglomerate interbeds. They are overlain by Ordivician and Silurian shales and greywackes. The Lower Devonian is composed of clastics with tuffogenic material, and locally of clays with pyrite and siderite at the top. These are overlain by a Middle and Upper Devonian carbonate series that strongly affects the Holy Cross Mts. relief. Lower Carboniferous carbonates and shales top the Palaeozoic section.

The Holy Cross Fault runs WNW-ESE on the southern side of the Łysogóry Range. The fault separates the Kielce region from the Łysogóry region. The latter is characterised by a complete sequence of Palaeozoic rocks. The sedimentary basin of the Łysogóry region was characterised by a continuous development, without longer breaks in sedimentation. The Palaeozoic succession starts with Middle Cambrian fine-grained clastics. They are overlain by quartzitic sandstones exposed as stone runs at the highest culmination of the Holy Cross Mts. Similar sedimentation took place during the Ordovician. After a short emergence, clay-marly sediments were deposited. In the Silurian section, they are represented by claystones, graptolitic shales and carbonates. Devonian sedimentation of this area was similar to that in the Kilece region. Several folds have been recognised in the exposed part of the Łysogóry region, in the most elevated part of the mountains. The Łysogóry Anticline is best exposed, with a succession of Cambrian, Ordovician and Silurian rocks. Other folds, situated further north, are in part covered with the Mesozoic formations of platform cover. Folds of the Łysogóry region are cut by faults of great amplitude. Some of them extend into the Mesozoic margin, indicating that they were rejuvenated.

The folded Palaeozoic formations are covered with the Permian-Mesozoic complex. It starts at the base by the Zechstein conglomeratic deposits with their characteristic rock type - the so called Zygmuntówka Conglomerate consisting of Devonian and Carboniferous limestone cobbles. Some intercalations contain copper and lead sulphides. They are overlain by Buntsandstein and Röt clastics, Muschelkalk limestones and marls, and Keuper claystones. The Liassic and Dogger successions are represented mainly by clastic sediments with ferruginous and carbonaceous intercalations. The Malm is composed of spongy limestones and marls, as well as platy and oolitic limestones.

The platform margin deposits occupy small areas located to the south of the Palaeozoic massif. To the north, they are exposed in a relatively low hilly range of the Opoczno Hills, extending northeastwards approximately 60 km away from the Łysogóry Range.

The Rhaetian and Muschelkalk deposits contain barite mineralization mostly developed near the contact with the Devonian limestones exposed in the anticlines. The barite mineralization is of vein and impregnation types and occurs also in the Cambrian sandstones as well as in the Devonian limestones and dolomites. The mineral deposits are not large. There is only one large deposit at Strawczynek; however, it is not mined because of small reserves. There is also sulphide mineralization dispersed in the Zechstein and Triassic deposits (Cu, Fe and Zn minerals). Vertical ore-bearing veins (containing Ag, As, Cu, Fe, Mn, Ni, Pb and Ba minerals), which developed in the Devonian limestones, occur in the Miedzianka deposit. The Miedziana Góra mineralization is associated with ore-bearing claystones that occur at the Devonian/Silurian tectonic contact. Cu, Fe, Pb, Sb and Zn minerals have also been found in this area. A pyrite, siderite and hematite deposit at Rudki near Nowa Słupia developed in a zone of transverse fault that cuts the Łysogóry Anticline. The ore lens occurs at the contact of the Silurian greywackes with the Middle Devonian dolomites.

THE LUBLIN UPLAND

In the Lublin Upland, the basement formations are overlain by a platformal sedimentary cover. The oldest deposits that outcrop in this region are Middle Jurassic rocks found in the core of the Annopol Anticline, and Albian sands with phosphate concentrations, overlain by Cenomanian marly limestones and gaizes. Maastrichtian deposits are of the largest extent and are represented by marls, marly limestones, gaizes, opokas and chalk. The Upper Cretaceous rocks are, in turn, overlain by a loess cover. No signs of ores are found in the Lublin Upland area.

THE CARPATHIAN FOREDEEP

The Carpathian Foredeep is situated between the uplands of the Meta-Carpathian Range and the Outer Carpathian overthrusts. It has a lowland landscape and is filled with Neogene deposits. River system of this area is the continuation of the Carpathian river systems. The Carpathian Foredeep is a relatively narrow structure; to the west, its width ranges up to several kilometres, while east of Cracow it expands to approximately 70 km. Its easternmost part is triangular in shape and is bounded by the Vistula and San river valleys.

Age of the rocks composing the basement of the foredeep is diversified (Precambrian, Ediacaran, ore-bearing Carboniferous formations, Permian and Mesozoic rocks). The Carpathian Foredeep is filled with unfolded Miocene deposits. Carbonate deposits dominate in its northern part, whereas shallow-water clayey sediments dominate in the southern area. There are also Miocene gypsums and genetically related native sulphur deposits (at Piaseczno, Machów, Jeziórko, Osiek–Baranów, Tarnobrzeg, Solec, Grzybów, Rudniki and Basznia). Gypsum deposits are also known from the Nida River valley and the Carpathian Foothills near Dynów. The Miocene rock salt deposits occur in a southern belt of the foredeep between Wieliczka and Tarnów (at Barycz, Wieliczka, Łężkowice, Moszczenica, Bochnia and Wojnicz). The salt series, which originally lied in a horizontal position, has been strongly folded in front of the Carpathian overthrusts. The Miocene sedimentation ended with the Sarmatian deposition that occurred over a significantly greater area including the southern part of the Lublin Upland.

A considerable part of the foredeep area is occupied by plateau composed of Quaternary deposits with predominant glacial tills and alluvial fans deposited by Carpathian rivers. The Miocene deposits crop out at the foredeep margins (e.g. in the Nida River valley). In the remaining area, the Miocene is known mainly from boreholes.

Extraction of the sulphur deposits (S and Sr minerals) has affected the geochemical conditions in the Carpathian Foredeep. The initial open-cast mining method has been replaced by exploitation by wells through the method of underground smelting. In addition, the leaching method is employed to extract rock salt (leaching through wells and underground leaching of chambers). Na, Cl, Br and J minerals migrate to the environment.

Sulphate-type groundwater occurs in the north of the foredeep. Chloride-type groundwater, locally with high iodine content, is found in the remaining area.

THE CARPATHIANS

Southern Poland is occupied by the northernmost part of the Carpathian Mts. chain. This part includes a small area of the Inner Carpathians and a portion of the Outer Carpathians (flysch deposits). Both areas are different with respect to age of rocks and folding. The Pieniny Klippen Belt constitutes a boundary between both these areas; there is a deep fracture zone running beneath the Pieniny Klippen Belt, which divides the Earth's crust into two blocks.

The Inner Carpathians are composed of crystalline rocks and Mesozoic deposits folded in Late Cretaceous time. The Tatra Massif is part of the Inner Carpathians. It is made up of crystalline rocks and Mesozoic sedimentary deposits. The Tatra Mts. is the only area in the country with a high mountain relief that is dependent on such factors as neotectonics (recent uplifting movements), complex geological structure and Pleistocene glaciation. The crystalline massif is composed of metamorphic rocks (gneisses, amphibolites) and granites. Sedimentary series of the Tatra Mts. show considerable variability. Sedimentary basin of the Inner Carpathians was several hundred kilometres wide and it expanded far to the south. Rock series that developed in the southern part of the basin (Sub-Tatric Series) have been thrust over the autochthonous High-Tatric Series. Permian conglomerates are the oldest rocks of the autochthonous cover. They are overlain by Lower Triassic clastics. The Middle Triassic carbonate sedimentation was followed by a period of tectonic movements that resulted in the division of the sedimentary basin into several zones of different mobility. The Late Cretaceous folding processes gave rise to the formation of nappes and slices. After uplifting and erosion of the orogen, a Palaeogene series of the Podhale Flysch was deposited. The nummulitic Eocene beds were the first to accumulate in this area. Uplifting movements of the massif started after the Oligocene and were active until the present.

Within the crystalline core, there is Ag, Au, Cu, Mo, Pb, Sb, barite, pyrite and siderite mineralization. Sedimentary rocks of the area contain iron ore and sporadically copper ore (especially in Lower and Middle Triassic marly clays). The Podhale Flysch contains frequent interbeds and concretions of ankerite. These small ore deposits were mined in the past centuries.

The Pieniny Klippen Belt, several hundred kilometres long, is very narrow up to a few kilometres in width. Its geological structure is very complicated and related to intense Alpine movements that took place both during the geological evolution of the sedimentary basin and during the folding phases. Among several series of different lithostratigraphic sections, the dominant rocks are carbonates, variegated shales and radiolarites.

The Pieniny Klippen Belt is an area of occurrence of volcanic rocks, i.e. andesites that intruded in Badenian time into the topmost klippen series and adjoining flysch formation.

Some ore veins occurring at Jarmuta near Szczawnica are associated with these volcanites; they were mined in the past for As, Ag, Au, Cu, Fe, Hg, Mn, Pb and Zn minerals.

The Outer Carpathians stretch north of the Pieniny Klippen Belt and are almost exclusively composed of flysch rocks deposited in a deep basin by turbidity currents. Claystones, mudstones, sandstones and conglomerates dominate in the flysch sediments. Medium- and coarse-grained rocks highly affect the landscape, whereas fine-grained rocks are predominant in the vertical geological section.

The original location and configuration of the sedimentary basin is unknown. Most likely, its width could be approximately 300 km. The basin was subdivided into deep-marine zones where the main lithostratigraphic series were deposited, emerged ridges, and shallow water zones of carbonate sedimentation. The flysch rocks were subjected to folding and thrusting. They are thrust over the Miocene deposits of the Carpathian Foredeep. Four main nappes can be distinguished in the geological structure of the Outer Carpathians. The lithostratigraphic division of each nappe exhibits some individual features although some lithostratigraphic units can be common with other nappes. In particular, it refers to the three lower nappes: the Skole Nappe, Sub-Silesian Nappe and Silesian Nappe. The uppermost nappe (Magura Nappe) shows the highest individuality. The lithostratigraphic variability entails a complicated nomenclature of rock formations, including numerous local names.

The lowermost nappe (Skole Nappe) extends east of the Dunajec River and continues onto the area between the edge of the Carpathians and the head of both the Sub-Silesian and Silesian nappes. Its characteristic feature is the largest exposure of sandstones of the Inoceramus Beds (Upper Cretaceous) and the Krosno Beds (Oligocene) with inserts of tuffogenic material.

The overlying Sub-Silesian Nappe occurs over the entire area of the Polish Carpathians. It is best exposed in its western part, where it forms a narrow and strongly folded zone in front of the Silesian Nappe. Its outcrops are found in the Cieszyn Highlands near Wadowice, in the vicinity of Żywiec, and in small patches at the Carpathian border (as far as the Raba River).

Further to the east, it forms a narrow zone that separates the Skole Nappe rocks from the Silesian Nappe deposits. In particular, it is well exposed in the folds at Węglówka near Krosno. It is composed mainly of shaly-marly deposits.

The Silesian Nappe is characterised by a complex structure, impressive thickness of its deposits and the most complete lithostratigraphic section with Upper Jurassic formation at its bottom. The overlying Upper Cieszyn Shales and Wierzów Shales occur throughout the Outer Carpathians area. Relief of the western part of the nappe is strongly affected by great masses of the Lgota, Godula and Istebna Sandstones passing eastwards into the Ciężkowice Sandstones. The Menilite Beds and the sandstone-shale Krosno Beds are well developed above these sandstone horizons, mainly in the eastern part where they fill the Jasło-Krosno Depression.

The largest area of the Flysch Carpathians is occupied by the Magura Nappe, which is the topmost one. It crops out between Istebna and Dukla and continues to the north of the Pieniny Klippen Belt towards Myślenice. Rocks of the lower nappes and slices crop out in this area in small tectonic windows. The Magura Nappe is composed of Upper Cretaceous and Palaeogene rocks. An especially characteristic formation is the Magura Sandstones (Upper Eocene-Lower Oligocene) composing the highest culminations of the Flysch Carpathians (Mt. Pilsko, Mt. Babia Góra, Mt. Turbacz and Mt. Radziejowa). This is an impressive series (approximately 1,400 m thick) of thick-bedded sandstones of variable granulation and mineral composition (glauconitic, micaceous and arkosic types).

Occurrences of ores are very scanty in the Outer Carpathians. Dispersed ore mineralization (with As, Cu, Fe, Pb, Sb and Zn minerals) occurs in fissures that developed in sandstones at Baligród. Fluorite veinlets can be found in the Cieszyn Limestones at Leszna Górna. In some areas (near Lesko, Żywiec, Strzyżowa, Tymbark and Limanowa), primary copper, malachite and azurite were discovered in variegated shales and marls. Phosphate, siderite, oligonite and rhodochrosite concretions occur in similar formations. Barite concretions are known from the Mszana Window. Baritocelestite (a biogenic origin of Ba and Sr) occurs in radiolarian shales of the Silesian Nappe at Międzybrodzie near Sanok. Uranium concentrations of up to a few tens of g/t (and even 600 g/t in individual samples) were discovered at the bottom of the menilite shales in the Lesko area. It is interesting that the uranium concentration is directly proportional to the bitumen content in the rock.

The area of Outer Carpathians is rich in mineral water of chloride-bicarbonate and bicarbonate types, enriched in carbon dioxide. The Poprad region is well known for its carbonated water in the spas of Krynica, Muszyna, Piwniczna and Szczawnica. Origin of these mineral waters is associated with the occurrence of Neogene volcanites. Mixed mineral waters developed as a combination of a number of factors: the presence of fossil connate waters in the sedimentary basin, palaeo-infiltration waters and recent infiltration waters.

This chapter was prepared based on literature review, including the following entries: Gucwa, Pelczar, 1986; Lis, Sylwestrzak, 1986; Malinowski (ed.), 1991; Osika (ed.), 1987; Paulo 1970b, 1979, Sokolowski (ed.), 1968, 1973.

THE POLISH LOWLANDS

Most of the area of Poland is composed of Quaternary deposits (Plate 1). Extensive outcrops of older rocks, mainly in southern Poland, are commonly covered with weathering mantles.

The Quaternary succession is composed largely of glacial deposits of different facies along with periglacial and fluvial deposits.

Several Pleistocene invasions of the Scandinavian ice-sheet deposited thick series of glacial tills. In their considerable part, the older glacial tills are weathered, sandy, in places with deep soil horizons developed mainly as podsols. Evidences of a periglacial environment are also visible and represented, among others, by boulder pavements that developed as a result of deflation. Those were upland areas, where an advanced process of downward migration of iron and manganese compounds developed, and where a relative enrichment of near-surface deposits with silica took place. A considerable part of the weathering mantle was washed down from numerous slopes to valleys. Due to this process, the less weathered basement was exposed on the surface.

Glacial deposits are less weathered in the area covered with the last late Pleistocene Scandinavian ice-sheet. Weathering processes did not reach deep and denudation was of a limited extent. For such reason, the original features of these deposits are detectable much easier. It refers, in particular, to geochemical features and petrographic composition of erratic boulders. These features give evidence of Scandinavian origin of glacigenic deposits and indicate their relation to the Scandinavian area with fresh crystalline rocks outcropping there. They contain a conspicuous admixture of rocks from the Baltic Depression and insignificant admixture of local rocks (Jurassic and Cretaceous in age).

In places, glaciofluvial deposits form extensive outwash plains. They are composed mainly of sands with a northward increasing admixture of gravel. Weathering processes are even less pronounced in some older outwash plains than in the glacial deposits. The glaciofluvial covers are well permeable; therefore, the process of leaching by rain waters plays an important role. Gravel aggregate deposits are relatively frequent among the glaciofluvial deposits of the last glaciation. They are extracted in many places in the north of the Polish Lowlands. Less common on the surface are fine-grained ice-dammed lake deposits. In general, they occur in topographic lows that mark the places where lakes developed near the ice-sheet front. Predominant muds and clays in these deposits do not create favourable conditions for rainwater percolation causing downward migration of some chemical compounds. Of similar character are some deposits in closed reservoirs that are not related to ice-dammed lakes. They commonly occur in the central parts of ancient large glacier lobes.

Sands and gravels in the terraces of ice-marginal valleys are the most common late Pleistocene fluvial deposits. There is no significant difference in their petrographic composition and lithology as compared with the outwash plain deposits. However, they have a more distinct admixture of usually weathered sands and gravels that have been brought to the ice-marginal valleys by rivers flowing from the south. They are also well permeable.

A distinct mosaic of surface deposits occurs in a periglacial area of Poland, south of the maximum extent of the Pleistocene ice sheet. An important part is played by loess. This sediment is well sorted and contains interlayers of variably developed fossil soils. Lithologic features of loess and its geological-engineering properties (porosity, settlement) are well recognised.

In addition to loess, periglacial slope covers are also common. In some areas, they are characterised by an inverse position in the stratigraphic section in relation to the basement structure. The slope covers are thin, variously grained, predominantly weathered and composed of material originally weathered prior to deposition.

Dune sands are the deposits relatively uniform with respect to their mineral composition, grain size, reworking and sorting. These late glacial, but predominantly Holocene sediments, occupy large parts of river valleys in the uplands; they are also common in the Baltic Sea coast zones (where they are still movable). Dune deposits are carbonate-free and highly permeable. In many places, fossil soils can be found in the lower part of the dune section. In general, they are of late glacial age; those at the sea coast are also of Holocene age. The fossil soils are represented by lithosol and podsolic types.

Holocene deposits are dominant particularly in valleys of major rivers, where they can form several morphogenetic horizons. Each of them is composed predominantly of fine-grained sands; interbeds of organic deposits, muds, peats, and similar facies are also common. These interbeds give evidence of variable positions of the river beds. Younger deposits of these facies contain a considerable admixture of industrial pollution, particularly common in southern Poland. They are called the "industrial mud".

A separate position is taken by carbonate-free deltaic deposits of the Żuławy area. They attain a thickness of more than 10 m. These deposits formed during the last 7–6 ka BP and are composed of sand-mud-clay covers with an admixture of organic matter and industrial pollution in their younger portion.

MINERAL DEPOSITS

This chapter deals with mineral deposits that can significantly affect the distribution of elements in surface waters, river and stream sediments, lacustrine sediments and soils. This approach causes a specific and selective treatment of information, which differs from that presented in textbooks on mineral deposits

On the one hand, such selectivity consists in limiting the presented data to certain groups of mineral products that are the source of metal, chemical and energy raw materials, and to only some rock materials. The last group exerts an insignificant effect on geochemical changes in the environment, although extraction of rock materials may have a negative environmental impact.

On the other hand, the information mainly concerns deposits under extraction, because in the course of mining and processing of mineral raw materials, individual elements, originally stable, become mobilized to migrate. Ore deposits cause the development of natural geochemical aureoles combined with anthropogenic anomalies. Thus, it is necessary to characterise some undeveloped deposits. In many cases, it is also necessary to mention historical ore deposits and mining sites to properly define the source of anomalous concentrations of elements, because the recent geochemical studies can even record pollution originated in many centuries ago.

METALLIC ORE DEPOSITS

Zinc and lead ores. Zinc and lead ores occur mainly in the Cracow-Silesia region, i.e. in the northern and eastern margin of the Upper Silesian Coal Basin. Signs of small but numerous deposits and mineralization are also known from the Holy Cross Mts. and the Sudetes. Zinc and lead ores, occurring in the Fore-Sudetic Monocline, accompany copper ores.

In the Silesian-Cracow region, zinc-lead deposits occur in some areas including Tarnowskie Góry, Bytom, Chrzanów, Olkusz and Zawiercie. The Tarnowskie Góry and Bytom regions are now historical. In the post-war years, the following deposits were mined in these regions: Orzeł Biały, Nowy Orzeł Biały-Marchlewski, Waryński, Nowy Dwór and Dąbrówka.

In the Chrzanów region, the Jaworzno and Matylda deposits were extracted. The Trzebionka deposit has recently been abandoned and the mine is currently under closure.

In the Olkusz region, the Klucze I, Olkusz and Pomorzany deposits are currently mined. Ore deposits from the Zawiercie region have not been developed yet.

Supposed economic resources of the zinc and lead ores are 79.01 million tons of ore containing 3.52 million tons of zinc and 1.48 million tons of lead (Szuflicki et al., 2012), as of December 31, 2012.

These are stratabound ore deposits. Ore bodies form stratified pseudo- beds, lenses, nests and brecciated fills of karst forms, mainly in Triassic ore-bearing dolomites, rarely in other formations. The primary sulphide ore contains galena with a silver admixture, sphalerite with cadmium, gallium, germanium and thallium, as well as substantial quantities of iron sulphides – marcasite and pyrite. In shallow-seated parts of the deposits, there are oxidized ores (so-called calamine) containing minerals such as smithsonite, cerussite, goethite, hemimorphite and hydrozincite (Żabiński, 1978).

The zinc-lead deposits cause the formation of natural aureoles of metal dispersion in the environment, mainly due to the shallow position of ore bodies (Serafin-Radlicz, 1972). The large areas of outcrops of ore-bearing dolomites are in a natural way polluted by zinc, lead and other metals. Considerable dispersion of metals in the surface environments (in water, sediments and soils) is also related to ore extraction and processing conducted over centuries (Klimek, Macklin, 1991). Of particular importance are zinc, lead and cadmium anomalies that occur in areas of historical exploitation of galena (until the 18th century). Those anomalies can be explained by dumping of very rich oxide zinc-lead ores as well as sulphide zinc ores as waste material (Przeniosło, 1995b). According to original historical records available since the 12th century (Grzechnik, 1978), galena was the first to be mined in the history of ore mining in the Silesia-Cracow area; subsequently galena and oxidized zinc and lead ores were mined. Next, the extraction concentrated on oxidized ores and zinc blende (ZnS), and lately (at the end of the 20th century) – on sulphide type zinc-lead ores. This variability of interest in different ores had an important bearing on locating mines and processing plants, and consequently on the natural environment (Lis, Pasieczna, 1995a).

Ore processing activities, in the past and at present, have been taking place in the vicinities of mining plants; similarly, metallurgical plants are also located in large areas of ore occurrence and in industrial regions of Upper Silesia.

The metallurgy industry is also based on imported concentrates, commonly rich in harmful admixtures. Zinc-lead ore processing and metallurgical processes are among the most troublesome to the natural environment. Sphalerite, galena and combined sphalerite-galena concentrates are recovered by the flotation process of sulphide-type ores (Bolewski et al., 1994). At present, ore processing is carried out at the Bolesław Mining and Metallurgy Company (Zakłady Górniczo-Hutnicze ZGH Bolesław). Dolomites and limestones are the waste materials. It is difficult to utilize them as they contain much zinc and lead remnants and some other harmful elements (Szuwarzyński, Kryza, 1993).

The concentrates were recovered from oxidized ores after mechanical pre-treatment (by crushing and milling) and thermal processing in rolldown furnaces. Raw zinc oxide dust was then subjected to a sintering process in the same furnaces. Calamine processing had been continued until 1990 at the Miasteczko Śląskie plant that closely cooperated with the Orzeł Biały-Waryński sintering plant and the Bolesław zinc oxide production plant. The latter still operates and currently it continues processing of oxidized ores exploited together with the sulphide ores. Sludge and calamine wastes, raw materials from mining heaps, ashes and slags, as well as zinc smelting waste are subjected to processing here. The oxidized ore processing causes serious dust emissions over large areas in the environs of the processing plants. Emitted dust contains heavy metal concentrates; migration of these pollutants to soils and groundwater is another environmental impact of the ore processing.

Metallurgical production of zinc from the concentrates is carried out at the Miasteczko Śląskie Zinc Plant using a pyrometallurgical method. An electrolytic method has been employed at the Bolesław Mining and Metallurgy Company (Zakłady Górniczo-Hutnicze ZGH Bolesław).

The lead metallurgy has significantly developed in the Silesia-Cracow area over the last years. According to the Chamber of Commerce for Nonferrous Metals, the production of refined lead increased by 48% in the period 2000–2006 (Orzeł Biały, 2012). The first and largest company involved in the recycling of lead-acid batteries in Poland is the Orzeł Biały SA company in Piekary Śląskie. It produces several types of products, including raw lead, soft lead, low-processed alloys, antimony alloys and calcium alloys.

In addition to zinc and lead as the main products of the metallurgical process, also cadmium, cadmium sponge, silver and sulphuric acid are extracted in the same process. Recovery does not include other ore components such as gallium, germanium, thallium and tellurium, which, together with zinc and lead, can migrate to the natural environment at different stages of ore processing and smelting. Before the Second World War, a part of thallium was recovered, eliminating it in this way from the circulation in the environment.

Lead deposits and frequent lead signs in the Holy Cross Mts. are found within the Devonian rocks (Rubinowski, 1970). Mining of lead ores has been carried out since the 14th or 15th century at Białogon, Jaworznia, Karczówka, Ołowianka and Szczukowskie Górki. Mineralization with lead sulphides is confined to veins and fissures, and to pockets of karstic origin. Currently, the lead ore concentrations in the Holy Cross Mts. are of historical importance only.

In the Sudetes and Lower Silesia, zinc and lead mineralization coexists with copper and arsenic mineralization occurring in different ore-bearing formations, and in barite deposits as well. Among the locations of these ore deposits are Czarnów, Miedzianka, Stara Góra, Lipa, Wleń Chełmiec, Stanisławów, Boguszów and Dziećmorowice. Dispersion of zinc and lead in surface deposits (soils, sediments and surface waters) of the Sudetes could occur not only as the result of ore extraction in old mines, but also by erosion of exposed rocks containing increased concentrations of metals.

Relatively large quantities of zinc and lead accompany the Zechstein copper ores. Part of lead is recovered by copper ore processing. Due to a significant depth to ore bodies, migration of the metals into the environment can only take place by the mining and processing activities.

Copper ores. Signs of copper mineralization are well known in south-western Poland (in the Sudetes and Fore-Sudetic Monocline). In the past, small copper deposits were mined at Miedzianka and Miedziana Góra near Kielce in the Holy Cross Mts. Combined copper, tungsten and molybdenum mineralization was discovered in Upper Silesia, in the eastern margin of the Upper Silesian Coal Basin (Piekarski, 1988).

Copper ores of the Sudetes were mined in the Kaczawa Mts. (near Chełmiec and Radzimowice) and in the eastern metamorphic aureole of the Karkonosze granite massif (Miedzianka-Ciechanowice deposit near Jelenia Góra). Copper mineralization is also known from the Rotliegend *Anthracosia* Shales of the Intra-Sudetic Trough. Copper-bearing shales outcropping at the surface in the North-Sudetic Trough have been mined here since the beginning of the 16th century. However, the copper mining development took place only in the 20th century (Lena, Nowy Kościół, Lubichów, Grodziec and Konrad copper mines). The copper mining activity was finished in 1989 in this area.

The copper ore deposits, discovered in the Fore-Sudetic Monocline (Wyżykowski, 1958), are the main basis for the copper industry. These are stratabound deposits occurring at the base of the Zechstein. They are represented by a copper-bearing shale layer constituting the most abundant mineralization zone. The copper-bearing shale is underlain by a sandstone layer, locally with mineralization, and is overlain by a limestone-dolomite series with copper mineralization and increased zinc and lead concentrations. The zone of mineralization occurs at a depth of approximately 600 m and dips monoclinally northwards. The deposit resources were evaluated at almost 56 million tons of metallic copper. The following elements coexist in the ore body: lead, zinc, silver, vanadium, cobalt, nickel, molybdenum, gold, arsenic, rhenium, selenium, platinum metals and sulphur. The active mines are those located at Lubin, Polkowice, Rudna and Sieroszowice.

Supposed economic resources of ores extracted by active mines are 1 494.85 million tons of ore containing 29.45 million tons of copper and 88.22 thousand tons of silver. Developed deposits account for about 83% of the total amount of supposed economic resources. Economic resources of the same deposits are 1,252 million tons of ore (Szuflicki et al., 2012). The production of copper ore in 2011 was 22,985 thousand tons of ore containing 459 thousand tones of metallic copper and 1,635 tons of silver. Almost the same is the amount of processing tailings. In addition to processing tailings, post-mining waste is also produced (about 380 thousand tons per year), and mine water is discharged (including saline water and brine). Brine is discharged into surface waters of the Odra River drainage basin by the Rudna mine drainage system. The production of concentrate takes place at the Lubin, Polkowice and Rudna plants that processes the ore from the Rudna and Sieroszowice mines. The total of copper concentrate goes to the production of refined metallurgical copper at the first stage, and of electrolytically refined copper at the second stage. Copper smelters are located at Legnica and Głogów.

Nickel ores. The occurrence of nickel silicate ores of weathering type is related to serpentinite massifs of ultrabasic rocks in the marginal zone of the Sowie Mts., i.e. the Szklary, Braszowice and Gogołów massifs (Fedak, 1970). The Sudetic ores are poor with respect to nickel content (the average content is 0.5–0.6%); however, the nickel content at Szklary was in excess of 1%. The Szklary deposit was of an industrial importance until 1983 when the mining ceased. The remaining reserves from the Wzgórze Koźmickie, Siodłowe and Szklana Góra deposits were evaluated at 14.6 million tons of ore containing 117 thousand tons of nickel.

Nickel is also the accompanying metal in the Zechstein copper deposits of the Fore-Sudetic Monocline (about 64.71 thousand tons). In 2011, 2481 tons of nickel sulphate was recovered by processing sulphide-type nickel ores (Mikulski, 2012).

Insignificant nickel admixtures can be found in other Sudetic ore deposits of sulphide type. However, they are not important from the economic point of view. In addition to nickel, cobalt is another accompanying metal here.

Arsenic ores. Arsenic ore deposits occur in the Sudetes. The most important one is that situated at Złoty Stok. This deposit is associated with metamorphosed calcareous-dolomite-silicate rocks. Mining activity continued in this area from the Middle Ages until 1962 (Dziekoński, 1972). Arsenic occurs as loellingite and arsenopyrite, both accompanied by magnetite, pyrite and chalcopyrite. Ores extracted in medieval times were gold-rich, with a gold content up to 40 g/t. Around 540 thousand tons of ore have been left untouched in the deposit. The unrecovered part of the deposit is estimated to contain almost 20 thousand tons of arsenic and approximately 1,500 kg of gold. The mining activity and processing stopped due to the lack of demand on arsenic and have left ore-depots at Złoty Stok with a considerable amount of arsenic and gold admixture (Wojciechowski, 1990). Arsenic also occurs in polymetallic deposits of the Kaczawa Mts. (Paulo, 1973). Arsenopyrite and gold-bearing pyrite of the Świerzawa and Wleń region were mined in the Middle Ages. At present, these deposits are not important from the economic point of view.

Some arsenopyrite deposits with admixture of magnetite or copper, zinc and lead minerals occur in the surroundings of the Karkonosze granitoid massif. Kowary and Czarnów are the examples of deposits occurring in this area. Small amount of arsenic co-occurs with the Zechstein copper ores. It is recovered as sodium arsenian, the total extraction of which reaches more than 150 tons annually.

Tin ores occur in the Sudetes, in the schistaceous Kamienica Range of the Izera Mts. Metamorphic Block. These are the Gierczyn and Krobica deposits, classified as non-economic resources (category C_2 and C_1). The resources are estimated at 4.6 million tons of ore with an average content of about 0.5% of tin (Mikulski, 2012). The Gierczyn deposit was mined until the beginning of the 19th century (Dziekoński, 1972; Jaskólski, 1967). The perspective resources in the schistaceous Stara Kamienica Range are estimated at approximately 20 million tons containing about 100 thousand tons of metallic tin. The tin ores are associated with ore zones of considerable concentrations of cobalt and nickel.

Iron ores occur in a number of geological formations, from the Sudetic metamorphic rocks (megnetite deposit at Kowary) through bog iron ores in the Quaternary formations. The iron ores can contain some accompanying elements that are harmful to the environment, and can be set in motion by mining.

Elements harmful to the environment, such as As, Pb, U and Zn, accompany the Sudetic iron ores at Kowary and Janowa Góra.

Liassic and Dogger deposits are the most important iron ore formations in Poland (Znosko, 1955). They contain clayey siderites, sideritic coquinoid limestones and ferruginuous sands. Deposits of prime importance are known from the Częstochowa, Kielce and Łęczyca regions. Mining was carried out in all these regions (locally since the Middle Ages); however, the mining activity was ceased in 1982 when the last mine at Wręczyca in the Częstochowa region was closed down. Until 1989, clayey siderites were extracted for the need of the Łęczyca cement industry. In the south of the Częstochowa region, oxidized iron ores contained considerable admixture of zinc and lead.

Due to disadvantageous geological conditions, and primarily low metal content and very thin beds, the sedimentary iron ore deposits in Poland are unsuitable for economic exploitation. Therefore, they have been removed from the state register of mineral reserves. The only one record that has been left valid in this register refers to the ilmenite-magnetite deposits at Krzemionka and Udryń in the Suwałki region. The deposits occur at a depth of several hundred metres below ground level, and therefore they do not affect any processes that develop in the surface environment.

ENERGY MINERAL DEPOSITS

Brown coal. Brown coal deposits of Poland are associated largely with Neogene formations of the Polish Lowlands. Main brown coal deposits occur in western and central Poland (Piwocki, 1993). Total economic resources in 90 brown coal deposits are estimated at 22,663.08 million tons, including 12 developed deposits containing 1.668 million tons. Brown coal extracted in the largest mines (Bełchatów, Turów, Adamów and Konin) in 2011 was almost entirely used by power plants (Dyląg, 2012).

In terms of environmental protection, the main problem is combustion of brown coal in power plants located near the mining areas. Flue dusts and slags are produced in the process of electricity generation, which are difficult to utilize. In addition, sulphur oxides, nitrogen, carbon sulphides and heavy metals-containing dusts are emitted to the atmosphere (Kurczabiński et al., 1995). The sulphur content in the coal is variable and the average values range from 0.3 to 4.0% (Piwocki, 1990).

In the recent years, there have been significant changes in the coal combustion technology for the benefit of the environment. Modern coal-burning units on a fluidized bed do not cause air pollution, because coal and its combustion products circulate in a closed circuit until complete dissolution; only CO_2 and water vapour are emitted to the atmosphere (Kasiński, 2011).

The problem of leaching pollution from ash landfills is eliminated by the construction of sealing screens made of materials of ion-exchange properties (beidellite-smectite clays), and by increasingly common petrification of combustion waste mass. The most difficult problem to solve is the emission of large amounts of CO_2. Actions taken to reduce the emissions is the use of modern, low-emission coal technologies (e.g. combustion in pure oxygen), especially CO_2 sequestration in deep geological structures. However, the requirement for zero-emission combustion greatly increases the cost of energy production from lignite (Kasiński, 2011).

Mine waters from the brown coal mines are of low mineralization. These are potable or industrial waters, utilized in their total volume.

Hard coal. Hard coal is currently mined in the Upper Silesian Coal Basin (USCB) and Lublin Coal Basin (LCB). In the Lower Silesian Coal Basin (LSCB), there are seven historical hard coal deposits that are abandoned at present.

The area of the Upper Silesian Coal Basin in the territory of Poland is approximately 5,600 km^2, and the currently mined hard coal deposits occupy an area of about 1,106 km^2. Prospective areas, with resources estimated for a depth of 1250–1300 m, occupy an area of about 1,291 km^2. Reserves of the Upper Silesian Coal Basin account for 80.2% of all supposed economic resources of hard coal in Poland (Malon, Tymiński, 2012). Over the last two decades, the number of coal mines, and consequently the production level, has significantly decreased. In 1989, there were 65 active coal mines. In 2006, only 33 coal mines continued their production. Coal mining is carried out in the conditions of rock burst, water flooding and gas hazards.

In the most coal-bearing areas, the total thickness of coal seams is about 65 m (down to 1000 m depth). The number of coal seams that can be mined, i.e. those whose thickness is more than 1 m, is about 200.

Hard coal resources in the Lublin Coal Basin, where 13 hard coal deposits have been documented, are estimated at 8.8 billion tons. The area of defined prospects for hard coal deposits is about 9,100 km^2, and the area of proved deposits is 1,022 km^2 (Malon, Tyminski, 2012). The Bogdanka Mine (the only one operating in the LCB) produces hard coal from a deposit covering an area of about 77 km^2. Hard coal resources of the LCB account for approximately 20.9% of supposed economic resources of Poland.

The least abundant in hard coal is the Lower Silesian Coal Basin. Mining activity was ceased here in 2000. The last mine, closed due to difficult geological and mining conditions resulting in unprofitable activities, was the Nowa Ruda mine. Economic resources of this coal basin are estimated at 359.72 million tons.

Economic hard coal resources are estimated at 48,541 million tons, as of December 31, 2011. Almost ¾ of the resources is represented by steam coal, and ¼ of the resources is represented by coking coal. Other coal types account for about 2% of the resources. Developed hard coal deposits currently account for 36.3% of economic resources and amount to 17,606 million tons (Malon, Tymiński, 2012).

The main environmental risks associated with hard coal mining and noted on geochemical maps are mine waters, the impact of mining waste dumps and tailings, as well as rock mass deformation. Gas emissions from coal combustion also cause environmental pollution.

Mine waters include saline waters and brines containing mainly chloride ions (Cl^{-}) and a small amount of sulphate ions (SO_4^{2-}). Saline waters and brines are mostly produced (over 90%) in the USCB. Contribution of the LSCB to saline water and brine production is 3%. Mineralization of groundwater in the LCB is relatively low and does not exceed 35 g/1 (which is the upper limit for saline waters). Saline waters and brines are discharged to surface waters of the Vistula and Odra drainage basins.

As the result of mining activity, mining waste rocks and processing wastes are produced in large volume. Mining wastes are mainly dumped, but a part of them is utilized as the filling material used for levelling the land surface and to some other engineering purposes. Waste rocks exert a negative impact on the environment not only by degradation of the landscape (mine dumps and waste banks), but mainly by polluting groundwater with chlorides, sulphates and heavy metals that are leached from the dumped wastes.

Rock mass deformation that is manifested by subsidence of land surface above extracted parts of coal seams is of destructive nature as hydraulic contacts between different groundwater bodies (normally separated from each other) can be opened. It can result in groundwater pollution, and some elements might be mobilized.

Industrial objects of coal combustion (power plants and, to a lesser degree, metallurgical and cement plants) cause air pollution by emissions of gases, fly ashes and metals. In contrast to brown coal (which is burnt in power plants located close to mines), hard coal is combusted in industrial objects located throughout the country (Chmura, Szczęśniak, 1990).

The average sulphur content in the most productive coal seams of the Upper Silesian Sandstone Series is 0.85%, while the ash content is 11.0%. Coal seams of the Cracow

Sandstone Series are the poorest with respect to sulphur and ash contents being equal to 2.0% and 16.2%, respectively (Buła, Zdanowski, 1993). Another negative feature of the Cracow Sandstone Series is a high uranium content, up to several hundred g/t. Uranium is abundant in near-fault zones, particularly in the eastern part of the area (Sałdan, 1965). Similar uranium concentrations have been measured in the coal seams of the Lower Silesian Coal Basin, especially in the contact zones between coal and porphyries. In the western part of this coal basin, at Okrzeszyn, uranium concentrations are high enough to be considered economic deposits within the coal seams. However, they have never been mined yet.

CHEMICAL RAW MATERIALS

Barite and fluorite. Barite or barite-fluorite mineralization is known from a number of occurrences in the Sudetes (Boguszów, Stanisławów, Rusinowa, Kletno) and the Holy Cross Mts. (Strawczynek, Hucisko, Wiśniówka). These deposits were mined in different periods. Numerous, although smaller barite and fluorite deposits are also known; however, they are not economic deposits. There are also some signs of barite mineralization in Triassic dolomites of the Upper Silesian Coal Basin margin; however, the barite concentrations are insufficient to form a deposit.

The most important economically are the Boguszów and Stanisławów vein-type deposits. They developed along NW–SE-trending fault zones. Polyphase barite and barite-fluorite mineralization co-occurs with a number of minerals, among which the most important are sulphides of Fe, Pb, Zn and Cu (Paulo, 1970a, 1972, 1973). Barite accumulations occur in fault fractures as steeply dipping veins of variable thickness, with the average $BaSO_4$ content of about 80%. The fluorite content ranges up to several percent. As a result of flooding of the Boguszów mine near Wałbrzych by a flood in 1997, the production of barite and fluorite was ceased and the deposits were included into subeconomic resources. In 1998, mining operations in the Stanisławów mine were stopped due to unprofitable extraction. Proven barite reserves are 5.66 million tons. Proven fluorite reserves are 0.54 million tons (Bońda, 2012).

Phosphorites. The occurrence of phosphorites is restricted to Albian (Upper Cretaceous) deposits in the north-eastern and northern margin of the Holy Cross Mts. between Gościeradów and Annopol in the east and Iłża and Radom in the west and north. Phosphorite deposits are also known from Burzenin near Sieradz. Phosphorites were mined in Annopol (from 1924 to 1970) and in Chałupki (from 1936 to 1956). Both mines were closed down due to unprofitable production.

All phosphorite deposits were removed from the national registry of resources and the demand for raw phosphate rock (for the production of phosphate fertilizers and phosphoric acid) is totally covered by imports. Processing of raw phosphate materials (in the Police, Gdańsk and Luboń plants) gives rise to emissions of hydrogen fluoride and the formation of solid waste (phosphogypsum), which often contain significant amounts of sulphur, rare earth elements and radioactive elements.

Sulphur. Native sulphur deposits occur in the northern part of the Carpathian Foredeep near Tarnobrzeg (Osiek, Baranów, Machów, Jeziórko), Staszów (Solec and Grzybów) and Lubaczów (Basznia). They are found within Tortonian rocks represented mainly by post-gypsum limestones, and form infills of small caverns and fractures (Pawłowski et al., 1987). The average content of sulphur in the rocks is 25–30%, the maximum values are 70% (Bońda, 2012). Native sulphur is currently extracted in the Osiek deposit only, using the underground melting method. This is the last large mine of native sulphur in the world.

When documenting native sulphur deposits, the boundary limits for economic resources are as follows: minimum sulphur content in the ore 10%; minimum average sulphur content in the deposit 10%; lowest acceptable mineral accumulation at least 150 m; maximum depth to the deposit floor 400 m.

Proven reserves of native sulphur are 512 million tons and its production in 2011 amounted to 681 thousand tons (Bońda, 2012).

Historical sites of sulphur extraction include Czarkowy on the Nida River, Posądza near Proszowice, Swoszowice near Cracow, and Kokoszyce near Rybnik (Osmólski, 1969).

The native sulphur deposits are associated with strontium mineralization (Osmólski, 1987, 1989). In sediment ponds near Tarnobrzeg (into which wastes of sulphur processing are disposed), the strontium content is over 1%.

A small amount of sulphur (for sulphuric acid production) is being recovered from the copper, zinc and lead ores. In the past, pyrite deposits situated at Rudki near Nowa Słupia (Holy Cross Mts.) and Wieściszowice (Sudetes Mts.) were also the sites of sulphur recovery.

Rock salt. Numerous and abundant rock salt deposits are associated with Miocene and Zechstein salt-bearing formations.

Miocene deposits occur in the marginal part of the Carpathian Overthrust from Upper Silesia (Rybnik–Żory–Orzesze) in the west through the Cracow–Tarnów–Przemyśl environs in the east (Garlicki, 1979). This type of rock salt includes the deposits that have been mined since the 13th century (Wieliczka and Bochnia, where mining activity stopped in 1996) as well as the deposits discovered after World War II. The complex geological structure of these deposits (with dominant fold and fold-sheet deposits; only the Rybnik–Żary–Orzesze deposit is of sheet type in a tectonic graben), variable quality of salt as well as water and gas hazards cause a very low production profitability of these salts. The historic mines (at Wieliczka and Bochnia) operate as museums, tourist facilities and recreation sites. Proven resources of the Miocene salt deposits are over 4.36 billion tons, accounting for 5.13% of the national economic resources of rock salt (Czapowski, 2012).

The Zechstein salt formation is the major source of salt in Poland. It occurs over an area of 2/3 of the territory of Poland, mostly in the Polish Lowlands. The Zechstein deposits are both sheet and dome-shaped. The former have been found in the north of Poland (Puck Bay) and in the Fore-Sudetic Monocline. Economic resources are estimated at nearly 25 billion tons, which accounts for 29.42% of national reserves (Czapowski, 2012). Rock salts of northern Poland are accompanied by magnesium-potassium salts (polyhalites) (Werner, 1970). Rock salt domes occur in Central Poland in the area extending from Rogóźno near Łódź through Kłodawa, Łanięta, Łubień, Góra, Mogilno and Damasławek, to Wapno in the Piła region. Rock salts are overlain by a 7 km thick overburden. They were locally uplifted to form a belt of diapiric salt structures.

A number of the shallowest-seated structures contain rock salt and potassium-magnesium salt deposits. Proven economic resources of the Zechstein dome-shaped salt deposits are over 55.6 billion tons, which represents 65.45% of all domestic resources (Czapowski, 2012). All of the national salt production originates from the Zechstein deposits (excluding salt production from the overburden of the Sieroszowice copper ore deposit). Currently, salt deposits are increasingly frequently used as extremely favourable geological objects to store crude oil, natural gas and fuel, as well as hazardous waste.

Other mineral deposits. Exploitation of rock raw materials such as dolomites, gypsum and limestones is hazardous to the environment due to emission of dust originated in the process of extraction, reworking of extracted materials, and the activity of industry located close to the deposits. In general, mining operations do not cause dispersion of the elements at the concentrations that are detectable by geochemical surveys. However, information on active quarries is essential due to the large-scale production of rock materials (many tons of rock material).

Dolomites are widely used in the steel industry, agriculture and glass industry, as well as in the construction and road building industries. Dolomite deposits occur in the regions of Silesia, Lower Silesia and Małopolska. Top quality parameter deposits are those from Devonian and Triassic rocks of the Silesia-Cracow region. The second type of dolomite deposits are lenses within metamorphic schists of the Sudetes. The most famous are the Rędziny and Ołdrzychowice-Romanowo deposits, located in the Kłodzko Valley. Production of dolomites amounted to 3,568 thousand tons in 2011 (Dyląg, 2012).

Calcium sulphate deposits (gypsum and anhydrite) occur in the Miocene and Zechstein evaporite formation, accompanying salt sediments. Economic resources, documented for 15 deposits, are close to 259 million tons. Economic resources estimated for the five active deposits are more than 127 million tons (Czapowski, 2012).

Miocene gypsum deposits of economic significance are located mainly along the northern margin of the Carpathian Foredeep (especially in the Nida River valley), where gypsum occurs over large areas in the form of a slightly tilted and weakly tectonically disturbed bed. They are exposed at the surface or occur under a thin cover. The currently extracted deposits are those at Borków–Chwałowice and Leszcze. Zechstein anhydrite and secondary gypsum deposits occurring in Lower Silesia are mined from the Lubichów, Nowy Ląd and Nowy Ląd–Pole Radłówka deposits.

Production of gypsum and anhydrite was approximately 1,226 thousand tons in 2011 (Czapowski, 2012).

Marls and limestones are mined for the need of cement industry. Limestones are also used by the lime-producing and chemical industries. Materials for these industries are quite common in a variety of geological formations, mainly in southern and central Poland. Nearly 60% of the proved reserves are Jurassic deposits. Also important are Devonian, Triassic and Cretaceous limestones. Most of the resources are located in the Opole, Cracow-Częstochowa-Wieluń, Holy Cross Mts. and Lublin regions.

Economic resources of this group of mineral deposits totaled 18,156.61 million tons as of the end of 2011, including 12,550.09 million tons (69%) from 71 deposits documented for the cement industry, and 5,606.52 million tons (31%) from 116 deposits documented for the lime-producing industry (Tołkanowicz, 2012).

METHODS AND SCOPE OF WORKS

FIELD WORK

The sampling program was accomplished in the 1991 and 1992 summer seasons. Based on the order placed by the Polish Geological Institute, the field sampling teams were organised from among the employees of the geological companies POLGEOL and SEGI in Warsaw and the field groups subordinated to the Department of Mineral Raw Materials and the Carpathian Branch of the Polish Geological Institute. Three teams operated in the field in 1991, and up to

14 teams in 1992. Each team included two technicians or geologists. One of them served an additional function of a driver. Prior to moving to the field, all team members were adequately trained.

Each team was equipped with topographic maps, samplers and other materials, and the instruction dealing with the field work procedure. Topographic maps of the *1965* State Coordinate System, scale l: 50,000, were used to locate the sampling points. Each map covering a surface area of 640 km^2 was divided into 28 squares (each 25 km^2 in size). Another division was applied in urban and industrial areas, where each 1:50,000 map sheet was divided into 160 squares. In this case, the squares were approximately 4 km^2 in size. Samples of soils, sediments of inland water bodies and surface waters were collected from each square. Soil samples were taken from a sampling point located as close to the centre of a given square as possible, within the squares of characteristic land use (farmland, meadow, forest). The soil sampling point was staked out in the field using a wooden stake with a sample number clearly marked out. Sediment and surface water samples were collected from banks of major rivers and streams, unnamed small watercourses, ditches, pools, ponds, lakes, man-made reservoirs, settling ponds etc.

The location of sampling points was marked on the maps using a combined number containing the following data: a coded type of the sampled material, the number of sheet map at scale 1:50,000, and the number of the square within a given map sheet. A special sampling cards were used to record the field observations – land development, land use, character of the surface water body, the type of collected material, as well as to draw a sampling point location sketch (Figs 1, 2).

An 80-mm hand-operated probe was used to collect soil samples. The sampling depths were 0.0–0.2 m and 0.4–0.6 m (Fig. 3). Samples were approximately 1,000 g in weight; they were packed in cloth sacks with an appropriate number clearly marked out.

Sediments samples of the finest grain-size material were collected using a scoop, and subsequently put into a dense cloth sack (Fig. 4). Each sample weighted approximately 1,000 g. Then, the sacks were placed in a plastic bag to avoid any direct contact between the individual samples during transportation.

Surface water samples (Fig. 5) were collected from the same sites. The water was filtered through a hard filter, and then placed in a 30-ml polyethylene container and treated with 0.5 ml of 6M HCl.

Location of the sampling sites for soils, sediments and surface waters is presented in plates 3, 29 and 51, respectively.

Re-sampling. One year after the completion of field work, the sampling of soils, sediments and surface waters was repeated to check the results. The re-sampling covered approximately 2% of the sampling points. The samples were subjected to chemical analysis and the results were compared with the results of the basic sampling analysis. Repeatability of the results from the re-sampling was estimated by the variation coefficient:

$$V_1 (\%) = s/x \times 100$$

where: s – standard deviation, x – average value

The results fall within the limits of error: 20–40% for soils, and 40–50% for sediments and surface waters. In some samples, whose content of elements is near the detection limit, the differences exceed 100%. Repeatability of the re-sampling results is sufficient, because the mean values, rather than single values were used to construct the geochemical maps, which allowed us to reduce the confidence intervals to $x \pm s/\sqrt{n}$. For example, for $x = 10$ mg/kg, $s = 3$ and $n = 10$, the confidence interval for the mean value is 10 ± 0.9 mg/kg.

PREPARATION FOR RESEARCH AND ARCHIVING OF SAMPLES

After preliminary drying in the field, the soil and sediment samples were transported to a sample storage for final drying at a room temperature. Then, they were sieved through nylon sieves (1 mm for soils and 0.2 mm for sediments). Subsequently, the samples were reduced by quartering, so that a 100 g sample could be stored in a polyethylene container. Surface water samples were exposed to ultraviolet radiation to cease growth of microorganisms.

Solid samples were stored in an adequately adopted compartment arranged according to the type of sampled material and particular map sheet (Fig. 6). Each sample was marked with an analytical file number.

Due to insufficient funds to cover the entire project, the soil samples collected at the depth of 0.4–0.6 m have not been chemically analysed. They have been stored and, in the future, might be used to prepare suitable geochemical maps of the subsoil. A comparative study of both topsoils and subsoils, which has been carried out in Upper Silesia (Lis, Pasieczna, 1995b), proved their applicability to differentiation between natural and anthropogenic anomalies.

LABORATORY WORK

Digestion of samples. Depending on the purpose of investigation, the geochemical analysis makes use of various methods of digestion of soil and sediment samples. Total decomposition of samples by their fusion with suitable fusing agents is a relatively rare method; more common is digestion with concentrated acids or their mixtures.

This Atlas focuses on the mobile (weakly bound) part of elements, that come from anthropogenic pollution or from weathering of ore deposits, from which the elements are released to the environment as the result of hypergenic processes. Therefore, the acid treatment was selected as the most suitable method of sample digestion.

When the acid treatment is used to digest samples, different amounts of elements are passing to the solutions depending on the form of their occurrence. The amounts can vary from several percent to 100%. Most resistant to digestion are such elements as silicon, aluminium, potassium, sodium, calcium, iron, magnesium originating from aluminosilicates (feldspars, amphiboles, pyroxenes), titanium, yttrium, REE, thorium, zirconium, and other elements that can replace each other in the rock-forming or accessory minerals, in general very resistant to weathering (zirconium, titanite, chromite, magnetite, etc.). The most soluble elements are those constituting the structure of carbonate, chloride and some sulphide minerals, or those occurring in sorbed forms.

Acid treatment is the most useful method in environmental protection studies, because only that part of the element content is released and subsequently detected, which is weakly bound with the medium (mainly in forms of sorption). These forms of chemical elements control the migration of elements regardless of whether they enter the environment due to economic activity of humans (anthropogenic sources) or their origin is related to natural sources (such as mineral deposits) and they are released as a result of hypergenesis. Due to weak bonds, some of highly mobile elements are the greatest hazard to living organisms, as they are readily assimilated by vegetation and subsequently participate in a food chain of other living organisms.

The method of acid treatment of geochemical samples also has economic implications on the study. It significantly decreases costs of projects with a huge number of chemical analyses.

The method is important from the point view of analytical technique too. In instrumental methods applied so far (ICP-AES and CV-AAS), it is required that the analysed solutions be of the lowest element matrix since its influence on detectability and precision of determinations is essential due to the effect of elements' interference.

Prior to commencement of mass determinations, many experiments were carried out to compare the results of different digestion techniques (Górecka et al., 1993). Based on those studies, a digestion method with the use of hydrochloric acid HCl (1 +4) was selected.

Table l was compiled to compare the results of very deep digestion of soils and sediments using HF, HNO_3, $HClO_4$, and HCl (1+4). The comparison shows that cadmium, lead, and zinc are the most readily HCl-digestible group among the trace elements (average is above 80%). Lower in the rank are cobalt and nickel (average approximately 60%); then follows a group including barium, copper and strontium (average is approximately 50%); and chromium (average is approximately 27%) is at the end of the list. The degree of extraction of calcium, magnesium and manganese is clearly related to their contents. Samples containing high concentrations of the elements are subjected to stronger extraction.

Determination of elements and acidity. To obtain an analytical solution, a 2-g sample was placed in a suitable vessel and treated with 20 ml HCl (1+4). Then the vessel was heated in an aluminium block for an hour at the temperature of 90°C. The solution was subsequently filtered into a 100-ml measuring flask and the flask was filled in to the line.

The ICP-AES method was employed to determine the concentrations of Ag, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V, Y and Zn in the soil and sediment samples. A Philips PV 8060 spectrometer (Fig. 7) was used to analyse the soil samples and a Jobin-Yvon JY 70 Plus Geoplasma spectrometer was employed to analyse the sediment samples.

The Hg content was measured with the CV-AAS method using a Zeiss AAS-3 spectrometer and a Perkin-Elmer 4100 ZL spectrometer combined with the FIAS-100 flow system.

Soil pH measurements in the aquatic environment were performed according to the standard used in soil sciences (Norma..., 1975).

A PV 8060 equipment from Philips (Fig.8) was employed for the analysis of water samples using the ICP-AES method. The following elements were determined in the water: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, SiO_2, SO_4, Ti, V and Zn.

Detection limits of the elements are specified in Table 2.

Quality control. Both the reference materials and internal standards were applied to check the analytical procedures. The following reference material were applied for soil samples: Montana Soil, SRM 2710, SRM 2711 and IAEA/Soil 7. For analytical procedures of sediments STSD l, STSD 2, STSD 3 and STSD 4 standards were performed. The SLRS and SRM 1643c standards were applied when checking the surface water analyses. The accuracy of the IPC-AES method in measurements of particular elements was very high: ±1–2%. Total repeatibility, which included sample heterogeneity, sample preparation, calibration and measurement determined from repeated analyses, expressed as:

$$V_2 (\%) = 2s/x \times 100$$

where: s – standard deviation; x – average value,

was variable and dependent on the elements concentration. The error exceeded 100% when the element content was close to its detection limit. For relatively high concentrations, the error was 10–30%. Correlation factors between basic determinations and checking determinations vary from 0.82 to >0.99 (for the Ag_1/Ag_2 couple with most results below the detection limit).

DATABASES AND MAP CONSTRUCTION

Base topographic map. A modified topographic map, at the scale of 1:2 500 000, developed for the printed version of the atlas published in 1995, was used as the base topographic map.

Databases. Separate databases have been created for:

– soil from a depth of 0.0–0.2 m (topsoil),

– sediments of inland water bodies (rivers, streams, ponds, pools, etc.)

– surface waters.

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

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

Coordinate measurements of sampling sites on the 1:50,000 sampling maps were performed on a Houston Instrument digitiser using the SINUS computer package. The resulting coordinates in the coordinate system *1965* were converted to the system *1942*, and then recalculated to the rectangular coordinates and the albers coordinates. Once created, the databases contain the source coordinates (*1965*) and transformed coordinates (*1942*, geographic, albers). These databases were used to generate geochemical maps. The results of chemical analyses include 825,516 determinations of elements in 36,773 samples.

Statistical calculations. The databases were used to extract database subsets for statistical calculations according to different environmental criteria, such as the content of elements in industrial area soils, forest soils, urban soils (Table 3), and in sediments and surface waters of various rivers and reservoirs (Tables 4–9), as well as to construct geochemical maps. The calculations of statistical parameters were performed for both the entire database sets and subsets of soils, sediments and surface waters. In case of some elements with the content lower than the detection limit value for the given analytical method, half of the detection limit value was taken. The arithmetic and geometric means, median, minimum and maximum values were calculated.

Geochemical maps. The geochemical maps were constructed based on a more or less uniform set of sampling points with known coordinates and assigned attributes of the content of elements. Depending on the map scale, there are two possible approaches to the development of geochemical maps:

- presentation of geochemical data from the unconverted (initial) set of points,
- processing of the set of points into the regular set and presentation of geochemical data based on the newly created set of points.

The first procedure provides good results only if the map is developed for a small area or if a small number of sampling points is available. As a presentation method, pie-chart thematic maps, usually with circular graphs, are used in this case. Maps of this type are included, inter alia, in the Geochemical Atlas of Warsaw (Lis, 1992), Geochemical Atlas of Kielce (Lenartowicz, 1994) and Geochemical Atlas of Finland (Lahermo et al., 1990; Koljonen, ed., 1992) and Fennoscandia (Bølviken et al., 1986). In this case, it is theoretically possible to use other presentation methods, e.g. a variable density grid method.

If the data are referenced to the environments of sediments or surface waters, ribbon diagram methods may be used. An example of this mode of presentation is the Atlas of river's pollution in the Vistula drainage basin (Woyciechowska, Morawiec, 1994), developed at the Institute of Meteorology and Water Management (IMiGW), based on monitoring of 11 rivers of the basin. Atlas of river's pollution in Poland, 1990–1992 (Korol et al., 1993) was constructed in a similar way by the State Inspectorate for Environmental Protection and IMiGW. This atlas was developed based on the basic monitoring covering 53 rivers.

Distribution of elements in soils of Poland is presented by isoline maps. It is a method commonly used in the construction of small-scale geochemical atlases (maps), such as Geochemical Atlas of Austria (Thalmann et al., 1989), Geochemical Atlas of Western Germany (Fauth et al., 1985), Geochemical Atlas of Southern Scotland (Williams, ed., 1993). In these cases, other ways of presentation (circular or ribbon pie-chart maps) are of little use.

While preparing the geochemical maps of soils, the whole territory of Poland was covered by a regular network of points that coincide with the nodes of the network of squares. The density of the regular network was selected in such a way to develop 1:2,500,000 scale maps, maintaining the data credibility. A characteristic value was calculated for each node. Among the many possible algorithms of procedures, after numerous attempts, one variant of the inverse distance method was selected. This algorithm procedure resulted in flattening and smoothing of the statistical sets, however maintaining all important geochemical anomalies. Flattening is an advantageous effect. On the one hand, it allows avoiding inevitable measurement errors and reducing uneven distribution of sampling points, on the other hand, it provides a more clear mapping image. Processed data are shown on the maps in the form of isolines. The method of isolines (contour lines) generally gives a clear and easy-to-read graphical image, but has a significant drawback – the isolines suggest a smooth variation of the intensity of the attribute in the space, which is not always the case with geochemical data.

The geochemical maps of sediments and surface waters have been developed in the form of circular point maps, assigning an appropriate colour to each class of content. Choosing the classes (ranges of content) on the contour maps and point maps, statistical analysis of the distribution of the contents of elements was taken into consideration. The classes are intervals corresponding to the value of percentile 25, 50, 75, 90, 95, 97%, presenting the proportion of samples with the concentration of a given element.

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

Soil type (divided into sandy, clayey and peaty soils), land development and land use are presented in the form of point maps.

Maps of radioactive elements were constructed based on the database of radiometric measurements made in 1992 using the gamma-spectrometry method, according to the guidelines of the IGP project No. 259 (Darnley et al., 1995). The results of these studies were published as radioecological maps of Poland at the scale of 1:750,000, Parts I and II (Strzelecki et al., 1993, 1994a). They presented a detailed methodology for measuring operations, their scope and measuring units used.

The following maps were constructed for the Atlas (Tables 4–77):

- land development,
- land use,
- soil pH,
- contents of Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V, Y and Zn in the topsoil (depth 0.0–0.2 m),
- contents of Ag, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in sediments,

– contents of Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, SiO_2, SO_4, Sr and Zn in surface waters,

– $^{137}Cs + ^{134}Cs$, ^{40}K, eTh, eU, gamma radiation dose.

Using the present Atlas, please remember that we are dealing with generalized images. If at any point we observe a high content of the element, it does not mean that the entire area is heavily contaminated. Only detailed research can show that the distribution of pollution is much more complicated. In addition to heavily contaminated areas, there are also regions where the element contents fall within the limits of the natural geochemical background. The geochemical image presented in the Atlas should be considered only as a signal to take a more detailed study to determine the actual extent of the natural or anthropogenic anomalies.

RESULTS

Based on the research and classification of geochemical anomalies (Xuejing, Binchuan, 1993; Darnley et al., 1995), two geochemical provinces have been distinguished (northern and southern), related to the geological structure of the country. Each province has a different geochemical background (natural contents) of a number of elements. The southern province, including the Sudetes, Upper Silesia and Carpathian Mountains, is characterized by a higher content of almost all of the elements in soils and sediments in comparison to the rest of the country. Geochemical diversity of the province is associated with the lithological and chemical composition of the bedrock. The Sudetic soils developed on igneous and metamorphic rocks, with a rich inventory of elements and abundant forms of mineralization. In the Carpathian Mountains and Upper Silesia, flysch and molasse deposits, containing material of magmatic origin, occur in the basement. In Upper Silesia, an additional factor contributing to the concentration of elements in the surface environment is ore-bearing and coal-bearing rocks.

The diversity of elements presented in the geochemical maps is the result of mathematical operations in the interpretation model and is not always consistent in details with the actual content of the element in a particular place. The accuracy of mapping of the actual content of elements depends on the density of observations (sampling) and, consequently, on the map scale.

Small-scale geochemical atlases illustrate general trends in the geochemical background that differentiates itself mainly based on the geological structure, and geochemical anomalies over large areas (agglomerations, industrial areas, intense fertilization areas, some outcrops of mineral deposits, etc.). These atlases can be the basis for the assessment of the general state of the geochemical environment of the country and for making further detailed studies.

In the case of the Geochemical Atlas of Poland, the soil sampling density averaged approximately 1 sample per 25 km^2. However, the maps are generated at a density of 1 sample per 35 km^2 due to reduction in the number of samples (lack of funds for all analyses) and a significant shortening of the project duration. In Upper Silesia, industrial areas and major urban areas, the increased density of sampling has been maintained (1 sample per approximately 4 km^2). The contents of the geochemical maps, obtained by interpolation procedures at this density of observations, should be read as a highly generalized image. Therefore, it is not appropriate to draw conclusions concerning the chemistry of the environment for objects whose surface is smaller than that resulting from the map scale and sampling density.

Surface water and sediment samples were collected from all available water bodies, based on the principle that each point represents a drainage basin area adequate in size to the map scale. The geochemical maps of these environments should be read in such a way that surface waters and sediments show specific contents of the elements in the particular area characterised by a defined concentration level. Remarks on the accuracy of the presented geochemical image of soils are also up-to-date, although to a lesser degree due to a greater homogeneity of the aquatic environment.

The geochemical maps of sediments can often be considered an "early warning" sign. This is due to the specific properties of sediments containing organic and inorganic compounds with a high sorption capacity of elements from the water. At relatively low contents of elements in the water (still undetectable by routine chemical analysis), there is a very remarkable concentration of elements in the sediments. At the same time, they migrate along with the solid components over considerable distances from the pollution sources. A thorough analysis of the map of sediments often allows locating point sources of pollution and trace the migration routes of toxic elements.

ACIDITY pH

Soils

The pH of soils of different land use

Soils pH – H_2O (Norma…, 1975)		Arable fields	Grazing land	Forests	Urban areas
		n = 822	n = 2985	n = 3806	n = 1109
		% of samples			
Very acidic soil	≤5	10,7	11,5	71,1	5,2
Acidic soil	>5 – ≤6	27,1	31,6	15,8	9,5
Slightly acidic soil	>6 – ≤6,7	24,6	21,6	5,3	14,0
Neutral soil	>6,7 – ≤7,4	28,2	28,0	5,3	39,6
Alkaline soil	>7,4	9,9	7,3	2,5	31,7

Soil pH is a result of geological and climatic factors as well as human activities. About 60% of the country is covered by very acidic, acidic and slightly acidic soils (pH ≤ 6.7). Very acidic soils with pH values <5 (often <4) occur mainly in forest areas. Neutral and local alkaline soils developed on Triassic, Jurassic and Cretaceous carbonates in the Silesian and Cracow regions, and on Cretaceous rocks of the Nida Trough and Lublin Upland. A higher pH is also observed in soils developed on loess sediments in the Wrocław Lowland and Sandomierz Lowland as well as in the Lublin Upland and Carpathian Foothills. Soils of this type also occur locally in the vicinity of Poznań and in Kujawy, i.e. in areas of highly developed agriculture.

According to the Regional Agricultural-Chemical Stations (Michna, ed., 1993), acidification of soils in the last decade has been greatly accelerated mainly due to the effect of acid immission. It is favoured by the extreme acidity of rainwater, especially in the Sudetes (Małecka, 1991).

Unreasonable fertilization (too much nitrogen and potassium fertilizers as compared to magnesium ones) also contributes to the lowering of the soil pH. An additional acidifying factor is the systematic drop in the groundwater table levels in recent years, leading to leaching of calcium and magnesium from the arable layer.

The soils of cities show the high pH values. Their alkalinisation occurs as a result of precipitation of industrial dust (mainly from coal combustion). Impact of urbanization on soil pH is observed even in forest and agricultural soils around urban areas. Among the prominent industrial plants, those producing cement highly contribute to the effect of alkalinisation through the emission of cement dust. In the immediate vicinity of the plants, pH values often exceed 8 (Dubińska, 1982).

Al ALUMINIUM

Surface waters. The aluminium content in most of the analysed waters does not exceed the standards adopted in Poland for acceptable water quality, which is 0.4 mg/dm^3 (Rozporządzenie..., 2004). Poor quality waters (containing >0.8 mg/dm^3 of aluminium) represent only 3%. The average aluminium contents in the waters of the Vistula and Odra rivers (taken in many areas for drinking purposes) are 0.1 and 0.2 mg/dm^3, respectively. The areas of remarkably higher aluminium contents (> 0.5 mg/dm^3) are Lower and Upper Silesia, part of the Wielkopolska region (between Wrocław and Kalisz) and the region extending south of Ciechanów. Over the rest of the country, anomalous aluminium concentrations (above 0.6 mg/dm^3) were recorded in few places only.

The aluminium concentration in surface waters of those areas results from acidification caused by the presence of acid-forming oxides of sulphur, nitrogen, and carbon in the atmospheric air. Lithology of basement rocks, type of soils developed on these rocks, and the land use can also result in acidification. Studies conducted by the Institute of Meteorology and Water Management (Graczyk et al., 1992) clearly indicate that the anthropogenic factor is the most important. As concluded from those studies, 1/3 of the Poland's territory remains under the threat of acid rains, the most acidic in Europe (pH 4.1).

The near-surface lithology of Poland is the important factor that affects the occurrence of acidic and strongly acidic soils. Surface runoff in areas covered with these soils leads to acidification of surface waters, and subsequently to increased solubility of aluminium. Elevated aluminium concentrations of more than 0.6 mg/dm^3, found in some areas of Lower and Upper Silesia, can likely be related to the weathering of various rock massifs. Studies of aluminium concentrations in headwaters the Intra-Sudetic Trough demonstrate a distinct dependence of the aluminium concentration on the chemistry of basement rocks (Dobrzyński, 1993). Particularly high aluminium concentrations in surface waters occur in areas where sulphide ores subjected to weathering are exposed to oxidation, e.g. in Upper Silesia where very acidic waters are common. Surface waters of this type can contain as much as several hundred mg/dm^3 of aluminium (Macioszczyk, 1987).

Ag SILVER

Soils. The silver content in soils do not exceed the detection limit of the analytical method (1 mg/kg), and elevated concentrations of >1 mg/kg can only be found in a few sites of Lower and Upper Silesia.

In Upper Silesia, soils containing increased silver concentration are found in outcrops of the Ore-Bearing Dolomite (Piekary Śląskie) and in waste-rock dumping sites of post-mining areas of Pb–Zn ore deposits (Bytom, Świętochłowice, Szopienice, Trzebinia).

In Lower Silesia, small silver anomalies are observed in soils of the Złotoryja and Lubin copper mining areas and in the Legnica and Głogów copper metallurgy region. There are also silver anomalies (up 20 mg/kg) in soils of old mining excavation areas due to the occurrence of lead ores in the Holy Cross Mts. (Lenartowicz, 1994).

Sediments. Silver content in most of analysed sediments, like in soils, do not exceed 1 mg/kg, and the anomalies are definitely of anthropogenic nature. In the Silesia-Cracow and Lower Silesian regions, the anomalies (>1 mg/kg, most often >2 mg/kg) may be of mixed geological-anthropogenic character.

The highest silver concentrations in Lower Silesia have been found in sediments of the copper mining and metallurgy areas of Bolesławiec, Legnica, Lubin and Głogów.

In the Silesia-Cracow region, increased silver concentrations are observed on the outcrops of Middle Triassic carbonates containing zinc and lead ore deposits. The maximum silver concentration (117 mg/kg) was detected in the Ropa Stream, a right-side tributary of the Chechło River, south of Trzebinia.

The maximum silver anomalies are commonly situated within the areas of historical and present-day mining, processing and metallurgy of ores (Lis, Pasieczna, 1995a).

Location of the anomalies indicates that they are of geological-anthropogenic origin.

In the Polish Lowlands, elevated silver concentrations are observed in sediments of streams flowing close to some large urban-industrial agglomerations (Warszawa, Łódź, Bydgoszcz, Białystok, Lublin).

Like in Poland, silver polluted areas are well known across Europe from highly industrialized regions. Sediments of the Elbe River near Hradec Kralove can serve as the example, with the silver concentration ranging from <l to 35 mg/kg (Veselý, 1991). Silver is a good indicator of environmental pollution related to industrial activity.

As ARSENIC

Soils. Average arsenic contents in the soils of Poland are relatively low and occasionally exceed 5 mg/kg. They do not deviate from those summarized by Dudka (1993) to be the background values for agricultural soils of Poland. That author concluded that the arsenic content in sandy soils range between 0.5 and 15 mg/kg, while in clayey and muddy soils, the values vary from l .4 to 10.0 mg/kg. Slightly elevated arsenic concentrations are observed in the soils of Lower Silesia, Upper Silesia and the Bieszczady Mts.

In the Bieszczady Mts., some arsenic minerals occurring in the Lgota and Istebna beds near Baligród (Gucwa, Pelczar, 1986) could be the source of increased arsenic content.

The maximum arsenic concentrations in the Lower Silesian soils (up to 3444 mg/kg) have been detected in the Złoty Stok area, in the valley of the Trująca Stream that is the right-side tributary of the Bystrzyca Kłodzka River. The source of this anomaly is an arsenic deposit mined from the 13th century until 1962 (Dziekoński, 1972). In the valley of the Bystrzyca Dusznicka River (at Polanica Zdrój), the arsenic concentration is 744 mg/kg. This anomaly is probably associated with the occurrence of arsenic rich mineral waters (Szmytówna, ed., 1970). An arsenic anomaly of above 100 mg/kg is observed near Kamienna Góra. This area is known from the occurrence of arsenic ores (Posnenenske, 1935; Banaś, 1967). Another anomaly (up to 269 mg/kg) found near the Głogów copper smelter is undoubtedly of anthropogenic origin.

In Upper Silesia, arsenic concentrations that are over 20 mg/kg are found in the urban areas of Świętochłowice, Bytom, Mysłowice and Sławków, and in the area of the Pomorzany Zn–Pb ores mine (between Olkusz and Bolesław). These anomalies are of anthropogenic origin and they are associated with the Zn–Pb ores mining and smelting (Lis, Pasieczna, 1995a). Observations of other authors (Verner et al., 1994) conducted in the Bukowno smelter area confirmed the occurrence of local arsenic concentrations above 150 mg/kg in the topsoil of nearby arable land and allotment gardens.

The same applies to arsenic contaminations of soils in areas with long-term mining and metallurgy of Zn–Pb ores in the UK (Xiangdong, Thornton, 1993). In mining areas, the content of this element ranged from 6.5 to 42.3 mg/kg. In the Derbyshire lead smelter area, the topsoil layer from a depth of 0.00–0.15 m contained 5.9–44.4 mg/kg of arsenic.

In the Polish Lowlands, small areas of soils enriched with arsenic are observed mainly in the north-eastern regions. These are probably natural anomalies related to iron accumulations in bog iron deposits. It is also proved by the high iron content, usually in excess of 3%. However, without additional verification it is difficult to preclude that some of them are of anthropogenic origin. An example could be the presence of a strong arsenic anomaly detected during geochemical mapping of Warsaw in a place of former tannery (Lis, 1992).

Most of soils contains <20 of arsenic mg/kg, so they can be classified into land use groups A and B (Rozporządzenie.., 2002). The content in excess of 60 mg/kg (group C) occurs only locally in Lower and Upper Silesia.

Sediments. The geochemical background of arsenic in the studied sediments is between <5 and 11 mg/kg, and local enrichment (up to 17 mg/kg) is observed in the SW part of the country (mainly in Upper and Lower Silesia).

Anomalous contents are characteristic at the Złoty Stok region, where arsenic ore was mined and processed over hundreds of years (Dziekoński, 1972). The highest arsenic concentration, attatining 6215 mg/kg, was found in alluvial sediments of the Trująca Stream flowing across the area. In alluvial sediments of the Jamnica and Mąkolnica rivers (tributaries of the Nysa Kłodzka River), located west of Złoty Stok, arsenic concentrations locally exceed 200 mg/kg, which is associated with the occurrences of arsenic mineralization near Mąkolno (Wojciechowska, 1969).

The arsenic concentrations in alluvial deposits of the Nysa Kłodzka River in its lower reach attain a level of 48 mg/kg. Even greater values (up to 134 mg/kg) were detected near the confluence of the Nysa Kłodzka and Odra rivers (Bojakowska, Sokołowska, 1993).

In the Kamienna Góra area, the arsenic concentrations in alluvial deposits of the Bystra stream (left-side tributary of the Bóbr River) are up to 175 mg/kg, which can be due to the fact that the stream flows across areas of Czarnów arsenic ore deposits, exploited with some breaks from the 18th century to 1925 (Websky, 1853; Petrascheck, 1933; Banaś, 1967; Dziekoński, 1972).

An extensive arsenic anomaly, observed in the Kaczawa River drainage basin, is associated with extraction, processing and metallurgy of historical copper deposits in the North-Sudetic Trough and contemporary processing of the ores in the Lubin-Głogów Copper District. Arsenic originates from arsenopyrite and löllingite that are components of the ores (Konstantynowicz, 1967; Lisiakiewicz, 1969; Harańczyk, 1972). The maximum arsenic content in the stream near the Legnica copper smelter is 1053 mg/kg.

Among the Lower Silesian rivers, the most contaminated by arsenic are alluvial deposits of the Kaczawa River (average 24; maximum 171 mg/kg) and of the Nysa Łużycka River (average 21; maximum 51 mg/kg).

The arsenic content in alluvial deposits of major Upper Silesian rivers falls within the range of geochemical background. Distinct enrichment in this element can be observed in alluvial deposits of the Biała Przemsza, Chechło and Sztoła rivers in the Vistula drainage basin. The maximum arsenic concentration (915 mg/kg) was detected in a small right-side tributary of the Woda Graniczna Stream (approximately 5 km to the northwest of Miasteczko Śląskie, with a long-term activity of a metal smelter).

Some arsenic anomalies described in soils from the Baligród area in the Carpathians are poorly distinct in the deposits (Bojakowska, Borucki, 1992).

Increased arsenic concentrations in sediments of the Polish Lowlands seem to be of similar origin as those in soils. They are associated with the occurrence of bog iron ores. The most characteristic anomaly of this type can be observed in drainage basins of the Orzyc, Omulew, Rozoga and Pisa rivers in north-eastern Poland. Another extensive arsenic anomalies in sediments are found in drainage basins of the upper Narew and middle Vistula rivers (east of Warsaw), in the Vistula and San river valleys (south of Sandomierz), and in the drainage basin of the upper Pilica and upper Radomka rivers. These are also related to the occurrences of bog iron ores (Białaczewski, 1987). High arsenic contents (locally >100 mg/kg) in sediments are due to surface runoff rather than the existence of point sources of pollution. They are observed in sediments of small streams and watercourses (unnamed), but not major rivers.

Surface water. Because of poor arsenic detectability by the analytical methods applied in this project (0.04 mg/dm^3), no map could be prepared to show the arsenic distribution in surface waters.

Arsenic contents in most sampled waters are below the detection limit of the analytical method. Very high arsenic concentrations at Lower Silesia have been detected in the waters of the Trująca and Jamnica streams near Złoty Stok (0.66–6.77 mg/dm^3) and of the Czarna Woda Stream, a right-side tributary of the Kaczawa River, near Legnica (0.5 mg/dm^3). In Upper Silesia, a small pond located on the eastern side of a railway station at Miasteczko Śląskie (Woda Graniczna Stream drainage basin) contains 1.71 mg/dm^3 arsenic, while the water of the Rawa River at Szopienice – 1.53 mg/dm^3.

B BORON

Surface water. The geochemical background of boron is between <0.02 and 0.17 mg/dm^3. Areas of higher background values are found in the regions of Upper Silesia, Lower Silesia, Tarnobrzeg, Kujawy, northern Carpathians and Carpathian Foothills. Increased boron concentrations are also observed in surface waters of the Warsaw and Łódź regions, Szczecin environs, and the Vistula River delta in Żuławy. Among major rivers of Poland, the Vistula, Odra and Przemsza rivers are those showing the highest boron concentrations. Of minor rivers, the Kłodnica River (Gliwice Canal) is worth mentioning because of the average boron content of 0.43 mg/dm^3 in its waters.

Discharges of industrial sewage and mine waters to the rivers are the most common sources of boron in surface waters. Increased boron concentrations in surface waters of both Lower and Upper Silesia are caused by disposal of mine waters and drainage of Carboniferous deposits and barren-rock dumping sites by surface runoff. Boron concentrations in Carboniferous barren rocks that accompany the coal seams (in the Paralic Series) can reach 350 mg/kg (Walker, 1964). The boron content in the Poręba Beds in the north-western part of the Upper Silesia Coal Basin is 210 mg/kg (Krzoska, 1981). These data indicate that boron can mostly be leached from both barren rocks and mine dumps. Most of the water samples with the boron concentration more than 2 mg/dm^3 were collected from the Upper Silesia Coal Basin. Increased boron concentrations were also found in mine waters of the Wałbrzych Coal District in Lower Silesia.

Anomalous boron concentrations in surface waters occur in the Kujawy region due to mining of rock salt and brine discharges. Rock salt is accompanied in this area by boron-rich sulphate deposits with the boron concentration of up to 500 mg/kg (Pasieczna, 1987). Salt clays can contain even 1000 mg/kg of boron (Polański, 1988).

Elevated boron concentrations in surface waters of the Tarnobrzeg area are related to discharges of mine waters from the mines of sulphate deposits. A small watercourse flowing near the Jeziórko sulphur mine contains the maximum boron concentration of 12.87 mg/dm^3.

In the Warsaw and Łódź agglomerations and other industrial centres, e.g. Tarnowskie Góry, boron originates most likely from industrial wasterwater and solid waste. Wastes produced by chemical, pharmaceutical, ceramic, optical and detergent-producing industries are the main sources of surface water pollution.

Ba BARIUM

Soils. Two geochemical provinces can be distinguished with respect to barium concentration in soils. The southern province, characterised by increased barium concentrations (> 55 mg/kg), includes the Carpathians, Upper Silesia and Lower Silesia. In the northern province, the average barium concentrations are below 55 mg/kg. Slightly higher barium concentrations are observed only in the Żuławy area. Several point anomalies occurring in this area should be thoroughly studied and explained.

In Upper Silesia, the barium concentrations are >100 mg/kg in areas of outcrops of the Carboniferous coal-bearing clayey-sandstone rocks. These values are due to elevated barium contents in clays, which are of natural origin, as well as those of anthropogenic origin. Among the Carboniferous sedimentary rocks, clay shales, which are soil forming rocks, show the greatest tendency to accumulate barium. They contain an average of 550 mg/kg (Čurlík, Šefčík, 1999, Kabata-Pendias, Pendias, 1999). Contamination of soil with barium around mining facilities is probably associated with the pumping of salt water that contains much barium and strontium chlorides precipitating while mixing with the sulphate water at the ground surface.

Barium is subjected to accumulation in coal as a biophile element. Burning of huge amounts of coal in power plants may enrich soils with barium due to coal ash fallout. As concluded from the study of Różkowska and Ptak (1995), the average barium concentration in the Upper Silesian coal is 176 mg/kg; in the coal ash, the content is 1,274 mg/kg.

In Lower Silesia, soils with increased barium concentrations (>100 mg/kg) are observed near Wałbrzych (Sowie Mts., Intra-Sudetic Trough), where numerous signs of barite mineralization occur (Lis, Sylwestrzak, 1986). A distinct barium anomaly in soils near Złoty Stok needs to be explained since barite occurs in minor amounts in the arsenic deposit (Petraschek, 1933).

Increased barium contents in soils of the Odra and Upper Vistula valleys should be related to river floods of waters enriched with barium, polluted by discharge of mine waters and municipal and industrial sewage. On a local scale, barium can accumulate around cement-producing plants due to dust fallout. An example is the soil near the "Warta" cement plant at Działoszyn, where the barium concentrations attain of 600 mg/kg (Dubińska, 1982).

Sediments. Most of the samples (75%) contain below 100 mg/kg of barium. The lowest concentrations are found in nearshore lacustrine sediments (average 16 mg/kg), and the areas of anomalous contents occur in Lower and Upper Silesia.

In Upper Silesia, most of sediments of the drainage basins of the upper Stoła, Mała Panew and Brynica rivers near Tarnowskie Góry, Miasteczko Śląskie and Świerklaniec contain >400 mg/kg of barium.

Relatively low barium contents are characteristic of small streams and watercourses (average 97 mg/kg), small water reservoirs (average 114 mg/kg), as well as fish ponds and man-made reservoirs (60 and 58 mg/kg, respectively) (Lis, Pasieczna, 1995a). Such a variable barium content in different surface water bodies suggests that the element originates from mine waters discharged to the rivers.

Alluvial sediments of the Odra River in the territory of Poland are rich in barium (average 234 mg/kg). The main sources of this element are mine waters discharged from both Upper Silesian and Lower Silesian coal basins. Similarly high barium contents were recorded in alluvial sediments of this river in the period of 1992–1994, during monitoring observations of sediments (Bojakowska et al., 1993; Bojakowska, Sokołowska, 1993, 1994).

Between Jelenia Góra and Kłodzko in the Sudetes, there is an area of elevated barium content in sediments. The area is known to contain numerous signs of barite mineralization. Enrichment of barite and galenite is observed among heavy minerals occurring in alluvial sediments of the Trująca Stream (Złoty Jar). Jęczmyk and Markowski (1990) are of the opinion that this is of anthropogenic origin. Sediments in the Polish Lowlands usually show anomalous barium contents (> 230 mg/kg) in urban areas, indicating that barium originates from industrial and municipal wastewater.

Surface water. The regional distribution of barium in surface waters is similar to those in soils and sediments, and is controlled by natural factors (Małecki, 1988, 1991). Over most of the Polish territory, the barium concentrations vary from <1 to 100 μg/dm^3. For example, Rejniewicz (1994) reported the contents of 48–121 μg/dm^3 in surface waters of the Netherlands, which are considered natural barium levels.

Anomalous barium concentrations are found in the rivers and streams that drain the Upper Silesian area. Worthy of mentioning are the Biała and Czarna Przemsza, Bobrek and Mleczna rivers in the Vistula drainage basin, and the Vistula River itself. Particularly high barium content (average 425 μg/dm^3*)* was recorded in the Mleczna River, which is a left-side tributary of the Gostynia River. Within the Odra drainage area, barium concentrations of more than 100 μg/dm^3 were found in the waters of the Bytomka, Kłodnica, Mała Panew and Stoła rivers.

Extremely high barium concentrations (average 362 μg/dm^3) were measured in the Stoła River waters (Lis, Pasieczna 1995a). Mine waters from both coal and metal ore mines are the main sources of this element.

The Intra-Sudetic Trough of Lower Silesia is the area of high barium contents probably due to the occurrence of basic magmatic rocks (palaeobasalts). In the Polish Lowlands, a distinct barium anomaly occurs in the Noteć River water, between Inowrocław and Bydgoszcz. It is most probable that the anomaly originates from disposal of mine waters pumped out from rock salt mines.

Be BERYLLIUM

Sediments. Beryllium concentrations in sediments are low (average <0.5 mg/kg). Only south-western Poland (Upper Silesia, Lower Silesia and Opole Silesia) are the areas of higher beryllium contents (between 0.5 and 1.0 mg/kg). It results from the chemistry of basement rocks as well as industrial activities. Unvarying contents and nature of distribution of beryllium in stream sediments of Poland have been confirmed by recent studies (Salminen, ed., 2005).

The main source of beryllium in sediments of Upper Silesia is dust emissions from coal combustion and leachates from landfills of the Siersza Jaworzno, Łagisza, Będzin and Cieśle power plants. According to the data cited by Kabata-Pendias and Pendias (1979), the beryllium content in coal ranges from 0.1 to 31.0 mg/kg, while in the flue dust of power plants it can be as high as 45.0 mg/kg.

In the Sudetes, the highest beryllium concentration (up to 20 mg/kg) was found in sediments of some streams in the eastern Karkonosze Mountains. These are natural enrichments associated with the Variscan granites. A similar effect of geology, mainly due to the presence of acid igneous rocks, distincted by the occurrence of beryllium concentrations in sediments (up to 84 mg/kg), was noted by Reid (1993).

On the industrial scale, beryllium has been utilized only recently. It is used to harden light copper and aluminium alloys. It is likely that the occurrence of the beryllium anomaly in sediments is associated with the discharge of industrial sewage to the Warta River (from the Częstochowa Steelworks), Kamienna and Radomka rivers (from industrial plants in Starachowice), and Wisłoka River (from the Stalowa Wola Steelworks).

Ca CALCIUM

Soils. The calcium content in soils is commonly less than 0.5%. Concentrations greater than 2% are observed in soils that developed on limestones (Upper Silesia, Opole region, part of the Cracow-Częstochowa Upland, Nida Trough, Lublin Upland) and in ice-dammed lake deposits near Pyrzyce (SE of Szczecin). Soils in loess-covered areas of the Sandomierz Valley (Basin), and Wisłoka River and upper San River drainage basins, as well as soils developed on glacial tills in NE Poland show the calcium content in the range of 0.5–1.0%. Soils of the last group, developed on the youngest glacial tills, contain noticeably more calcium as compared with the soils developed on older tills (Kern, Pietraś, 1981).

Increased calcium contents in soils of the Poznań, Kujawy and Bydgoszcz regions seem to be related to a high agriculture level (lime fertilization). Soils of these regions also show high pH values.

Sediments. The pattern of areal distribution of calcium in sediments is generally consistent with its distribution in soils. Basement lithology is the main factor controlling the calcium distribution; the anthropogenic factor is of secondary importance.

The Ca concentrations >5% are observed in the Silesian-Cracow region, Lublin Upland, Nida Trough and Flysch Carpathians. Sediments of the Kujawy, Poznań, Bydgoszcz and Szczecin regions are also rich in calcium. Elevated calcium contents (>2%) are found in most sediments of watercourses draining glacial tills of the youngest glaciation, which is well marked in the Pomeranian Lake District.

Surface water. The values of calcium concentrations vary between individual regions, as it is the case with sediments and soils. 90% of samples contain <140 mg/dm^3 of calcium.

Such areas as Lower Silesia, Upper Silesia, Opole region, Nida Trough, Lublin Upland and Carpathian Foreland with the calcium content ranging between 100 and 200 mg/dm^3 can be distinguished from the remaining area of Poland characterised by lower contents (<110 mg/dm^3). Increased calcium contents can be explained by chemical weathering of basement rocks containing this element (calcites, aragonites, dolomites, gypsums and anhydrites). Literature data indicate that the concentration of calcium in surface waters is dependent on its content in basement rocks. Streams flowing across lowland areas of the Netherlands contain 16 to 36 mg/dm^3 calcium, while those flowing down the carbonate areas have a content of 55 to 74 mg/dm^3 (Rejniewicz, 1994).

Surface waters of northern Sweden, in the area of metallic ore mining in magmatic rocks, contain very low amounts of calcium (2.7–14.5 mg/dm^3) Ek (1974).

It is most probable that agrotechnical treatments (liming) are the reason for enrichment of surface waters with calcium in Wielkopolska, Kujawy and Mazowsze.

A distinct calcium anomaly is observed in waters of the Noteć River drainage basin between Lake Gopło and Bydgoszcz city. It is thought that the discharge of mine waters from a rock salt mine might be a source of calcium. The maximum calcium concentration (6,400 mg/dm^3) was found in a stagnant water ditch close to the cement plant at Ogrodzieniec; it is of anthropogenic nature.

Cd CADMIUM

Soils. In most soils, the cadmium concentrations are below 0.5 mg/kg. Slightly increased contents (0.5–1 mg/kg) are found in soils of the Carpathians, middle part of the Sudetes, as well as in the upper Vistula River (downstream to Sandomierz) and upper Odra River valleys.

Soils of the Silesian-Cracow region are characterized by the highest cadmium concentration, frequently in excess of 2 mg/kg. The maximum concentrations (>16 mg/kg) are observed in areas of mining, ore processing and metallurgy (Bytom, Chrzanów, Katowice, Szopienice, Miasteczko Śląskie and Olkusz regions). Verner et al. (1994) proved that the topsoil layer in the vicinity of the Bukowno zinc smelter (Olkusz region) contains 25–133 mg/kg of cadmium.

A study by Xiangdong and Thornton (1993) on cadmium concentrations in regions of ore mining and processing in Great Britain shows that the maximum cadmium contents of up to 372 mg/kg occur in ore mining areas, whereas in the topsoil layer near metallurgical plants, the values range between 0.2 and 19.7 mg/kg.

Cadmium concentrations in soils of various countries vary from 0.2 to 1.05 mg/kg (Kabata-Pendias, Pendias, 1999). In the topsoil of Slovakia, the cadmium contents are <0.1–8.9 mg/kg (Čurlík, Šefčík, 1999). Arable soils of Poland contain 0.01–24.75 mg/kg of cadmium (Terelak et al., 1995).

In terms of land use, the maximum cadmium content is characteristic of soils in city parks (with the average content of 4.6 mg/kg), urban lawns (average 2.7 mg/kg), and arable land of urban agglomerations (average 2.7 mg/kg). Previous studies on land use (allotment gardens and ploughland) in the Katowice Voivodship showed that the cadmium content was between 0.3 and 143 mg/kg (Marchwińska, Kucharski, 1990). Increased cadmium concentrations in urban soils are locally observed in other areas of Poland. In Warsaw, the cadmium concentration in soils ranges from <0.3 to 5 mg/kg (Lis, 1992), with the maximum of 41 mg/kg (Czarnowska, Gworek, 1988). In Cracow, the urban soils contain <0.5 to 27.3 mg/kg of cadmium (Lis, Pasieczna, 1995c).

Out of the total area of soils under agricultural use in Poland, only 2.8% represent soils containing 1–5 mg/kg of cadmium (tolerable values); no cadmium concentrations in excess of 5 mg/kg have been recorded, which are considered toxic contents. Increased cadmium concentrations in soils (>l mg/kg) are mainly observed in southern Poland, where heavy clayey soils are predominant. Such soils strongly bind cadmium in sorption complexes.

In Upper Silesia, 53.6% of cultivated soils contain between l and 5 mg/kg of cadmium. Soils that contain more than 5 mg/kg of cadmium account for 8.6%. These concentrations are of anthropogenic origin and are associated with Zn-Pb ores mining activity and metallurgy. Only the topsoil layer is polluted by cadmium over large areas; however, the cadmium content is quickly decreasing with depth (Lis, Pasieczna, 1995b).

Sediments. In general, the cadmium geochemical background in sediments varies between <0.5 and 2.6 mg/kg, and is below 1 mg/kg in 75% of the investigated sediments.

There are some regions of elevated cadmium concentrations. The most extensive anomaly is that observed in the Silesian-Cracow region. In part, its origin is natural (outcrops of the Triassic Ore-Bearing Dolomite with Zn–Pb ores); partly it is of anthropogenic origin (related to ore mining and ore metallurgy). Among major rivers flowing across the area, average cadmium contents over 10 mg/kg were detected in sediments of the Biała Przemsza, Brynica, Baba, Chechło, Sztoła and Vistula rivers (in the Vistula drainage basin) and of the Bytomka, Mała Panew and Stoła rivers (in the Odra drainage basin). The maximum concentrations occur in the Woda Graniczna Stream (a tributary of the Stoła River) and in sediments of its drainage basin (up to 8,735 mg/kg). Similar cadmium anomalies in sediments of the Upper Silesian rivers were recorded as the result of river monitoring conducted in the period 1992–1994 (Bojakowska, Sokołowska, 1993, 1994). Other authors also confirm the occurrence of contamination with cadmium in this region. Sediments of the Biała Przemsza River contained between 0.9 to 73.0 mg/kg of cadmium, measured along nine cross-sections (Ryborz, Suschka, 1993). Helios-Rybicka (1994) reported the maximum cadmium content in sediments of the Przemsza River, which is 500 mg/kg. Sediments of the Chechło River (from 40.8 to 130.1 mg/kg; average 70.8 mg/kg) and the Stoła River (from 6.3 to 290.3 mg/kg; average 31.0 mg/kg) are particularly enriched with cadmium. The effect of the Upper Silesian cadmium anomaly is detectable far away from this anomaly's sources in sediments of both the Vistula and Odra rivers.

Alluvial sediments of the Vistula River near Cracow contain 86.9 mg/kg of cadmium that migrates to soils in this river valley as the result of floodings. In the upper stretch of the Vistula River the cadmium concentration in sediments can reach 160 mg/kg, and intensified accumulation of cadmium takes place in the river sections of low flow velocity (Leńczowska-Baranek, 1991).

The maximum cadmium concentration in Lower Silesia (50 mg/kg) was detected in sediments of a small stream being a tributary of the Leśna Woda Stream in the Boguszów area near Wałbrzych.

Increased cadmium concentrations in sediments of the Polish Lowlands are mostly of anthropogenic origin, except in the drainage basins of the Skrwa, Wkra, Orzyc, Omulew and Rozoga rivers. The increased cadmium contents are found in natural bog iron ores that also contain anormally high concentrations of arsenic and iron.

Near Warsaw, drainage basins of the Utrata and Jeziorka rivers are among the most polluted areas. The cadmium concentration in one of the Jeziorka River tributaries was at the level of 1,100 mg/kg in 1990 (Lis, 1992). High cadmium concentrations in sediments of the Jeziorka River have sustained for years at a level of >100 mg/kg (Bojakowska, Sokołowska, 1994).

Anthropogenic pollution highly contributes to the abnormal cadmium concentrations (up to 47 mg/kg) in drainage basins of the Warta and Bzura rivers near Łódź and its environs. In drainage basins of the Bystrzyca and Wieprz rivers near Lublin, the concentration of cadmium reaches 123 mg/kg, and its content in sediments of the Warta River between Poznań and the confluence with the Obra River is 112 mg/kg. The content 39 mg/kg of cadmium is observed in the upper part of drainage basins of the Radomka and Kamienna rivers near Starachowice. These anomalous concentrations are genetically related to the discharges of industrial sewage of metallurgic, dyeing, electronic and plastics industries.

Surface water. The average cadmium content in surface waters is lower than 3 μg/dm^3 (detection limit). Only some waters in the Upper Silesian area contain a higher amount of cadmium. There are some isolated cadmium anomalies in surface waters near Ogrodzieniec and between Bolesław and Bukowno, with the concentrations of more than 5 μg/dm^3. Very strong anomalies (locally exceeding 100 μg/dm^3) occur in the Szopienice and Mysłowice areas and in drainage basins of the Mała Panew and Stoła rivers north of Tarnowskie Góry. The latter anomaly, with the maximum concentration of 238 μg/dm^3 found in the Woda Graniczna River drainage basin, is consistent with another very strong cadmium anomaly in sediments.

In nature, cadmium is associated with zinc; and its increased concentrations are common in surface water bodies in historical metal ore mining districts. There are some indications in the literature that surface waters in old Zn-ore mining regions can contain even greater cadmium concentrations than those in Upper Silesia. One example refers to Wales where surface waters in the vicinity of old mines contain 2,500 μg/dm^3 of cadmium, whereas in the whole drainage basin of the mining district, the values varied between 6.5 and 15.6 μg/dm^3 (Fuge et al., 1991). In Germany, cadmium contents reaching 48 μg/dm^3 are well known in surface waters of the Rhenisches Schiefergebirge and the Bodenmais area in the Bavarian Forest (Fauth et al., 1985). Relatively slightly polluted waters of the Biały Dunajec River drainage basin contain up to 43 μg/dm^3, which is interpreted as the impact of chemical industry (Małecki, 1988).

Co COBALT

Soils. Geochemical properties of cobalt are similar to those of iron. Areal distribution of both elements in soils is also similar. In general, the cobalt content in soils is very low (<3 mg/kg); however, in the southern part of the country, where silty soils prevail (the Sudetes, the Carpathians), cobalt occurs at the concentrations between 5 and 10 mg/kg. In the north, similar contents can be observed in the Vistula River delta (Żuławy) and along the north-eastern state border. Distribution of cobalt in the soils is of natural character, dependent on the chemistry of basement rocks (in the Sudetes, Carpathians and Lublin Upland) or is due to site-specific properties of soils (muddy soils of Żuławy).

In Lower Silesia, the maximum cobalt content in soils was recorded near the Legnica copper smelter (up to 24 mg/kg) and near a sludge pond of the copper mine at Leszczyna near Bolesławiec (21 mg/kg). It is likely that dust fallout from the metallurgic plant is the source of cobalt enrichment in the soils.

Enrichment of soils with cobalt is a characteristic feature of the upper Vistula and upper Odra river valleys, which occurs due to floodings. The higher cobalt concentrations in soils of the upper drainage basin of the Kamienna and Radomka rivers are of anthropogenic origin due to development of metallurgical industry in this area. Other industry sectors, e.g. oil refineries, can also contribute to the enrichment of soils with cobalt. Soils of the area around the Płock refinery contain 16 mg/kg of cobalt (Biernacka, Liwski, 1986). Cobalt compounds are also utilized as dyes in the ceramic and glass-making industries, causing environmental pollution.

Sediments. The distribution pattern of cobalt in sediments is very similar to that in soils, with the concentration ranging from <1 to 5 mg/kg. In many areas, anthropogenic pollution greatly affects the amount of cobalt in sediments.

Anomalous cobalt concentrations in Lower Silesia (>5 mg/kg) have a local character of natural enrichment associated with the occurrence of basic rocks (Szumlas, 1963) or anthropogenic pollution (due to copper mining and metallurgy). The Lower Silesian copper ores contain minor amounts of cobalt minerals such as cobaltite and safflorite (Lisiakiewicz, 1969; Harańczyk, 1972). However, cobalt does not accumulate in alluvial sediments of the Odra River (average content 6 mg/kg). Similar contents (4.8–7.2 mg/kg) were recorded by Jędrczak and Czyrski (1990) in the Odra sediments between Nowa Sól and Kostrzyń.

A regional cobalt anomaly in the Silesian-Cracow region is characterised by the concentrations exceeding 10 mg/kg. Similar values were measured in the Radomka and Kamienna drainage basins. The maximum concentration (160 mg/kg) was found in a small tributary of the Radomka River. Other anomalies, most likely of anthropogenic origin, are situated near Częstochowa (iron metallurgy), Mielec and Lublin (aircraft industry, metallurgy). An anomaly (up to 357 mg/kg) occurring in the middle Warta River drainage basin near Jarocin still needs a more detailed study and explanation.

Surface water. Determination of cobalt concentrations is impossible due to the poor detectability (5 $\mu g/dm^3$) of the analytical method used for this study. The maximum cobalt concentrations (136 $\mu g/dm^3$) were found in a small pond and a stagnant-water ditch (85 μg/dm^3) in the Czarna Przemsza River drainage basin. Most likely, the anomalies are associated with discharges of industrial sewage. Geological factor seems to be insignificant, as evidenced by previous determinations of cobalt contents near a zinc-lead mine (Pasternak, 1973), which were 7 μg/dm^3 in the Biała Przemsza River and 2–9 μg/dm^3 in the upper Vistula River.

Stream sediments of Germany contain 1–540 μg/dm^3 of cobalt (Fauth et al., 1985). However, no suggestion was offered on natural sources of the cobalt anomalies there, concluding its anthropogenic origin.

Cr CHROMIUM

Soils. The main factor controlling the chromium content in soils is geological structure, to a lesser extent pollution related to economic activity. Soils that are not affected by anthropogenic factors show concentrations of chromium dependent on its content in the parent rocks. The ranges of chromium contents in soils of the neighbouring countries are as follows: 0.6–133.6 mg/kg in Lithuania (Kadūnas et al., 1999), <5–6096 mg/kg in Slovakia (Čurlík, Šefčík, 1999) and <3–610 mg/kg in Saxony (Rank et al., 1999).

In southern Poland, comprising the Sudetes and the Carpathians, the chromium concentrations are typically >7 mg/kg. In the Sudetes, the chromium concentrations exceeding 15 mg/kg were found in soils developed on metamorphic rocks of the eastern margin of the Karkonosze Mts. (Rudawy Janowickie), in the Kaczawa Mts. and between Świdnica and Złoty Stok.

The enrichment is natural and results from the presence of basic rocks (greenschists, serpentinites, gabbroes, paleobasalts). A small chromite deposit, the only one in Poland, is known to occur in this region in serpentinites at Tąpadła near the Sobótka Mt. (Kossman, 1890). Chromium contents reaching 800 mg/kg (Ciemniewska, 1970) were reported in soils that developed on serpentinites (in the Szklary area).

Increased chromium concentrations also occur in soils developed on glacial deposits of the youngest glaciation in northern Poland, Żuławy and the Lublin Upland.

In the north of the Polish Lowlands, the chromium contents are <4 mg/kg.

Urban agglomerations and valleys of major rivers (Vistula, Odra and Kamienna rivers) are the areas where chromium-related pollution of anthropogenic origin is most common. A distinct chromium anomaly in soils of Częstochowa and its environs, probably associated with iron metallurgy, needs further study and explanation. Soils can be highly polluted by chromium due to metallurgy, chromate production and tannery industry. An example is the chromium anomaly of 870 mg/kg that occurs at a dumping site of the Siechnice smelting plant near Wrocław (Twardowska, 1993).

Sediments. Variability of chromium content in sediments is greater than in soils. Over most of the territory of Poland, sediments contain below 10 mg/kg of his element. In southern Poland (including Lower Silesia, Cieszyn Silesia and the Carpathians), the enrichment (10–20 mg/kg of chromium) is associated with the geological structure.

In the Sudetes, in areas of the occurrence of basic rocks, accumulations of eroded rocks generate a chromium anomaly (>1,000 mg/kg). In the Nysa Kłodzka drainage basin (near Złoty Stok), the maximum chromium concentration is 4000 mg/kg. Low chemical mobility of chromium is the reason why this element is subjected to mechanical transportation over a long distance from the source areas. This phenomenon is well visible in sediments of the Kaczawa, Bystrzyca and Nysa Kłodzka rivers, exhibiting enrichment in chromium along the entire courses. Part of sediments of the Vistula and Odra rivers contain chromium originating from erosion of rocks in southern Poland. For this reason, there are problems in attempting to evaluate the content of chromium supplied from anthropogenic sources.

Distinct chromium anomalies (>80 mg/kg) are common in Upper Silesia near industrial plants and railway junctions. The strongest anomaly (up to 12,251 mg/kg) occurs in the Kozi Bród Stream (left-side tributary of the Biała Przemsza River), near the Jaworzno-Szczakowa transhipment railway station (for iron ore).

A relatively strong chromium anomaly in the Centara Stream (right-side tributary of the Biała Przemsza River) is the result of an undefined source of pollution in Wolbrom. Other anomalies located near Strzybnica, Alwernia, Oświęcim and Babice occur near industrial plants or railroad tracks. In Alwernia, post-chromium sludge from a chemical plant is probably the source of a chromium anomaly.

As concluded from the study of Helios-Rybicka and Wardas (1989), chromium in the fraction <63 μm is almost entirely associated with a ferruginous phase of the sediments. Chromium concentrations in sediments of the upper Vistula River (downstream of the confluence with the Przemsza River) can be explained by mining and metallurgical activities in Upper Silesia.

In the Polish Lowlands, where the basement rocks contain no natural sources of chromium, strong anomalies are of anthropogenic origin (from point sources). It is evidenced by a very low chromium content in sediments of small watercourses (6 mg/kg), pools (6 mg/kg), lakes (2 mg/kg) and fishponds; although there are some local concentrations in these inland water bodies.

Anomalously high chromium contents often occur in areas of large industrial centres, especially metallurgical centres discharging sewage produced in the chrome plating process: Częstochowa (upper Warta drainage basin), Mielec (Wisłoka drainage basin), Rzeszów (Wisłoka drainage basin), Lublin (Bystrzyca Lubelska and Wieprz drainage basin), Warsaw (Vistula drainage basin) and Starachowice (Kamienna drainage basin).

Chromium anomalies also occur in regions of large centres of leather industry near Radom (Radomka drainage basin) and Sochaczew (Bzura and Utrata drainage basin). Chromium originates in these areas from sewage and wastes produced at tanneries, which contain over 1% of chromium (Bojakowska, 1994).

The chemical industry, especially the production of dyes, generates chromium anomalies by discharging wastewater. These types of chromium anomalies occur in Tomaszów Mazowiecki (Pilica drainage basin), Płock (Vistula drainage basin) and other smaller industrial centres.

In addition to the main potential sources of chromium, there are also point sources that locally can highly contaminate the environment. These originate from small plants and workshops (electroplating workshops, small tanneries etc.), e.g. in a drainage basin of a small stream of Buchnik that drains the right-bank side of Warsaw, where the chromium concentration exceeds 4,000 mg/kg (Lis, 1992).

Surface water. Almost all surface waters of Poland (99% of samples) contain below 10 μg/dm^3 of chromium.

In Lower Silesia, chromium anomalies are strongly dependent on the occurrence of basic rocks. The chromium concentrations of 4,040 and 10,801 μg/dm^3 were recorded in the Trująca Stream near Złoty Stok.

Surface waters are often enriched with chromium introduced with sewage from smelters. Near the Siechnice smelting works, the chromium concentration is as high as 1,250 μg/dm^3 (Sławski et al., 1989), and the harmful effect of this element on living organisms is enhanced by the alkaline pH of the waters, which stabilizes chromates (CaO is used in furnace processes).

A very strong chromium anomaly in Upper Silesia was detected in the Kozi Bród Stream waters near the Jaworzno-Szczakowa railway station, with the maximum chromium concentration of 4,445 μg/dm^3. A less extensive anomaly was found south of Alwernia. Both these anomalies coincide with the chromium anomalies recorded in sediments and soils.

Chromium anomalies in surface waters are known to occur near Częstochowa (Warta drainage basin), Radom (Radomka drainage basin), and north of Łódź (Bzura drainage basin).

They are observed in the areas of chromium anomalies found in sediments. In addition, both these anomalies originate from the same sources. Less impressive anomalies require some more detailed studies.

Among anthropogenic sources, leachates of furnace wastes containing fire-resistant materials contaminate surface waters by chromium. Near the Rejowiec cement plant, the chromium concentration ranges from 840 to 1,560 µg/dm^3 (Smuszkiewicz, Jaworski, 1991). Chromium-related pollution of surface waters in some areas of Wielkopolska can originate from surface runoff from soils that are fertilized with sewage sludge.

Cu COPPER

Soils. Copper is a common element in nature and necessary to the functioning of living organisms. Both deficiency and excess of copper in the diet cause disturbances in the functioning of plant and animal organisms.

The total copper content in uncontaminated soils in different countries varies within the limits of 1–140 mg/kg (Kabata-Pendias, Pendias, 1999). In the soils of Lithuania, the copper concentrations range between 0.4 and 70.8 mg/kg (Kadūnas et al., 1999). Higher concentrations, from 2.5 to 570 mg/kg, were found in the soils of Saxony (Rank et al., 1999). In Slovakia, the values are <1–22 360 mg/kg, and the median is 17 mg/kg (Čurlík, Šefčík, 1999).

The soils of Poland contain small amounts of copper (commonly 3–10 mg/kg) and large areas of the country are characterised by deficiency of this element with respect to plants' needs. The geochemical background, expressed by the median, is 5 mg/kg. Similar copper concentrations were reported by Terelak et al. (1997) and Czarnowska and Gworek (1987) in arable soils of Poland; the average is 6.5 mg/kg (in case of a stronger chemical decomposition of samples).

A regional variability in the copper distribution is clearly visible, which is controlled by the lithology of basement rocks. Clayey soils of southern Poland contain higher copper concentrations (20–25 mg/kg). They contrast with sandy soils occurring in the remaining part of the country, which are poorer in copper. Among the latter, alluvial soils of the Vistula River delta (Żuławy) are conspicuous by increased copper contents (>10 mg/kg). In the Lublin Upland, increased copper concentrations occur in soils that developed on Cretaceous rocks (rendzinas) and younger loesses.

Against such a background, a number of local anomalies in soils developed on glacial deposits of the youngest glaciation can be identified in the Polish Lowlands. They are probably of anthropogenic origin. The maximum copper concentrations are found at some places in Kujawy and Mazovia (80–100 mg/kg), which can be related to agrotechnical treatments (such as application of crop protection chemicals or fertilization with sewage sludge).

Copper mining and metallurgy is the main pollution factor affecting soils in Lower Silesia, in both the Sudetes (deposits in the Intra-Sudetic Trough) and the Legnica-Głogów Copper District. The strongest anomalies can be observed near the copper smelters at Legnica (up to 3,490 mg/kg) and Głogów (up to 6,401 mg/kg). The study by Drozd et al. (1984) shows that the copper concentrations in soils occurring in the immediate vicinity of the Legnica copper smelter are as high as 16,400 mg/kg, and the clay fraction in soils from the area of the Głogów copper smelter contains as much as 7,875 mg/kg of copper (Borkowski et al., 1991). Mining activity is less destructive to soils. In the Lubin region, the maximum copper concentration is 101 mg/kg, and in the Polkowice area 696 mg/kg.

In Upper Silesia, distinct copper anomalies are situated close to historical and active metallurgical plants developed in a belt extending from Zabrze to Szopienice. The maximum copper concentration of 805 mg/kg was recorded at Tarnowskie Góry, which is likely associated with the activity of a chemical plant. Minor anomalies occur also near Trzebinia (metallurgical plants) and Oświęcim. Trafas et al. (1990) are of the opinion that metallurgical processes of Zn–Pb ores do not contribute to the increase of copper concentration in soils. In the immediate vicinity of the Boleslaw Mine and Metalurgical Plant, those authors found that the copper concentration in soils does not exceed 40 mg/kg. Another opinion was expressed by Lorek (1993) who claims that the copper concentration in soils near the zinc smelter increased from 20 to 36 mg/kg over a period of 11 years, and near the "Katowice" steelworks, it increased from 3 to 37 mg/kg during the same period.

Urban agglomerations and associated industries as well as intensity of motor transport constitute other factors controlling the copper concentration in soils. Elevated copper concentrations in urban soils have been found in Wrocław (up to 612 mg/kg), Warsaw (up to 427 mg/kg), Szczecin (up to 205 mg/kg) and Cracow (up to 83 mg/kg). For comparison, it is interesting to mention some data from Lux (1993) on soils from the Hamburg agglomeration where the topsoil layer (0–5 cm) contains <2–3,688 mg/kg (average 103 mg/kg) of copper. High vehicular traffic seems to be the factor contributing to the increased copper content. As reported by Czerwiński (1987), copper contents in the roadside of high intensity traffic are up to 67 mg/kg, whereas it is only 17 mg/kg at a distance of 300 m away.

Sediments. Variability of copper content in sediments is much greater than in soils. The natural background, controlled by surface runoff and the geological structure, is enhanced by numerous anomalies of mostly anthropogenic origin.

In the Polish Lowlands, the copper concentration in sediments commonly varies from 3 to 15 mg/kg. In the southern geochemical province, the values range between 10 and 30 mg/kg. Copper mining and metallurgy are the main pollution sources in Lower Silesia, in both active centres (Lubin-Głogów Copper District) and historical areas (North-Sudetic Trough). The level of copper-related pollution originating from copper smelters is manifested by the maximum concentrations recorded in a small water course in the upper part of the Czarna Woda drainage basin (tributary of the Kaczawa River) near the Legnica smelter (15,460 mg/kg), and in sediments of the Rzychowska Struga (tributary of the Odra River) near the Głogów smelter.

Both copper mining and ore processing significantly affect the development of copper anomalies. In the Polkowice region, close to the mining plant and a post-flotation settling pond of Żelazny Most, the maximum copper concentration was 5,598 mg/kg. Sediments of the Zimnica Stream (a tributary of the Odra River), close to the Lubin mine, contain as much copper as l,664 mg/kg, and sediments of the Mały Bóbr Stream (tributary of the Bóbr River) near the Konrad mine (at Iwiny near Lwówek Śląski) – 1,029 mg/kg. Another geological anomalies (copper content of several hundred mg/kg) are known to occur in the Sudetes, near Jelenia Góra, Wałbrzych and Świdnica.

A wide belt of copper anomalies is observed in sediments of Upper Silesia. It extends from Tarnowskie Góry through the most urbanized part of Upper Silesia to Olkusz and Bolesław. The maximum copper concentration was detected in sediments of the Bytomka River (average 125 mg/kg) and Stoła River (average 216 mg/kg) within the Odra drainage basin, and in sediments of the Chechło River (average 197 mg/kg) in the Vistula drainage basin. Industrial sewage (from metallurgical, dye-producing, pharmaceutical and plant protection chemical industries) is the main source causing pollution of sediments by copper. The other sources are municipal sewage, burning of coal and intense vehicular traffic. Monitoring of sediments in some major rivers of the region indicates the average copper concentrations between 54 and 84 mg/kg (Bojakowska, Sokołowska, 1994).

Anthropogenic copper anomalies in sediments are also common in central Poland. The highest copper concentrations are found in sediments of the Utrata River (tributary of the Bzura River) between Sochaczew and Warsaw, with the maximum values locally exceeding 2,000 mg/kg. The vicinities of other urban and industrial agglomerations are also highly polluted, as sediments contain up to 481 mg/kg of copper near Łódź, 969 mg/kg near Cracow, 722 mg/kg south of Rzeszów, and 573 mg/kg near the Kozienice power plant. Wastes produced by electrical, rubber, dying and pharmaceutical industries are the main sources giving rise to high copper concentrations in sediments.

Surface waters. The average copper content in surface waters of the world is determined to be 30 µg/dm^3 (Freedman, 1989). Copper concentrations in surface water of Poland are lower (< 5–20 µg/dm^3), and commonly do not exceed 7 µg/dm^3.

Concentrations of 7–20 µg/dm^3 are common in waters of south-western Poland, mainly in drainage basins of the Kaczawa, Bóbr and Ślęża rivers. Copper is most likely of natural origin due to penetration of copper-rich basic rocks by rainwater.

Surface waters naturally enriched in copper occur in streams draining loess areas of the Lublin Upland (7–20 µg/dm^3).

The maximum copper content in the areas of copper mining and metallurgy does not exceed 100 µg/dm^3 (except for one sample from the Czarna Woda Stream near the Legnica copper smelter, with the content of 171 µg/dm^3). In the Odra River, downstream the site of mine water discharge from the Legnica-Głogów Copper District, the average copper concentration is approximately 100 µg/dm^3 (Łanowy et al., 1989). Generally, copper concentrations in surface waters in the region of copper mining and metallurgy in Poland are lower than in other mining areas of the world. For example, in the Canada's ore-bearing region where volcanogenic Cu–Zn ore deposits are extracted, the copper concentration in surface water near ore mines frequently exceeds 20,000 µg/dm^3, and the maximum value is as much as 43,950 µg/dm^3 (Percival et al., 1992).

Interpretation of the copper distribution pattern and the source of this metal in surface waters face serious difficulties without detailed studies. High copper concentrations are recorded for small water bodies existing in areas where clearly visible sources of pollution are missing (excluding those of agricultural origin).

Fe IRON

Soils. Variability of iron content in soils of Poland shows a specific pattern. Soils of northern Poland, in the area covered by glacial deposits of the youngest glaciation, contain 0.50–1.00% of iron. Enrichment in iron is observed in alluvial sediments of the Żuławy region (>1.00%).

As indicated in the study by Gworek (1985b), higher iron concentrations (1.6% on the average) are noted in soils developed on the youngest glacial formations, whereas the soils developed on older tills show the average iron concentrations of 1.40%. Iron concentrations of

4–5% are observed in small patches of alluvial soils in the Polish Lowlands. Similar iron concentrations of up to 4% were also recorded in alluvial soils of the Odra River valley (Laskowski, Szozda, 1985).

Iron-rich soils (>1.00%) occur in the southern geochemical province. In the Sudetes, iron-rich soils (>2%) developed on basic metamorphic and igneous rocks. Increased iron concentrations in the Carpathians can be associated with interbeds of ferruginous rocks (siderites) mined at the end of the 19th century (Osika, 1987).

Sediments. The average iron content in sediments is 0.75%. Its distribution is controlled mainly by geological factors such as the abundance of iron in the basement and the occurrence of bog iron ores in the Polish Lowlands. Sediments of the northern geochemical province commonly contain 0.50–1.00% of iron, whereas in the south, its content increases to 1.00–2.00%.

Distinct iron anomalies in sediments of Lower Silesia (north of Zgorzelec and near Opole), Częstochowa environs and the Holy Cross Mts. (including their margin) are most likely associated with the occurrence and former exploitation of sedimentary iron ore deposits (Osika, 1987).

There are also distinct iron anomalies in the Vistula River delta and near the Odra River mouth. They are of anthropogenic origin. High iron concentrations (up to 7.70%) in muddy soils of the Szczecin Lagoon were reported by Chudecki and Niedźwiecki (1987), explaining their occurrence by the abundance of floatable matter in the sediments.

Surface waters. The majority of surface waters in Poland contain ≤1 mg/dm^3 of iron. Higher concentrations occur in south-western Poland, in the Odra River drainage basin. Among the major rivers, the highest average iron content are recorded in the following: the Kłodnica River (Gliwice Canal)(2.45 mg/dm^3), Mała Panew River (1.78 mg/dm^3), Widawa River (1.31 mg/dm^3), Barycz River (1.84 mg/dm^3), Nysa Łużycka River (1.03 mg/dm^3) and Prosna River (1.16 mg/dm^3) in the Odra drainage basin, as well as the Przemsza and Czarna Przemsza rivers (1.07 mg/dm^3), Brynica River (1.01 mg/dm^3) and Biała Przemsza River (1.04 mg/dm^3) in the Vistula drainage basin. The lowest iron concentrations were found in lake waters (average 0.18 mg/dm^3).

Very high iron concentrations in Upper Silesia are characteristic of the areas of hard coal deposits and mine water discharges (Lis, Pasieczna, 1995a). The assumption that mine waters from dewatering of hard coal mines contribute to the contamination of surface waters has been confirmed by high iron concentrations in the waters of the Gostynia, Pszczynka and upper Vistula rivers.

Hg MERCURY

Soils. The average mercury content in soils of Poland is below 0.05 mg/kg, which is comparable with the average mercury concentration (0.06 mg/kg) in soils of the world (Freedman, 1989). A regional increase in the mercury geochemical background (0.06–0.10 mg/kg) is observed in the area between the Vistula and San rivers, in the Żuławy region and in areas of mercury mineralization in the basement rocks of the Sudetes.

Local anomalies of mercury in the Polish Lowlands (near Szczecin, Gorzów Wielkopolski, Włocławek, Biała Podlaska, Częstochowa, Mielec) are associated with the activity of different industries and fuel combustion processes. A serious danger is posed by the textile industry (which uses mercury as a catalyst in fibre production), as well as chemical, engineering and electrical industries.

Geochemical anomalies of mercury (>0.10 mg/kg) in Lower Silesia occur in the Wałbrzych area of cinnabar and metacinnabar mineralization in coal seams (Huyssen, 1863); Petrascheck, 1933; Kwiecińska, 1967). In Upper Silesia, mercury concentrations of over 0.15 mg/kg were recorded in urban soils of Bytom, Katowice, Chorzów, Siemianowice, Świętochłowice, Ruda Śląska, Zabrze, Myszków, Mrzygłód and Poręba. In general, the amount of mercury in urban soils is two to four times higher than in soils outside urban areas. Emissions from coal burning in power plants are supposed to be the source of mercury in these regions. Estimates of the mercury contamination level in Europe indicate that 69% of the metal in the environment originate from fuel combustion (Szpadt, ed., 1994).

The maximum mercury concentrations (up to 7.55 mg/kg) occur in a small area near Jaworzno. An anomaly is also observed in the Wąwolnica Stream valley, where strongly contaminated soils occur in industrial areas and in the area of a landfill of Organika-Azot chemical company, that has produced plant protection chemicals for over 60 years. After World War II, a mercury electrolysis method was used in the production processes of this company (Proksa, 2008), and the produced plant protection products contained, inter alia, mercury, arsenic and organo-chlorine compounds. Mercury anomalies are also known from the area of Wrocław (6.60 mg/kg), Łódź (5.82 mg/kg), Gdańsk (5.50 mg/kg), Tarnów (3.76 mg/kg) and Legnica (5.13 mg/kg). Unclear is the case with a relatively extensive mercury anomaly in the upper Pilica River drainage basin. A detailed survey of urban soils showed the maximum mercury concentrations of 10.78 mg/kg in Warsaw (Lis, 1992) and 1.38 mg/kg in Cracow (Lis, Pasieczna, 1995c).

Sediments. Most of sediments under study (75%) contain <0.07 mg/kg of mercury. Some enrichment (>0.15 mg/kg) found in sediments has a distinct character of anthropogenic pollution associated with industrial activities, especially hard coal mining and coal burning, soda and chlorine production, metal processing, manufacturing of paints, lamps, batteries, ammunition and fungicides.

The textile industry, which uses mercury as a catalyst for fibre production, is considered the source of pollution. It gives rise to an extensive anomaly in the Łódź agglomeration (which includes Łódź, Pabianice, Zgierz and Poddębice) in the drainage basin of the Bzura and Ner rivers. Frequently, mercury concentrations are in excess of 1 mg/kg and can reach a maximum of 7.75 mg/kg in sediments of the Ner River north of Pabianice. Of the same type are the anomalies in the Bzura River drainage basin near Żyrardów (2.82 mg/kg in sediments of the Pisia Gągolina River), in the Supraśl River (up to 1.69 mg/kg in the Narew River drainage basin near Białystok – textile industry at Fasty) and in in the Bystrzyca River drainage basin (up to 1.77 mg/kg in sediments of the Pilawa River near Dzierżoniów, Lower Silesia). Discharges of sewage from the machine-building and electronic industries are also the sources of mercury-pollution of sediments. Anomalies occurring near Warsaw (at Falenica, up to 6.73 mg/kg) and near Radomsko (up to 5.66 mg/kg) are of this category.

In Upper Silesia, increased mercury contents (>0.15 mg/kg) in sediments are observed in a broad belt from Gliwice in the northwest to Oświęcim in the southeast, in the Stoła River drainage basin near Tarnowskie Góry and Miasteczko Śląskie, as well as in the upper Warta and Biała Przemsza drainage basins. The maximum mercury concentration (10.5 mg/kg) was recorded in sediments of a small pond in the Bytomka River drainage basin. Strongly contaminated sediments were also found in small watercourses near a railway transport base and numerous mine dumps at Koszutka (Katowice), near Jaworzno, close to chemical plants in Oświęcim and Murcki. Sediments of major rivers and streams are not distinct with respect to the mercury content, except for those of the Bytomka River with the average concentration reaching almost l mg/kg.

A relatively uniform distribution in sediments of various water reservoirs in Upper Silesia indicates, that mercury originates mostly from dust fallout and gas emissions related to coal combustion, in contrast to the sources of other elements whose elevated concentrations are associated predominantly with discharges of mine waters (Cd, Pb, Zn from Pb-Zn mines and B, K, Li, Na from hard coal mines).

Local mercury anomalies can be related to the chemical industry (Oświęcim, Jaworzno). An anomaly at Murcki requires additional studies to explain its origin. A portion of mercury is discharged to the Odra and Vistula rivers. Alluvial sediments of the Vistula near Cracow locally contain up to 2.15 mg/kg of mercury.

In Lower Silesia, apart from the above-mentioned anomaly in the Dzierżoniów area near Świdnica, another anomaly was detected in the Wałbrzych region (with the maximum values of 1.72 mg/kg near Sobięcin and 1.38 mg/kg near Boguszów). This anomaly can be of both anthropogenic (coal burning, mine waters) and natural origin, as the occurrences of cinnabar mineralization are known to occur in barite veins of coal seams in these areas (Petrascheck, 1933; Kwiecińska, 1961). Enrichments in mercury (0.97–0.63 mg/kg) have also been found in sediments of the Bystrzyca Dusznicka River in Polanica near Kłodzko.

A closer study is necessary on the anomaly in the Barycz River drainage basin, in sediments of the Krzycki Rów Stream (up to 2.38 mg/kg) and the Kanał Polski Stream (up to 9.07 mg/kg). The anomaly occupies an area on the right bank of the Odra River, to the north and east of the Głogów copper smelter. A high mercury content (up to 3.58 mg/kg) was recorded in the Odra drainage basin in the immediate vicinity of the Legnica copper smelter. Post-mining waste can be the source of this anomaly. A zone of copper ore containing up to a few hundered mg/kg of mercury was identified in the Lubin and Polkowice mining areas and in the Rudna mine (Banaś et al, 1980). The zone occupies an area of approximately 10 km^2.

Among sediments of other major rivers of Poland, sediments of the Odra River show distinct enrichment in mercury, especially between Wrocław and the confluence with the Warta River. There are eight sites of elevated mercury concentrations exceeding 1 mg/kg (up to 2.49 mg/kg).

K POTASSIUM

Surface waters. The average potassium content (expressed as the median value) is 5 mg/dm^3, but the concentrations are highly variable in the waters of various regions of Poland and dependent on the type and size of water reservoirs. Variability of the potassium content, associated with the type of reservoir, points to a clear relation with the surface runoff, leading to enrichment of small streams with this element. In the case of small stagnant-water reservoirs, enrichment as a result of evaporation may be an additional factor. A smaller amount of potassium in river waters and major streams may be due to its ability to be sorbed (mainly in clay minerals) and transported in the form of solid phase.

Elevated potassium concentrations in the Vistula and Odra rivers (especially in the upper river reaches) are the result of discharges of mine waters from the Upper Silesian and Lower Silesian coal basins.

High potassium concentrations dominate mainly in western and south-western Poland, especially in the areas with heavy artificial fertilization with potassium fertilizers (Sudetic Foreland, Wrocław Lowland and Wielkopolska). A high potassium concentration in the Inowrocław region may also be the result of discharges of mine waters from rock salt mines. River waters in the coastal area are enriched with potassium due to the influence of marine waters of the Baltic Sea.

In Upper Silesia, hard coal mining along with brine discharges to the rivers is the main factor controlling the potassium concentration in surface waters. The potassium content in Palaeozoic aquifers of this region is usually in excess of 350 mg/dm^3 (Płochniewski, Bidzińska, 1970). Potassium concentration in brines may reach 15,500 mg/dm^3. In the light of the presented data, an assumption can be made that only a small fraction of potassium contained in surface waters may originate from agricultural and industrial pollution, whereas the main source of potassium is related to brines. The most potassium-polluted rivers are: Gostynia, Mleczna (in the Vistula drainage basin) and Vistula, as well as Bierawka, Bytomka, Kłodnica, Rokitnica and Ruda (in the Odra drainage basin). Small watercourses and ponds are usually free of such contamination.

Li LITHIUM

Surface waters. The geochemical background of lithium has not been determined in Poland because of too low sensitivity of the analytical method applied (0.02 mg/dm^3). The lithium concentration was below the detection limit in 96% of the analysed samples.

Lithium anomalies (>0.03 mg/dm^3) are of anthropogenic origin. The most extensive anomaly (> 0.04 mg/dm^3) is observed in Upper Silesia, where the maximum lithium contents in some waters are 2.78 mg/dm^3. Prevoius studies (Lis, Pasieczna, 1995a) showed that lithium originates from discharges of mine waters from coal mines. The most lithium-rich waters are those in the Bierawka River (up to 0.63 mg/dm^3), Bytomka River (up to 0.15 mg/dm^3), Kłodnica River (up to 0.24 mg/dm^3) and Rokitnica River (up to 1.05 mg/dm^3) in the Odra drainage basin, as well as the Bobrek and Gostynia rivers (up to 0.67 mg/dm^3) in the Vistula drainage basin. Lower lithium concentrations are observed in the Mikołów, Sosnowiec and Jaworzno regions where no saline waters are disposed of from coal mining.

In Lower Silesia, the effect of coal mining clearly appears in Wałbrzych and in the vicinity of Nowa Ruda. Lithium pollution from the Wałbrzych coal deposits affect the Pełcznica River waters (up to 0.19 mg/dm^3), and then the Strzegomka River waters (up to 0.10 mg/dm^3). The Ścinawka River (left-side tributary of the Nysa Kłodzka River) in the Nowa

Ruda area is also highly polluted by lithium (up to 0.19 mg/dm^3). Pollution of surface waters by sources related to copper mining is of little importance. There is only a small anomaly, located near Polkowice, detected in small water reservoirs (up to 0.32 mg/dm^3).

As the result of mine water discharges in the Upper Silesian Coal Basin, river waters of the Vistula and Odra rivers are especially enriched in lithium, which is observed mainly in the upper courses of the rivers. In the Cracow area, the Vistula River water contains 0.14 mg/dm^3 of lithium.

Burning of hard coal in power-generating plants leads to the increase in lithium concentration in surface waters in their immediate vicinities. The lithium content in small watercourses flowing near the plants is up to 0.92 mg/dm^3 in Połaniec and up to 0.31 mg/dm^3 near Kozienice. Another source of lithium is gypsum rocks and related deposits of native sulphur. A small anomaly (0.09 mg/dm^3) occurs in the Iwisa Stream flowing close to a gypsum open mine at Niwnice (near Lwówek Śląski) in Lower Silesia. Lithium-related pollution is observed in the Trześniówka Stream (up to 0.50 mg/dm^3) that receives water from the Grzybów sulphur mine and processing plant. Small watercourses flowing near the former sulphur mine at Piaseczno are also polluted by lithium.

There are some streams in the Carpathian Foreland with increased lithium concentrations that are related to the extraction of natural gas and discharge of formation waters. A similar situation is observed in the area of rock salt mining near Inowrocław.

Increased lithium concentrations in the Wieprz-Krzna Canal reflect the effect of mine waters discharged from the Lublin Coal Basin.

In northern Poland, saline waters of the Baltic Sea can affect the lithium content level in the Szczecin Lagoon and Żuławy regions.

Mg MAGNESIUM

Soils. Different magnesium concentrations in soils of Poland reflect the chemical variability of basement rocks. In the northern geochemical province, the magnesium content ranges from <0.01 to 0.12%. Increased concentrations are observed in the soils developed on glacial deposits of the youngest glaciation (0.10–0.20%) in NE Poland. In southern Poland, the concentrations are typically >0.12%, reaching a level of >0.30% in some areas.

In the Sudetes, high concentrations are related to magnesium-rich basement rocks occurring in the eastern metamorphic aureole of the granitic Karkonosze Massif and Kaczawa Mts. (Teisseyre, 1963, 1973; Narębski, 1964). Magnesium enrichment in soils is also associated with ultrabasic and basic rocks in the surroundings of the Sowie Góry gneiss block (Dziedzic, 1989; Gunia, 1992) and near Złoty Stok (Kowalski, 1966; A. Muszer, 1995).

In Upper Silesia, high magnesium concentrations occur in the soils developed on carbonates (0.80–1.60%). An anthropogenic factor is also responsible for increased magnesium contents in soils of urban areas of the Upper Silesian agglomeration. Magnesium concentrations in urban soils (lawns, parks, allotment gardens, fallow lands) are twice the concentration in cultivated soils. It is likely that the fallout of industrial dust originated in the process of coal combustion is an important source of magnesium in the urban soils. Dust fallout in the Katowice industrial district supplies approximately 9.4 kg Mg/ha/year (Lorek, 1993). The amount of magnesium in soils is dependent on land use. The average magnesium content in agricultural soils is 0.07%. Especially low concentrations (average 0.02%) are observed in forest soils.

Sediments. The regional variability of magnesium in sediments is similar to that observed in soils, and is mainly dependent on the geological structure. The geochemical background is between <0.01% and 0.50%. Sediments in the Carpathians, part of Upper Silesia and some areas in the Sudetes are remarkably enriched with magnesium. The magnesium enrichment in all these regions is due to the presence of magnesium-rich rocks subjected to weathering.

Washing out of loess is the reason for the abundance of magnesium in sediments in both the Sandomierz Upland and the Lublin Upland. The source of detrital material could be the weathering of mafic massifs. Sediments in the Zemborzycki Zalew reservoir (on the Bystrzyca Lubelska River) may be the case. The total magnesium concentration in its waters ranges between 0.30 and 2.11% (Misztal, Smal, 1980).

Surface waters. The regional variability in the distribution of magnesium in surface waters differs from that observed in soils and sediments. The average magnesium concentration in surface waters is 11.6 mg/dm^3.

Over large areas, increased concentrations (>20 mg/dm^3) occur in Wielkopolska and the Sudetic Foreland that are characterised by a high level of agriculture. It is likely that magnesium has originated from many years' application of agrotechnical treatments (liming of soils, use of magnesium fertilizers). Mg-rich surface waters are also known from the Kujawy region and NE Poland.

Magnesium concentrations higher than 50 mg/dm^3 occur in Lower Silesia in drainage basins of the Kaczawa, Bystrzyca and Ślęża rivers that drain the area composed largely of magnesium-rich basic rocks.

Discharges of mine waters from hard coal mines are the factor contributing to the occurrence of anomalous magnesium concentrations (> 50 mg/dm^3) in surface waters of Upper Silesia. Groundwater of that region contains 300–1,000 mg/dm^3 of magnesium, although some Carboniferous brines can contain as much as approximately 4,000 mg/dm^3 (Płochniewski, Ważny, 1971). Impact of mine water discharges is clearly visible in surface waters of the Vistula and Odra rives, especially in their upper courses.

The Baltic Sea coast from Szczecin to the Vistula Lagoon is the area where increased magnesium concentrations (often more than 30 mg/dm^3) in river waters demonstrate the influence of sea waters.

Mn MANGANESE

Soils. Manganese concentrations in the northern geochemical province of Poland do not exceed 350 mg/kg. Some point anomalies observed in the Polish Lowlands (near Kępno, Siedlce and Kielce) require additional verification. A similar natural content (320 mg/kg of manganese) in soils of central and northern Poland is reported by Gworek (1985b) and Czarnowska and Gworek (1987), with the most frequent values of about 370 mg/kg (Czarnowska, 1989). Studies by Czarnowska et al. (1992) prove that the manganese concentration in soils is clearly dependent on the chemical composition of parent rocks and it does not show any correlation with elements (such as zinc, copper and lead) accumulated as a result of anthropogenic factors.

Greater manganese concentrations (>350 mg/kg) are common in the southern geochemical province (in the Carpathians, the Sudetes and Upper Silesia). In the Sudetes, manganese-rich soils are related to the occurrence of basic magmatic rocks abundant in manganese and iron (Kaczawa Mts., eastern aureole of the Karkonosze Massif, Nowa Ruda, Kłodzko and Złoty Stok regions).

Increased manganese concentrations (>500 mg/kg) characterise some urban soils of Upper Silesia between Strzebnica, Ruda Śląska and Będzin. Local studies focusing on manganese concentration in the topsoil layer were conducted between 1977 and 1988 by Lorek (1993) in the immediate vicinity of the Katowice Steel Works and the zinc smelter at Miasteczko Śląskie, indicating the concentrations ranging between 10 and 360 mg/kg.

Enrichment in manganese of soils in the Carpathians and the Bieszczady Mts. is mainly due to its occurrence in the basement rocks (Maciaszek, 1983). The same author found that the manganese concentration in the soils that developed on the Flysch Carpathian shales could be up to 2,360 mg/kg. Manganese minerals such as rhodochrosite, pyrolusite and psilomelane were also observed in the flysch deposits (Gucwa, Pelczar, 1986).

Low concentrations (average 71 mg/kg) of manganese and many other elements are a characteristic feature of forest soils. However, there is a clear enrichment in manganese of cultivated clayey soils (average 303 mg/kg) in contrast to sandy soils (with the average content of 182 mg/kg).

Sediments. Variability of manganese concentration in sediments is closely related to the type of water reservoir. Manganese concentrations in sediments of some major rivers are twice as high as in sediments of small watercourses (average 273 mg/kg) and small reservoirs (average 170 mg/kg). The low manganese concentrations are typically observed in sediments of coastal lakes (average 75 mg/kg) and fish ponds (average 71 mg/kg). Noteworthy is the fact of significant accumulation of manganese in large water reservoirs. The Szczecin Lagoon is such the case, with the manganese concentrations ranging from 100 to 2,300 mg/kg as reported by Chudecki and Niedźwiecki (1987). The data indicate that surface runoff is of minor importance for manganese concentrations as compared with point sources. Accumulation of manganese in sediments of major rivers is enhanced by its properties. Soluble manganese compounds in aquatic environment are subject to quick precipitation in the form of colloidal suspension. Thus, manganese is transported to distant places as colloidal suspension or hydrated oxides, which can accumulate far away from the source area.

In the cartographic image of the manganese distribution, there are distinct anomalies in drainage basins of the upper courses of both the Vistula and Odra rivers (>1500 mg/kg, and locally > 4,000 mg/kg), and a number of point anomalies that need to be closely studied.

Surface waters. Over 50% of the analysed waters contain >100 µg/dm^3 of manganese. The low concentrations (average 45 µg/dm^3) were measured in lake waters. Low manganese contents also occur in the Carpathians, Sudetes, Nida Trough and Lublin Upland in southern Poland, and in most areas of the Masurian and Pomeranian lake districts. Low manganese concentrations observed in surface waters of the Lublin Upland are a long-term phenomenon, as proved by the Kabata-Pendias and Bolibrzuch studies (1979) conducted on the waters of the Bystrzyca River drainage basin near Nałęczów.

Discharges of mine waters in the Lublin Coal Basin result in increased manganese concentrations in the Wieprz-Krzna Canal (up to 1,600 µg/dm^3). It is proved by the study of Janiec (1993) who found manganese in the canal waters at a concentration of 2,700–3,300 µg/dm^3, which imposes a negative impact on the waters in the Łęczna-Włodawa Lake District, also due to enrichment in other harmful components. Surface waters of the Sudetic Foreland, Carpathian Foothills, Wielkopolska and Upper Silesia are also rich in manganese (often >300 µg/dm^3). Abundance of manganese in surface waters of the Carpathian Foothills is consistent with high Mn concentrations in groundwater (500–2,500 µg/dm^3; Karwan, 1983).

In Upper Silesia, manganese-rich waters (>300 µg/dm^3) were found in areas of hard coal mining, especially near the sites of mine water discharges. Similar concentrations (average 248 µg/dm^3) were reported by Vesely (1991) from the Elbe River waters, in a brown coal mining area.

Na SODIUM

Surface waters. Average sodium concentrations in surface waters range between < l and 50 mg/dm^3. In Upper Silesia, Kujawy and some stretches of the Vistula and Odra rivers, the values are >100 mg/dm^3. The maximum concentrations (up to 5,723 mg/dm^3) are observed mainly in mining areas of hard coal and rock salt.

The upper courses of both the Vistula and Odra rivers contain waters rich in sodium and chlorides. Sodium-related pollution migrates down the river due to excellent solubility of chlorides. This can be evidenced by the average rate of water pollution in the Vistula River in a cross-profile of Cracow, which was 785 mg/dm^3 in 1993 (Cydzik ed., 1994).

Approximately 2.9 million tons of salt (equivalent to NaCl) were disposed to the surface water system in Upper Silesia in the period 1991–1992 (Przeniosło ed., 1994). This is due to exploitation of deeper and deeper coal seams, because the rate of mineralization of Carboniferous formation waters increases with depth, ranging from 1 g/dm^3 to 150 g/dm^3. The waters of increased mineralization (> 5 g/dm^3) are of chloride type (Derdzińska, Pałys, 1970). Mine waters pumped out from deeper formations predominantly contain much sodium and potassium chlorides. Mine waters occurring at shallow depths are polluted mainly by sulphates (Szymańska, 1990).

Mine waters are the major factor affecting mineralization of the Vistula River waters. About 50% of all mine waters from the Silesian mines are discharged to this river. Studies conducted by Gajowiec and Różkowski (1988) revealed that the Vistula waters at Goczałkowice (upstream of the discharge site of mine waters) show very low mineralization of approximately 0.3 g/dm^3. However, in a cross-profile of Bieruń, the mineralization rate rises up to 3.5 g/dm^3, and the waters are of Na-Cl type.

In the Vistula drainage basin, the most sodium-polluted rivers are Gostynia (average 385 mg/dm^3) and its tributary Mleczna (average 325 mg/dm^3). In the Odra basin, the most polluted rivers are Bierawka (average 517 mg/dm^3), Bytomka (average 472 mg/dm^3), Kłodnica (average 564 mg/dm^3) and Rokitnica (average 302 mg/dm^3).

The effect of coal mining in the Wałbrzych and Nowa Ruda Coal Basin was lower. However, it is clearly visible, like the effect of mine water discharges in the Legnica-Głogów Copper District.

In the Polish Lowlands, anomalous sodium concentrations in surface waters are observed in areas of rock salt mining where borehole mining methods are used. In the 1960s, iron ore mines were also active in this region (near Łęczyca). The most polluted surface waters of the region occur in the upper courses of the Bzura and Noteć rivers. Salt-polluted waters from the Noteć River are discharged through the Bydgoszcz Canal to the Vistula River.

The effect of sea waters is marked by increased sodium concentrations in the waters of Pomerania and the Vistula River delta. Enrichment of waters in sodium also occur in areas of great agglomerations (Łódź, Warsaw and Wrocław).

Ni NICKEL

Soils. The average nickel concentration in most soils is below 7 mg/kg. For arable soils of Poland, the concentration is determined at 7.4 mg/kg (Dudka, 1993). Slightly higher nickel concentrations (10–20 mg/kg) are observed in the soils developed on glacial deposits of the youngest glaciation in NE Poland. The average nickel concentration in the soils developed on the youngest tills is 14 mg/kg, and in the soils developed on older glacial deposits – 12 mg/kg (Gworek, 1985).

Nickel concentrations in excess of 7 mg/kg occur in southern Poland (in the Sudetes and the Carpathians) and in alluvial soils of the Vistula River delta. In the Sudetes and the Carpathians, nickel concentrations >20 mg/kg are observed in the soils developed on rocks rich in this element (igneous and metamorphic basic rocks and some flysch rocks).

Ciemniewska (1970) provided a case study of nickel concentrations in the soils covering gabbroes and amphibolites of the Ślęża Massif. The nickel content in that area is 200 to 6,000 mg/kg. Sudetic serpentinites contain from 20 to 4,000 mg/kg of nickel (Szumlas, 1963). In the Szklary serpentinite massif, there is a small nickel deposit of weathering type with the nickel concentration of 0.5–1% (Spangenberg, Miller, 1949; Niśkiewicz, 1963).

A content of >20 mg/kg is a representative value for some soils of the Lublin Upland, that developed on Cretaceous sedimentary rocks and younger loess sediments of the Lublin region and Sandomierz Lowland. Elevated nickel contents were also reported by Sapek and Skłodowski (1976) from rendzina soils (average 21 mg/kg).

Enrichment in nickel is also observed in alluvial soils of the Vistula valley between Cracow and Sandomierz. Locally, the values are in excess of 40 mg/kg, and nickel likely originates from industrial sewage, mainly from iron smelters in Cracow, Stalowa Wola and Mielec.

Sediments. The nickel distribution pattern in sediments of Poland is similar to that observed in soils. Based on several years' monitoring of sediments, a conclusion can be drawn that nickel concentrations in unpolluted areas remain stable at the level of <10 mg/kg (Bojakowska, Sokołowska, 1994). Increased nickel concentrations (>20 mg/kg) are observed in Lower Silesia and the Carpathians. They result from the occurrence of nickel rich rocks at the surface (basic magmatic rocks in Lower Silesia and flysch shales in the Carpathians).

A number of nickel anomalies that occur in many areas of the country developed as a result of economic activity. The most hazardous is the metallurgy industry. Investigations performed on lacustrine sediments of Norway indicate that elevated concentrations of nickel occur only in areas situated near smelter plants (Rogenurd, Field, 1993).

In Upper Silesia, anomalous nickel concentrations (>30 mg/kg) are associated mainly with discharges of industrial sewage from the metallurgy industry. Of anthropogenic origin are also the distinct nickel anomalies observed in Wielkopolska region (between Głogów and Leszno, and in drainage basins of the upper Obra and upper Prosna rivers) and in the Częstochowa, Bydgoszcz, Radom, Lublin, Warsaw and Włocławek areas. They require systematic studies to define the sources of contamination.

Surface waters. The nickel concentrations in surface waters of Poland are commonly below 10 μg/dm^3. Due to its detection limits of 8 μg/dm^3, it is impossible to define precisely its geochemical background. Unpolluted rivers usually contain 1–5 μg/dm^3 of nickel, however, its concentrations in many rivers of Western Europe is reported to be even as high as 75 μg/dm^3 (Kabata-Pendias, Pendias, 1993).

There are some regions of Poland (Wieprz-Krzna Canal, Krosno region, area between Szczecinek and Chojnice, Brodnica, lower Biebrza River region), where the nickel concentration can locally be as high as 100 μg/dm^3. These anomalies as well as another very strong anomaly near Żyrardów in the Masovia region, where the nickel concentration is up to 1,326 μg/dm^3, require a closer look.

P PHOSPHORUS

Soils. The average phosphorus content in soils of Poland is moderate and amounts to 0.033%. Increased phosphorus concentrations (>0.050%) are observed in the Sudetes and their foreland, in Pomerania, Żuławy, and in north-eastern Poland. Some alluvial and peaty soils contain >0.100% of phosphorus. The phosphorus content is highly dependent on the origin of soil. Acid cambisols appear to be the poorest with respect to phosphorus content while the alluvial soils are very rich in phosphorus (Andruszczak, Czuba, 1984).

In terms of land use, forest soils are the poorest with respect to phosphorus concentration (0.018%). Some earlier studies revealed that forest soils of different regions of Poland contain 0.003 to 0.055% of phosphorus (Pokojska, 1979). The average phosphorus concentration increases to 0.038% in cultivated soils and to 0.040% in grassland soils. Sandy soils generally contain smaller amounts of phosphorus than clayey soils (Table 3).

Sediments. In sediments, phosphorus is genetically related to erosion of basement rocks, application of phosphorus fertilizers and discharge of industrial and municipal sewage. There is a regional variability in the phosphorus content in sediments of Poland, but the source of phosphorus-related pollution is difficult to define.

Phosphorus concentration in sediments is strongly dependent on physical and chemical conditions existing at the interface of solid and liquid phases, but primarily on the pH of the environment and abundance of components with high sorption ability. The presence of sorbents and favourable conditions cause phosphorus to bind quickly. Among the sorbents, iron and manganese hydroxides are the main sediment components that accumulate phosphorus. This is evidenced by a high consistency of both iron and phosphorus distribution patterns in the maps. Sediments containing the greatest amounts of phosphorus (over 1%) usually contain several to 27% of iron and from several hundred to 13,610 mg/kg of manganese.

The effect of point sources on phosphorus-related pollution of sediments is marked by the occurrence of sediments poor in phosphorus in a close proximity to strong anomalies. An example is the Szczecin Lagoon with its sediments containing 0.033% phosphorus (Chudecki, Niedźwiecki, 1987). Alluvial soils around the Police chemical plant contain up to 0.991% of phosphorus.

Sediments in the Silesian-Cracow region are abundant in phosphorus (<0.100% and frequently even >0.200%).

Sediments of of rivers and streams in the Carpathians and northern Poland are the poorest with respect to phosphorus content (<0.100%). Sediments in the Lublin and Kielce regions are also relatively poor in phosphorus. Investigations carried out within this project confirm the results of previous study by Misztal and Smal (1981) who reported phosphorus concentrations in sediments of the Bystrzyca Lubelska River ranging from 0.027 to 0.112%.

In Lower Silesia and central-eastern Poland, the phosphorus contents in sediments vary from 0.100 to 0.200%. Against this background, there are both anomalies (with the maximum of 5.886%) and sediments containing small amounts of phosphorus (<0. 034%).

Surface waters. The average phosphorus concentration is 0.16 mg/dm^3. The lowest values (<0.08 mg/dm^3) were measured in streams flowing in the forested land of the Carpathians, Holy Cross Mts., Roztocze, and Pomeranian and Masurian lake districts. The highest concentrations (>1 mg/dm^3) are found in waters of central Poland (Wielkopolska and Kujawy), Upper Silesia and eastern part of Lower Silesia.

The average phosphorus concentrations in different types of reservoirs are similar (aproximately 0.20 mg/dm^3) except in lake waters where the concentrations are significantly lower (0.09 mg/dm^3). Investigation of phosphorus concentrations in the Vistula River and small watercourses confirms that phosphorus concentrations in major rivers are close to those in small water bodies (Tonderski et al., 1994).

Among the major rivers of the Vistula drainage basin, the Krzna and Bzura rivers are the most abundant in phosphorus (average values 1.10 mg/dm^3 and 1.33 mg/dm^3, respectively) (Table 8). In the Odra drainage basin, the highest phosphorus concentration was reported from the Kłodnica River (average 2.44 m mg/dm^3) (Table 9).

It is very interesting to compare the phosphorus content in different surface water bodies. It appears that the highest concentrations are observed in small streams and stagnant water reservoirs, whereas lakes are characterised by low phosphorus contents (Table 7).

Phosphorus is considered the main biogenic component that exerts a real threat to surface water quality (Giercuszkiewicz-Bajtlik, 1992; Słota, Zieliński, 1993). It is introduced into surface waters due to irrational mineral fertilization consisting in application of too high doses of fertilizers as compared with actual requirement by crops. As assessed by Giercuszkiewicz-Bajtlik (1992), surface runoff of phosphorus from arable land reaches a value of 0.29 kg/ha/yr, whereas the phosphorus flux from urban built-up areas can be as high as 0.90 kg/ha/yr.

The necessity of stopping degradation of surface waters became a popular idea in West Europe some years ago. Accordingly, since January 1, 1992, a regulation has been enforced in Germany providing limitation in fertilization (up to 120 kg/ha of phosphorus), supported by periodic analyses of phosphorus abundance in soils.

The most important source of phosphorus in surface waters is the run-off of fertilizers in cultivated land. Concentration of phosphorus in groundwater under arable land (0.14–0.73 mg/dm^3), even in the case of poor fertilization, is twice as much as its concentration in groundwater of afforested areas (Misztal, Smal, 1991). An especially intense process of phosphorus run-off occurs in light soils. Some authors are of the opinion that enrichment of surface waters with phosphorus is caused in 90–98% by surface runoff (Taylor et al., 1992).

Small phosphorus concentrations in surface waters are natural. On the other hand, the highest contamination of waters in streams and lakes of urban and industrial areas indicates a considerable proportion of point pollution sources associated with discharges of industrial and municipal sewage.

Surface water bodies of Upper Silesia are the exemplary cases of significant participation of pollution originating from point sources (Lis, Pasieczna, 1995a). The phosphorus concentrations broadly range from 0.04 to 45.12 mg/dm^3 in that area. There is also a remarkable regional variability. Phosphorus occurs to be less abundant (<l mg/dm^3) in surface waters from areas of dominant agricultural activities. It seems likely that surface runoff resulting from erosion of rocks and phosphorus fertilization is the most important source of phosphorus in those areas. In urbanized and industrial areas, point sources are another factor contributing to the increase of phosphorus concentrations. As the result, phosphorus concentrations increase to 2–8 mg/dm^3. The maximum average contents of phosphorus were detected in surface waters of the rivers, whose sediments are enriched with this element. These include: Bierawka River (1.46 mg/dm^3), Bobrek River (1.18 mg/dm^3), Bytomka River (2.53 mg/dm^3), Kłodnica River (2.36 mg/dm^3) and Stoła River (4.13 mg/dm^3). Small water bodies (such as streams, ditches and ponds) are usually less abundant in phosphorus, although high concentrations can be found in places.

Pb LEAD

Soils. The amount and forms of lead in soils are controlled by their acidity and the content of components of proper sorption capacity. At the pH> 6.5, lead is immobilized by precipitation in the form of carbonates and phosphates. In acidic soils, it is predominantly bonded in organic compounds, some of which are soluble and are subject to migration (Kabata-Pendias, Pendias, 1999).

Lead is a toxic element to plants and animals. Plant diseases are a result of both the extraction of lead from the soil and the absorption of dust settling on the leaves. In areas of dust emissions from zinc smelters, plants can accumulate several to 300 mg/kg of lead in the tissues (Kucharski, Marchwińska, 1990; Sawicka-Kapusta et al., 1990).

The content of lead in uncontaminated soils is controlled mainly by its presence in the parent rocks, and it varies within quite wide limits. The geometric mean of lead content in sandy soils of the Frisian Islands (Germany) was determined at 7.9 mg/kg (Severson et al., 1992). In mineral soils of Scotland, the average is 13 mg/kg of lead. In organic soils, it is 30 mg/kg (Reaves, Berrow, 1984). The geochemical background of lead concentration in soils of Slovakia is estimated at 20 mg/kg (Čurlik, Šefčik, 1999), in Lithuania – at 15 mg/kg (Kadūnas et al., 1999), and in Saxony – at 53 mg/kg (Rank et al., 1999).

On the one hand, the geochemical pattern of lead distribution is constrained by the geological structure; on the other hand, it is controlled by anthropogenic factors. In soils of central, north-eastern and eastern Poland, the lead concentration exceeds the value of 13 mg/kg only locally. Slightly higher values (up to 25 mg/kg) are observed in north-western and western Poland as well as in the Bieszczady Mts. and its foothill. Still higher lead concentrations are found in soils of some areas in the Sudetes and Holy Cross Mts.

Anomalous lead concentrations (locally >100 mg/kg) are observed in the Silesian-Cracow region. Two factors affect the lead concentrations in the Upper Silesian soils: geological structure related to the occurrence of Ore-Bearing Dolomites, and anthropogenic activity due to Zn-Pb ore mining, processing and metallurgy. A wide belt extending from Tarnowskie Góry and Ruda Śląska to Chrzanów and Olkusz is the area of anomalous lead concentrations. The strongest anomalies (>200 mg/kg) of anthropogenic origin occur in the regions of concentrated Zn-Pb ore mining, processing and metallurgy: Bytom-Piekary Śląskie-Tarnowskie Góry, Chrzanów-Trzebinia and Olkusz-Bolesław-Sławków. The most contaminated soils occur in the regions of historical and contemporary iron and non-ferrous metallurgy industry of Bytom, Świętochłowice, Katowice, Szopienice and Miasteczko Śląskie.

Combined effects of polymetallic ore mining and copper metallurgy are the main anthropogenic factors controlling the development of lead anomalies in Lower Silesia, because the copper-bearing ores mined in the past in the North-Sudetic Trough and in those currently extracted in the Fore-Sudetic Monocline contain galena (Lis, Sylwestrzak, 1986). The highest lead concentrations were measured in the immediate vicinity of the Legnica smelter (up to 970 mg/kg) and the Głogów smelter (up to 1,963 mg/kg). A high concentration (554 mg/kg of lead) was also detected near a sludge pond of an old inactive copper mine at Leszczyna (near Złotoryja). In the Eastern Sudetes, the highest lead concentrations in soils were measured in the vicinity of an old inactive galena mine at Lutynia near Lądek Zdrój (Petrascheck, 1933) – up to 955 mg/kg. Galena was also found in the Złoty Stok arsenic ore deposit (Traube, 1888). The lead concentrations in soils of this region reach a level of 460 mg/kg.

In the Holy Cross Mts., there is a strong lead anomaly near Kielce. This is a combined geological and anthropogenic anomaly and its origin is related to periodic exploitation (from the 14th century to the beginning of the 19th century) of galena from numerous small deposits of vein types, occurring in the Devonian limestones (Rubinowski, 1971). The maximum lead concentration (3,872 mg/kg) was recorded in the vicinity of an inactive copper and lead metallurgical plant at Białogon. A strong lead anomaly (up to 1,360 mg/kg) was also detected in this area by a geochemical study conducted by Lenartowicz (1994).

Anthropogenic factors also affect the lead content in soils of the Polish Lowlands, where the geochemical background values are generally low. Local enrichments in lead are associated mainly with urban agglomerations. Detailed studies of urban soils were conducted in Warsaw (Czarnowska et al., 1983; Czerwiński, Pracz, 1990; Czarnowska, Gworek, 1991; Lis, 1992), Łódź (Czarnowska, Walczak 1988), Bydgoszcz, Gdańsk, Poznań, Szczecin and other smaller towns (Pasieczna, 2003). Motor transport is the dominant factor that determines the pollution level of urban soils by lead. Some point sources (industrial plants) can also contribute to the occurrence of elevated lead concentrations in urban soils. Lead concentrations reaching 850 mg/kg were found in soils near Oława, where zinc white and minium is being produced (Roszyk, Strojek, 1983).

Lead content values are dependent on land use. The average lead concentration in sandy soils of arable land is 11 mg/kg; in clayey soils, it is 15 mg/kg. Grassland soils contain 15 mg/kg, forest sandy soils 12 mg/kg and forest clayey soils 26 mg/kg of lead. The maximum concentrations (average 41 mg/kg) are found in urban soils of lawns and city parks.

In Upper Silesia, the highest lead concentrations are attributed to city parks (average 153 mg/kg), lawns (average 111 mg/kg) and cultivated arable land of urban agglomerations (average 110 mg/kg). Cultivated soils of Upper Silesia show lead concentrations three times the lead concentrations in cultivated soils of other regions of Poland (39 and 13 mg/kg, respectively). Previous studies of point pollution of soils in allotment gardens in the Katowice Voivodeship confirmed local strong contamination by lead of up to 4959 mg/kg (Gulbicka, 1993).

Among all cultivated soil samples analysed from the area of Poland (excluding Upper Silesia), only 0.43% contain 100–1000 mg/kg of lead. In Upper Silesia, 15.21% of analysed samples of cultivated soils contain between 100 and 1,000 mg/kg of lead; and 0.78% contains more than 1,000 mg/kg of lead. Such high lead concentrations in Upper Silesia are mostly of anthropogenic origin, related to mining and metallurgical activities. In areas outside outcrops of ore-bearing formations, only the upper, topsoil layer is lead-polluted, and the lead concentration rapidly decreases with depth (Lis, Pasieczna, 1995b).

Sediments. The regional variability of lead concentrations in sediments is similar to that observed in soils. Areas of increased lead concentrations (>50 mg/kg) include Upper Silesia, the Opole region and Silesian-Cracow region.

In Upper Silesia, the areal range of enrichments of lead (>200 mg/kg) in sediments overlaps the area of high lead content in soils. The highest lead contents (>1,600 mg/kg) occur near active and historical zinc smelters. The strongest anomalies are found near Miasteczko Śląskie and Bukowno. The maximum lead concentration (43,878 mg/kg) was detected in sediments of a stagnant-water ditch situated in the north-eastern part of the Miasteczko Śląskie smelter. The sediment was also reported to contain a considerable amount of zinc (43,963 mg/kg), cadmium (508 mg/kg), arsenic (229 mg/kg), copper (216 mg/kg) and silver (10 mg/kg). Lead concentrations exceeding 200 mg/kg were noted in sediments of the following rivers: Baba, Biała Przemsza, Bobrek, Brynica, Chechło, Kozi Bród, Sztoła and Trzebyczka in the Vistula River drainage basin, as well as in the Bytomka, Rokitnica, Stoła and Warta rivers in the Odra River drainage basin. Particularly high concentrations were recorded in sediments of the Chechło River (163–8,795 mg/kg; average 2,042 mg/kg).

The strongest anomalies in Lower Silesia are of anthropogenic origin; they occur in the Legnica-Głogów Copper District. They are a consequence of mining activity; however, both ore processing and copper metallurgy seem to be the most important factors. The maximum lead concentration (11,310 mg/kg) developed due to the activity of the Legnica copper smelter and was detected in a small unnamed tributary of the Kaczawa River near Legnica. A sediment sample collected from a ditch situated near the "Żelazny Most" sludge pond contained 1,214 mg/kg of lead. In sediments of the Rzechowska Struga Stream, draining the Głogów smelter area, the concentration was 1,140 mg/kg.

An extensive lead anomaly (>100 mg/kg, with a maximum of 13,545 mg/kg) occurs in the Bystrzyca River drainage basin near Dzierżoniów, Świebodzice, Boguszów and Świdnica, in sediments of a small tributary of the Pilawa River in Świdnica. Its origin seems to be natural in part only. The origin of a very strong anomaly (up to 7,996 mg/kg) in sediments of the Trująca (Złoty Jar) Stream near Złoty Stok needs a more detailed study. As resulted from a panning prospection, considerable amounts (>500 g/m^3) of lead minerals (including galena, lead oxides and metallic lead) were discovered in that area (Jęczmyk, Markowski, 1990). The presence of lead oxides (litharge) and metallic lead is easy to explain since lead was imported mostly from the Silesian deposits to be used in metallurgical processes of arsenic ores for gold recovery (Dziekoński, 1972). High lead concentrations were also detected in sediments of the Bystrzyca Dusznicka River at Polanica (1,759 and 1,117 mg/kg).

In the Holy Cross Mts., a distinct lead anomaly is associated with both the occurrence of lead-bearing ores and discharges of industrial wastewater. A detailed study by Lenartowicz (1994) revealed that the lead concentration in sediments of the Sufraganiec Stream (a tributary of the Bobrza River) is 1,740 mg/kg.

Anthropogenic lead anomalies in sediments of the Polish Lowlands occur in urban agglomerations, particularly those with intense industrial development (Warsaw, Łódź, Płock, Białystok, Gdańsk and Szczecin). A several-point anomaly observed in the Liwa River drainage basin, north of Iława, should be investigated and explained. One of the samples collected from alluvial sediments of a small watercourse discharging into Lake Jeziorak contained 40,546 mg/kg of lead.

Surface waters. Because of too low sensitivity of the applied lead determination method, geochemical background values for lead have not been determined in surface waters. The maximum lead concentration (1.87 mg/ dm^3) was recorded in the Dąbrówka Canal (left-side tributary of the Biała River in the Przemsza drainage basin) in Upper Silesia, which receives wastewater from the "Bolesław" and "Olkusz" mine areas (Wójcik et al., 1990). The sample also contained 3.181 mg/dm^3 of zinc.

S SULPHUR

Soils. In the moderately humid climate of Poland (with prevailing aerobic over anaerobic conditions and weak evaporation), sulphur is subjected to oxidation to sulphates that can easily migrate into groundwater. Thus, organic compounds of sulphur are the most common forms of sulphur appearance in soils.

The sulphur content in various types of soils worldwide ranges from 0.025 to 0.080% (Siuta, Rejman-Czajkowska, 1980). The average concentrations of sulphur in soils of Poland are much lower (0.005–0.020%) and poorly variable. The smallest concentrations of sulphur (0.007% on the average) are found in forest soils. The maximum concentrations were recorded in peaty soils (0.050%). These data are in agreement with those acquired for organic soils – 0.040% (Laskowski, 1991). According to data presented by Siuta and Rejman-Czajkowska (1980), the sulphur concentration in peaty soils can be as high as 0.350%, and the most common forms of sulphur occurrence are sulphates.

Sulphur rich soils clearly tend to occur towards the south of the country. Sulphur concentrations >0.010% are common in soils of Roztocze and the Holy Cross Mts. margin, as well as over large areas of the Pomeranian Lake District. In the Polish Lowlands, the areas of highly increased sulphur concentrations occur most often in river valleys filled with peats. Two strong regional anomalies are associated with the occurrence of gypsum rocks (in the Nida Trough) and native sulphur deposits (in the Tarnobrzeg region). Smaller, but also distinct anomalies are observed near Kłodzko and Kąty Wrocławskie.

Industrial processes are of minor importance for accumulation of sulphur in soils. Studies on the sulphur occurrence in the immediate vicinity of the Legnica smelter show that the sulphur concentration varies from 0.016 to 0.058% (Andruszczak et al., 1986). Increased sulphur concentrations (up to 0.210%) were found only east of the plant (Drozd et al., 1984), which can be explained by prevailing westerly winds transporting sulphur emissions. Atmospheric sulphur emissions more distinctly affect the soils around the Głogów smelter, where the sulphur concentrations attain a level of 0.393 % (Roszyk, Szerszeń, 1988b). The sulphur concentrations in soils near the Ubocze phosphorus fertilizer plant range between 0.030 and 0.076% (Andruszczak et al., 1984) and do not deviate from figures acquired in other regions of Poland.

Sediments. In most of sediments, the sulphur content is less than 0.100%. This element rarely accumulates at concentrations greater than 0.500%, and the most sulphur-enriched sediments are found in Upper Silesia. Local sulphur contents of >1.000% are almost always associated with a high iron content. These concentrations indicate the presence of sulphide phases that formed in reducing conditions. The smallest concentrations of sulphur (<0.040%) are characteristic of sediments deposited in rivers and streams of the Polish Carpathians and NE Poland.

The maximum sulphur content (8.610%) was detected in sediments of a small pond in the Nida River drainage basin, in the area covered by gypsum rocks.

SO_4 SULPHATES

Surface waters. The waters of Poland are much more contaminated by sulphates (average 58 mg/dm^3) than other European countries: e.g. 15–30 mg/dm^3 in the waters of the Netherlands (Rejniewicz, 1994). Their regional variability is very well pronounced.

Surface waters of Upper Silesia, Sudetic Foreland, Silesian Lowland, part of Wielkopolska, Kujawy and part of Masovia contain >100 mg/dm^3 of sulphates.

High sulphate concentrations in surface waters of Upper Silesia (often >250 mg/dm^3) dominate over the entire coal district area (excluding the Mikołów area) and considerable part of its eastern margin (Pb–Zn ore mining areas). The highest average sulphate concentrations were found in surface waters of the following rivers: Bierawka (381 mg/dm^3), Bytomka (520 mg/dm^3), Gostynia (456 mg/dm^3) and Rokitnica (526 mg/dm^3). The contamination is due to mine water and sewage discharges from other industrial branches. Municipal sewage and leachates from mine dumps rich in sulphides are another source of increased sulphate contents in surface waters (Twardowska et al., 1988; Bojakowska, 1994).

Discharge of mine waters in Lower Silesia, from the Wałbrzych and Nowa Ruda hard coal mines, results in distinct sulphate concentrations in surface waters. Along the entire upper course of the Odra River, the sulphate contents exceed 100 mg/dm^3, and locally even 200 mg/dm^3. The sulphate concentration in the Odra River waters in the period 1991–1992 was twice as much as concluded from the previous study conducted by Kowal and Kowalski (1987). As reported by both authors, analysis of the physical and chemical composition of the Odra River water revealed sulphate concentrations in the range of 70–130 mg/dm^3, which, already at those times, disqualified this water even for cooling and other industrial purposes.

A well-marked sulphate anomaly occurs in surface waters near Police (north of Szczecin); it is likely associated with the industry of phosphorus fertilizers.

Sulphate-rich waters occurring in the Nida Trough are closely related to the occurrence of gypsum in the basement. Native sulphur deposits of the Tarnobrzeg area are manifested by elevated sulphate concentrations (>400 mg/dm^3) in surface waters.

Sulphate contents are variable depending on the type of surface water body. The smallest contents are characteristic of lake waters. It is clearly manifested in the Pomeranian Lake District. Sulphate contents in small watercourses, small stagnant reservoirs and larger streams and rivers are similar, indicating that surface runoff is the main source of sulphates.

SiO_2 SILICA

Surface waters. The average silica content in surface waters of Poland is over a dozen mg/dm^3. It shows a considerable regional variability, ranging between <0.3 and 22.8 mg/dm^3. The lowest silica concentrations are found in waters of the Carpathians and NE Poland.

Especially high silica concentrations (>25 mg/ dm^3) are reported from surface waters in the Lublin Upland. Most likely, basement rocks (gaizes, decalcified opokas) are the main source of silica. They contain considerable amounts of amorphous silica, solubility of which is twenty times greater than the solubility of quartz (Macioszczyk, 1987).

Enrichment in silica (>15 mg/dm^3) is also observed in surface waters of the eastern part of Lower Silesia, Opole region, Cracow-Częstochowa Upland, Nida Trough, and between Rzeszów and Przemyśl.

In the Polish Lowlands, increased silica concentrations occur in some surface waters of Wielkopolska and Masovia, Vistula River delta, as well as of the Szczecin, Lidzbark

Warmiński and Kętrzyn regions. Increased silica concentrations in areas composed of carbonate rocks or loess (Cracow-Częstochowa Upland, Nida Trough and Lublin Upland) suggest that the elevated silica content is related to high pH values of these waters because silica concentrations in strongly alkaline waters can attain several hundred mg/dm^3. It seems likely that the increased pH of surface waters in central Poland and Lower Silesia, in areas of well-developed agriculture and intensive agrotechnical treatments, may also be the reason for a higher solubility of silica. This idea is of hypothetic nature only, as the lack of water acidity measurements makes it impossible to interpret the phenomenon in a univocal way.

Sr STRONTIUM

Soils. The main source of strontium in the surface environment of the Earth is the combustion of coals. Strontium compounds are used to produce glass, fireworks and paint materials, television picture tubes, as well as ferrites in magnets. They can be a source of contamination of soils around industrial plants.

Strontium content in soils depends on its concentration in the parent rocks. In soil profiles, strontium migrates from the surface to deeper layers in acidic and aerobic conditions. Depending on the soil type, considerable variability in strontium concentration can be observed in the topsoil, ranging from 5 to 1000 mg/kg.

In the neighbouring countries, strontium concentrations in the topsoil are as follows: 21–706 mg/kg in Slovakia (Čurlik, Šefčik, 1999) and 4–320 mg/kg in Lithuania (Kadūnas et al., 1999).

The strontium distribution in soils of Poland significantly follows the distribution of calcium. This similarity results from the fact that both elements can replace each other. It causes calcium minerals (such as calcite, aragonite, anhydrite, gypsum and apatite) to be the main carriers of strontium.

Over most of Poland, strontium concentrations are relatively low (<10 mg/kg). Higher concentrations (>30 mg/kg), forming regional anomalies, are observed in the soils developed on limestones in Upper Silesia, Opole region, Lublin Upland and part of the Cracow-Częstochowa Upland, and on gypsum rocks in the Nida Trough. Carbonate rocks are the natural source of strontium as its concentration in these rocks reaches 400–600 mg/kg (Ważny, 1969). High strontium concentrations are also typical of Quaternary ice-dammed lake deposits of the Pyrzyce and Szczecin region.

Increased calcium and strontium contents in soils of the Wielkopolska, Kujawy and Bydgoszcz regions seems to be caused by soil liming.

The Tarnobrzeg strontium anomaly is associated with native sulphur deposits. Co-occurrence of sulphur and strontium in this region (also in the Nida Trough) as well as the presence of numerous accumulations of crystalline celestine indicate that strontium occurs in a sulphate form. Strontium replaces isomorphic calcium in anhydrites and gypsums. Additionally, it forms its own minerals: celestine, and less common strontianite. Their presence in sulphate deposits and Miocene limestones of the Carpathian Foredeep was reported many times (Łaszkiewicz, 1957; Tyniec, 1961; Kowalski et al., 1980; Pilichowska, 1984; Kasprzyk, Osmólski, 1989; Parafiniuk, 1989). Strontium concentrations in gypsum deposits of the Carpathian Foredeep are as high as 2,000 mg/kg. Gypsum deposits of the Nida Trough contain 1,800 mg/kg of strontium (Parafiniuk, 1987). An extensive strontium anomaly in the vicinity of Tarnów needs closer studies. Most likely, it is associated with the activity of chemical plants situated nearby.

Sediments. The areal extent of sediments contaminated by strontium is more or less consistent with the areal distribution of its concentration in soils. Most of sediments contain <1–40 mg/kg of strontium. Enrichments in this element (>70 mg/kg) are observed in sediments of the Nida Trough (in watercources draining gypsum rocks), Tarnobrzeg region (near mining areas of native sulphur deposits) and in the Lublin Upland composed of Cretaceous carbonate-marly rocks and loess deposits. The maximum strontium concentration (7,628 mg/kg) was found in a sludge pond of the Machów sulphur mine. Strontium originates from the sulphur ore enrichment process that leads to sulphur accumulation in waste tailings. For example, the average strontium content in sludge from the Piaseczno sulphur mine is 15,500 mg/kg (Osmólski, 1987).

It seems likely that a distinct strontium anomaly (with a maximum of 3,966 mg/kg of strontium) in sediments near Bolesławiec (Lower Silesia) is related to the activity of the Wizów Chemical Plant that generates phosphogypsum waste.

High stromtium concentrations are observed in sediments of the Bug River and the Wieprz-Krzna Canal. They can originate from different sources such as erosion of Cretaceous marls and limestones, or discharges of mine waters from the Lublin Coal Basin, as well as from sulphur deposits in Ukraine.

In Upper Silesia, mine waters discharged to the Bobrek, Bytomka, Kłodnica and Rokitnica rivers are of essential importance for strontium enrichment in alluvial sediments. As a consequence, they are one of the sources of strontium in sediments of the upper Vistula River and the upper Odra River (Lis, Pasieczna, 1995a).

Increased strontium concentrations in sediments of the Pyrzyce and Szczecin region as well as in the Vistula River delta seem to be related to erosion of ice-dammed lake and alluvial deposits.

Surface waters. There is a very close similarity in the strontium distribution in surface waters, sediments and soils. The lowest strontium concentrations (<150 µg/dm^3*)* are observed in the Pomeranian and Masurian lake districts. Determination of the strontium background in the Biała Białostocka and Biały Dunajec river waters (Małecki, 1991) revealed similar figures of about 150 µg/dm^3.

In other regions of Poland, strontium concentrations in surface waters are higher (350–650 µg/dm^3) and the sources of anomalies are of different origins, among which is erosion of carbonate rocks or calcium-rich soils in the Nida Trough, Lublin Upland and the Szczecin and Żuławy regions. Considerable amounts of strontium are introduced into surface waters by discharging mine waters from hard coal mines in Lower Silesia, Upper Silesia and the Lublin Coal Basin, as well as from native sulphur mines in the Tarnobrzeg region, or rock salt mines in the Inowrocław region. The extreme cases of enrichments refer to mine waters from the Machów sulphur area, where the strontium concentrations reach a level of 35,600 µg/dm^3 (Smuszkiewicz, 1969).

Surface runoff from soils subjected to fertilization with strontium-enriched lime can also be the source of strontium-related pollution (in Wielkopolska and Kujawy).

Ti TITANIUM

Soils. The total content of titanium in soils ranges from 1,000 to 5,000 mg/kg (Gworek, 1990). Its amount and distribution is controlled by the chemistry of parent rocks rather than soil-forming processes (Gworek, 1990).

The structure of titanium-containing heavy minerals (ilmenite, titanomagnetite and rutile) is only insignificantly affected by the applied method of sample extraction using hydrochloric acid. Acid extraction results in the release of only a portion of titanium in the structures of both clay minerals and iron oxides. Accordingly, the content of HCl-extractable titanium in the soils of Poland was found to be very low (average 26 mg/kg).

The titanium content in majority of soils in central and eastern Poland does not exceed 25 mg/kg. Increased concentrations (50–100 mg/kg) are common in the soils developed on the youngest glacial deposits in both the Pomeranian and Masurian lake districts.

In Lower Silesia, distinct titanium anomalies (>100 mg/kg) result from the occurrence of some titanium-rich basement rocks. The Upper Silesian soils, which developed on the Carboniferous clastic formations, exhibit insignificant enrichment in titanium.

Sediments. Weak mobility of titanium in surface environments is the reason why this element appears in sediments at small concentrations (<50 mg/kg).

In Lower Silesian sediments, the titanium concentrations reach locally 5,354 mg/kg. Basement rocks composed of basis magmatic and volcanic rocks, along with some basic metamorphic rocks, are the source of titanium in this region. The maximum titanium concentrations were measured in sediments of the Bystrzyca, Bóbr and Kwisa rivers.

Surface waters. In 90% of surface waters of Poland, the titanium concentrations are below 10 $\mu g/dm^3$. In some areas of the Polish Lowlands, the values vary between 10 and 20 $\mu g/dm^3$, and anomalous concentrations (>20 $\mu g/dm^3$) were reported from Lower and Upper Silesia.

V VANADIUM

Soils. Chemical composition of parent rocks is the major factor affecting vanadium contents in soils. Over most of the country, the vanadium concentrations in soils are below 10 mg/kg. Increased vanadium concentrations (>10–20 mg/kg) are observed in soils of the southern geochemical province, in particular in the Sudetes and the Carpathians, as well as in the soils developed on post-glacial deposits of northern Poland.

Vanadium is the element of considerable susceptibility to concentration in biolithes. Its content in hard coal ash is over 1,000 mg/kg (Kabata-Pendias, Pendias, 1993). Similar enrichment in vanadium can be observed in graphitic shales of the Sudetes (Mańkowska, 1960; Subieta, 1960). The shales are probably the source of vanadium in some soils of this region. Organic matter-rich menilite shales of the Carpathian flysch formations contain up to 1,081 mg/kg of vanadium (Gucwa, Wieser, 1980). It is likely that the increased vanadium concentrations in the Carpathian soils are related to this organic matter.

Vanadium can also accumulate as the result of anthropogenic pollution. Distinct vanadium enrichment in soils (up to 120 mg/kg) was observed in areas exposed to emissions from oil refineries (Biernacka, Liwski, 1986). Similar enrichments occur near metallurgical plants, coal-fired power plants and cement mills.

Sediments. Vanadium concentration in sediments of Poland, like in soils, is dependent on the chemistry of the geological basement. Most of sediments contain low amounts of vanadium, less than 10 mg/kg. Enrichment in vanadium (20–40 mg/kg) is observed in the Carpathians and Lower Silesia.

Surface waters. The water samples subjected to analyses contained <8 μg/dm^3 (detection limit) of vanadium. The analytical method applied in this study is insufficient to determine the geochemical background of vanadium in surface waters.

Y YTTRIUM

Soils. The pattern of yttrium distribution in the northern geochemical province differs from that in the southern one. In the northern geochemical province (Polish Lowlands), local anomalies (>7 mg/kg) are observed against the low geochemical background (<0.5–5 mg/kg) mainly in alluvial soils. A similar increase in yttrium concentration is observed in alluvial soils of the Vistula River delta in Żuławy and in the area covered with deposits of the youngest glaciation in the Masurian Lake District.

Slightly higher yttrium concentrations (5–10 mg/kg) occur in the southern geochemical province in Upper and Lower Silesia, Cracow-Częstochowa Upland, in the Carpathians and their foreland, and in the eastern part of the Lublin Upland. Increased concentrations in these areas are usually related to heavier clayey soils. The maximum yttrium concentration of 62 mg/kg was found at Szklarska Poręba (in the Sudetes), in areas of pegmatites containing yttrium-rich minerals (Websky, 1868).

Surface waters. Most of the water samples (95%) contained <0.5 μg/dm^3 of yttrium. The yttrium concentrations in some surface waters of Lower and Upper Silesia and the Polish Lowlands were >1 μg/dm^3.

Zn ZINC

Soils. Zinc content in soils is related to its concentration in parent rocks and the type of soil. In Germany, the average zinc concentration in soils is 83 mg/kg, in Austria 65 mg/kg, in Scotland 58 mg/kg (Kiekens, 1995). Zinc content values in the soils of Slovakia vary from 3 to 14,925 mg/kg, and the average geometric value is 62 mg/kg (Čurlik, Šefčik, 1999). The soils of Lithuania contain 1–185 mg/kg of zinc (Kadūnas et al., 1999), and in the soils of Norway the average zinc concentration is 40 mg/kg (Reimann et al., 1998).

Zinc is readily absorbed by plants and is involved in many biochemical processes, but both its deficiency and excess leads to tissue damage. In animal organisms, zinc is the element of enzymes involved in the metabolism of proteins, carbohydrates and fats.

Zinc is one of the most commonly used non-ferrous metals. It is predominantly (over 90%) applied in a metallic form and is used for coating of steel and production of cast iron in order to protect against corrosion (for example, in cars and in the construction sector). Dispersion of metallic zinc is insignificant, but zinc compounds can easily migrate. They are used for the production of rubber, plant protection chemicals, fertilizers, pharmaceuticals and cosmetics. Roasting of ore as well as storage of mining and ore processing wastes result in emissions of particulate matter and water pollution. An important source of soil contamination with zinc is also the production of paints, combustion of coal, tire wear, wastewater discharges and leachates from landfills.

Over most of Poland, the zinc concentrations in soils are below 50 mg/kg. Higher average contents (60–125 mg/kg) are observed in Lower Silesia, in the Western Carpathians and in the Polish Lowland (as anomalies of small areal extent mainly in urban areas). The producers of zinc white, e.g. in Oława, where the zinc concentration is 3,690 mg/kg, are important pollution sources (Roszyk, Strojek, 1983). Similar situation is observed at Helenów near Pruszków (cable factory), where the zinc concentration is 1,432 mg/kg (Lis, 1992).

Against this slightly differentiated background, zinc anomalies (>200 mg/kg) in soils of the central part of Upper Silesia are strongly contrasted (Lis, Pasieczna, 1995a). These anomalous zinc contents occur in the area extending from Tarnowskie Góry and Ruda Śląska in the northwest to Chrzanów and Olkusz in the southeast. The maxima of the anomalies (>800 mg/kg) appear in areas of concentrated extraction and processing of metals and metallurgy, including: Bytom, Piekary Śląskie, Świętochłowice, Chorzów, Siemianowice Śląskie, northern parts of the Katowice and Ruda Śląska districts, western part of the Sosnowiec and the area along the border between the Dąbrowa Górnicza–Olkusz and Jaworzno–Chrzanów districts. The highest zinc concentrations also occur in soils near historical and currently active metallurgical centres, such as Bytom, Świętochłowice, Katowice, Szopienice and Miasteczko Śląskie.

In terms of land use in Upper Silesia, the highest zinc concentrations are found in soils of city parks (average 442 mg/kg), urban lawns (average 340 mg/kg) and cultivated areas within urban agglomerations (average 306 mg/kg). As compared with cultivated soils in other areas of Poland, the zinc concentration in Upper Silesian soils under cultivation is three times greater (average concentrations are 34 and 99 mg/kg, respectively).

Zinc related pollution of soils in areas of exploitation and processing of Zn–Pb ores is a serious hazard in other countries, too. As reported by Xiangdong and Thornton (1993), the Zn concentrations in soils of the Shipham area (in the UK) can reach a level of 45,900 mg/kg, with lead occurring in these soils at a concentration of 3,470 mg/kg. Soils near old dumps in West Chiverton contain 14,790 mg/kg of zinc and 37,000 mg/kg of lead (Merrington. Alloway, 1994). The same authors reported that soils in the vicinity of similar dumps at Wemyss contained 3,800 mg/kg of zinc and 19,900 mg/kg of lead.

In Lower Silesia, increased zinc concentrations in soils (>100 mg/kg) are common in the Sudetes (Kaczawa Mts., Wałbrzych, Świdnica and Złoty Stok) and near Legnica and Głogów.

Outside Upper Silesia, only 0.25% of cultivated soils contain 300–600 mg/kg Zn, which is considered a tolerable content. About 0.10% of soils contain >600 mg/kg Zn. Such concentrations are toxic to organisms (Eikmann, Kloke, 1991). In Upper Silesia, 8.44% of cultivated soils contain 300–600 mg/kg zinc, and 5.19% of cultivated soils are characterised by the concentrations exceeding 600 mg/kg. To a large extent, these are anthropogenic contaminations associated with the activity of mining and metallurgy of metals.

Sediments. The average zinc concentrations in sediments do not exceed 100 mg/kg, although there is a regional variability. The Upper Silesian area within the Vistula and Odra drainage basins shows a distinct character. Increased zinc values of the regional background are also observed in the left-side sector of the Odra drainage basin in both the Sudetes and the Sudetic Foreland, and in some regions of central Poland.

In Upper Silesia, the area of elevated zinc concentrations (>800 mg/kg) in sediments overlap the area of high zinc contents in soils. The greatest concentrations (more than several thousand mg/kg) are observed close to both currently operating and inactive zinc metallurgical plants. The strongest anomalies occur in the vicinity of Miasteczko Śląskie and Bukowno. The highest value (in excess of 40% zinc) was measured in sediments of a drainage ditch near a railway station at Bukowno. The sediments were represented by almost pure zinc oxide with admixture of lead (1,439 mg/kg), copper (1,432 mg/kg), cadmium (34.9 mg/kg) and sulphur (0.459%).

Among the major rivers of Upper Silesia, the average zinc concentrations over 1,000 mg/kg are observed in the Biała Przemsza, Brynica, Chechło and Sztoła rivers (in the Vistula River drainage basin) and in the Bytomka and Stoła rivers (in the Odra River drainage basin). Especially high zinc concentrations were detected in sediments of the Chechło River (from 2,076 to 14,151 mg/kg, average 235 mg/kg) and the Stoła River (from 1,040 to 12,148 mg/kg, average 3,984 mg/kg). The Upper Silesian region is responsible for a remarkable increase of zinc concentrations in sediments of both the Vistula (average 235 mg/kg) and Odra rivers (average 426 mg/kg). The effect of the Upper Silesian mining and metallurgy on pollution of sediments of these rivers is most manifested in the upper courses of the rivers. The zinc concentrations in sediments of the upper Vistula River (between the Przemsza confluence and San confluence) range from 198 to 2,759 mg/kg (average 790 mg/kg). The respective figures for the Odra River sediments (upstream of Opole) are in the range of 142–3,755 mg/kg (average 968 mg/kg).

Among the major rivers of Lower Silesia, sediments of the Bystrzyca and Kaczawa rivers show the maximum average zinc concentrations (109–1,177 mg/kg, average 333 mg/kg; and 51–1,457 mg/kg, average 232 mg/kg, respectively). Most likely, the zinc content in sediments of both rivers is the effect of discharge of mine waters from coal mines of the Wałbrzych Coal District and copper mines of the North-Sudetic Trough and Lubin-Głogów Copper District. High zinc concentrations in the Eastern Sudetes were found in the Bystrzyca Dusznicka River (tributary of the Nysa Kłodzka River) (up to 1,894 mg/kg) and in the Trująca (Złoty Jar) Stream near Złoty Stok (up to 2,896 mg/kg).

Increased zinc concentrations in the Polish Lowlands were found in sediments in large urban agglomerations or in areas of concentrated industry (such as the Warsaw, Łódź, Wrocław, Bydgoszcz, Białystok regions, etc.). A relatively extensive zinc anomaly is observed in the Prosna drainage basin (between Kalisz and Ostrów Wielkopolski – up to 2,111 mg/kg). A very high zinc concentration was detected in sediments of the Mikośka Stream near the Połaniec power station.

Surface waters. Zinc concentrations in surface waters of Poland are regionally diversified and vary between <5 to 16,414 µg/dm^3; the average is 36 µg/dm^3. In south-western Poland, the values commonly range from 30 to 120 µg/dm^3; in eastern and northern Poland – from <5 to 30 µg/dm^3.

A number of anthropogenic anomalies, mostly on a local scale, occur in the Polish Lowlands. Zinc concentrations above 250 µg/dm^3 (and only occasionally 1,000 µg/dm^3*)* are observed most commonly in the waters of small streams, which indicates local pollution sources of limited extent. Areas of increased zinc contents are situated near Warsaw (in the Wkra and Utrata drainage basins) and near Kalisz and Ostrów Wielkopolski (Prosna drainage basin). These areas partly coincide with the areas of increased zinc concentrations in sediments.

The pattern of zinc concentrations in surface waters of Upper Silesia is very similar to the distribution of this element in sediments. It is likely that zinc enrichments are controlled by the same factors: the geological factor (responsible for a high geochemical background) and the anthropogenic factor (contributing to the formation of most anomalies).

Anomalies of zinc (>500 µg/dm^3) occur in surface waters near Miasteczko Śląskie and Strzebnica, in Bytom and Katowice, between Bukowno and the ArcelorMittal Smelter (former Katowice Smelter) and near Chrzanów. Average zinc concentrations >200 µg/dm^3 were detected in the Baba, Bobrek, Biała Przemsza, Brynica, Chechło and Sztoła rivers (in the Vistula drainage basin) as well as in the Bytomka and Stoła rivers (in the Odra drainage basin). Hydrochemical studies of groundwater (Serafin-Radlicz, 1972) conducted in the north-eastern part of Upper Silesia (Pomorzany-Bukowno) revealed that the zinc concentrations are up to 1,500 µg/dm^3. As claimed by that author, concentrations in excess of 400 µg/dm^3 provides geochemical indication on the occurrence of zinc-bearing ores.

Surface waters of Lower Silesia, containing increased zinc concentrations, occur primarily near Wałbrzych and Nowa Ruda. It is likely that the elevated contents are related to discharges of mine waters from the Lower Silesian Coal District mines.

RADIOACTIVE ELEMENTS

Cs CESIUM (^{137}Cs + ^{134}Cs)

When studying distribution of radioactive cesium isotopes in Poland, the following should be taken into consideration:

– the essential dose of cesium has entered the environment after the Chernobyl disaster in April and May, 1986;

– regional pattern of cesium fallout following the Chernobyl disaster was dependent on the meteorological conditions; other environmental factors, such as soil type, seem to have been of secondary importance;

– some amount of cesium can be associated with military nuclear tests, carried out mainly between 1959 and 1962.

Results of surveys indicate that more than 90% of the territory of Poland is characterized by low cesium concentrations ranging from 0.1 to 8 kBq/m^2.

The highest cesium-related pollution is observed in the eastern part of the Sudetic Foothills and Silesian Lowland. The polluted area is part of a zone of increased cesium concentration, stretching from the SW to the NE, from the Polish-Czech border in the Kłodzko Valley through Nysa, Opole and Radomsko to the Warsaw region. There are three very distinct anomalous areas within this zone:

– the Opole anomaly covering 4,500 km^2, with the highest cesium concentrations in Poland reaching a level of 96 kBq/m^2 in the Nysa area;

– the Radomsko anomaly situated north of the town; its extent is not large and the concentrations are up to 20 kBq/m^2;

– the Warsaw anomaly extending from Rawa Mazowiecka in the southwest to Wołomin in the northeast, with the cesium concentrations attaining 30 kBq/m^2 near Pruszków and Wesoła.

Apart from this anomalous zone, the following cesium-polluted areas have been detected in Poland:

– in southern Poland: in the Beskid Niski Mts., Beskid Mały Mts. and Oświęcim Basin, where the cesium concentrations reach a level of 25 kBq/m^2;

– in the Karkonosze Mts. and western part of the Sudetic Foothills near Pińsko, with the cesium concentration of up to 25 kBq/m^2;

– in eastern Poland, in the Siedlce Upland an the Bielsk Podlaski Upland, as well as between Kock, Siedlce and Czeremcha, with the cesium concentrations of up to 100 kBq/m^2 in the Nurzec-Milejczyce area. Towards the northwest, there are anomalies of similar values near Myszyniec in the Kurpie Forest and in the Masurian-Mrągowo Lake District;

– single occurrences of cesium exceeding 15 kBq/m^2 have been recorded between Ińsko and Maszewo, and near Prabuty.

There is no correlation between the cesium concentration and the soil and vegetation type. It suggests that meteorological conditions were the main factor controlling the distribution of cesium pollution in Poland (Strzelecki et al., 1994b). Unfortunately, there are no weather charts available presenting the weather situation during the first 10 days after the Chernobyl disaster, which would allow analysing directions of air-masses and rain movement to relate those data to the cesium concentrations.

Data on the movement of polluted air-masses over the European continent allow concluding that:

1. Within the first 30 hours after the disaster, contaminated air-masses were transported from Chernobyl north-westwards, but did not reach the Polish territory. This conclusion is supported by a very poor cesium concentration in the eastern part of the Suwałki and Białystok regions.

2. During the next days after April 27th, contaminated air-masses changed their movement direction to the western (according to Belorussian data) and moved towards Poland. Polish data indicate that the contaminated air-masses reached the area of Poland through Podlasie and the northern Lublin region. Then, they headed north-westwards over the eastern part of Masovia and reached the Olsztyn-Mrągowo Lake District. Deposition of cesium from these air masses was not high (at a maximum of 40-50 kBq/m^2). Cesium anomalies are of local extent and the concentrations over the prevailing area range from 8 to 15 kBq/m^2. Such a level

of contamination resulted from the weather conditions.

3. A change in meteorological conditions resulted in a change of movement direction of contaminated air masses to the south-western. On April 30th and May 1st, the air masses reached south-western Poland, Czech Republic and southern Germany causing serious cesium contamination. Its level was dependent on local weather conditions, particularly on the occurrence of rainfall. In the Opole region, the cesium concentrations reached 100 Bq/m^2, while in Bavaria - 40 kBq/m^2.

^{40}K POTASSIUM

There are three natural potassium isotopes in the environment: the ^{39}K isotope accounts for 93.08% of the total amount, the ^{41}K isotope – 6.91%, and the radioactive ^{40}K isotope – 0.0119%. The quantitative isotopic relations are constant.

Analysis of a gamma-spectrometric survey demonstrates that the average potassium concentration in Poland is 0.68%. The maximum value is 2.80%. The highest values have been recorded in the Sudetes, the Carpathians and north-eastern Poland.

Its regional distribution is clearly related to geology. In particular, this is clearly manifested in the Sudetes. The highest potassium content is associated with granitoid massifs.

In the Karkonosze Massif, composed of different types of granites with abundant potassium feldspars, the potassium content varies from 1.5 to 2.0%. The potassium contents in the Strzegom granites are of the same order. The lowest contents (<0.75%) were measured in the Cretaceous carbonates of the Kłodzko Valley.

The concentrations of ^{40}K in the Carpathians range between 0.75 and 1.25%, showing a weak relation to the geological structure. It is worth noting that very low potassium contents are characteristic of the eastern part of the Carpathian Foredeep. Quaternary alluvial sediments of the San and Tanew river valleys contain less than 0.25% of potassium. An area of potassium contents <0.25%, extends westwards through the Nida Trough and the northern part of the Cracow-Częstochowa Upland to the eastern part of the Silesia Lowland.

Potassium concentrations in the Lublin Upland and Holy Cross Mts. are higher, reaching 1.5%. Interesting is the fact that the highest content is associated with loess deposits overlying Cretaceous rocks in the Holy Cross Mts. Similar potassium contents (1.0–1.25%) are recorded for the loess cover between Cracow, Miechów and the Nida River valley. Quaternary deposits of the Polish Lowlands are highly differentiated with respect to potassium content. The lowest values (<0.5%) were measured in alluvial sediments, especially those of Holocene age. The highest values are typical of glacial tills of frontal moraines of the Vistula Glaciation, containing considerable amounts of erratics. In north-eastern Poland (Lidzbark Warmiński region), the potassium content is up to 1.5%. Lower potassium concentrations, between 0.75 and 1.25%, are characteristic of glacial tills of older glaciations, while glaciofluvial deposits contain 0.5–0.75% of potassium.

eTh THORIUM

The isotopic composition of thorium is simpler than that of uranium due to the fact that terrestrial thorium is practically in 100% composed of isotope ^{232}Th that gives rise to the thorium decay chain.

The distribution of thorium in the topsoil is similar to those of other natural radionuclides. The average thorium concentration in Poland is 2.2 mg/kg. The highest concentrations are noted in the Carpathians and the Sudetes, and the concentrations exceeding the average value are also known from the Lublin Upland and Roztocze, and from the southern Holy Cross Mts. In the Polish Lowlands, the concentrations >4 mg/kg occur in Żuławy and north-eastern Poland, mostly in glacial tills of the last glaciation.

eU URANIUM

The uranium concentrations in the topsoil layer of Poland vary from 0.1 to 13.3 mg/kg, and the average is 1.1 mg/kg. Uranium concentrations above 2 mg/kg occur in the Sudetes and the Carpathians, in the Holy Cross Mts. and in the Lublin Upland.

In the Sudetes, the uranium concentration over almost the entire area exceeds 2 mg/kg. The Izera-Karkonosze Block is distinctive by the average concentrations ranging between 3 and 5 mg/kg, and the maximum values recorded at some places are above 13 mg/kg. The Strzegom and Strzelin granitoid massifs also show high uranium contents. The lowest concentrations (<2 mg/kg) are recorded in Upper Cretaceous and Lower Carboniferous (Culm) carbonates of the Intra-Sudetic Trough. Considerable variations in uranium concentrations are observed in the Fore-Sudetic Block. In general, the uranium contents in Quaternary deposits overlying older formations are <2 mg/kg. An exception is loess, as it is characterised by the maximum concentrations of up to 6 mg/kg uranium (a patch of loess NNE of Wrocław).

Extensive areas of the uranium content between 2 and 4 mg/kg (much higher than the average for Poland) are situated in the Carpathian Flysch areas, which is associated with a significant proportion of shales, especially menilite bituminous shales.

Similar values of uranium concentrations have been recorded in that part of the Holy Cross Mts. that is composed of Palaeozoic and Triassic rocks. This similarity in uranium concentrations is observed in both the basement and the overlying loess deposits. In the northern margin of the Holy Cross Mts., composed mostly of Jurassic carbonates, the uranium concentrations are below 2 mg/kg.

Noteworthy is the south-eastern part of the Lublin region and Roztocze, covered with loess, where the uranium concentrations are 2-4 mg/kg. There are also uranium concentrations as high as 7 mg/kg, however of limited areal extent, found in the Wisłoka River sediments near Mielec. These sediments and the loess deposits require further more detailed studies.

In the postglacial deposits of the Polish Lowlands, uranium concentrations in excess of 2 mg/kg are scanty. They are usually related to glacial tills, particularly those deposited by the Vistulian Glaciation in the Masurian Lake District. The very majority of glacial tills, glaciofluvial, aeolian and Holocene fluvial deposits contain <2 mg/kg of uranium.

GAMMA DOSE RATE

The gamma radiation is a combined effect of radiation produced by natural radionuclides of uranium ^{238}U, thorium ^{232}Th, potassium ^{40}K, as well as cesium $^{137+134}$Cs that is artificially introduced to the environment. All of them are considered environmental pollutants.

The average dose of gamma radiation in Poland is 30.9 nGy/h. The highest gamma radiation rates are recorded in southern Poland (in the Sudetes and the Carpathians), Holy Cross Mts. and the Lublin region. Low radiation rates are observed in northern and central Poland, excluding some areas in the Masurian Lake District and Suwałki region. Such a distribution of gamma radiation in Poland is related to the geological structure. Considering the total area of the country, the distribution pattern has been only slightly altered by fallout of radioactive dust after the Chernobyl disaster.

The highest doses of gamma radiation (>70 nGy/h) have been measured in the Sudetes, in the Karkonosze Mts. and Izera Mts., in the areas of outcrops of Carboniferous and Permian rocks in the Intra-Sudetic Trough, Śnieżnik Massif, Złote Mts. and the south-eastern part of the Sudetic Foreland (western part of the Opole region). The highest doses are associated with the presence of rocks containing increased concentrations of natural radioactive nuclides, which are exposed at the ground surface. These are granitoids, gneisses and crystalline schists in the Karkonosze and Izera Mts., Permo-Carboniferous sedimentary rocks (shales, sandstones) and volcanic rocks (rhyolites) in the Intra-Sudetic Trough, and Precambrian metamorphic and magmatic rocks in the Złote Mts. and Śnieżnik Massif. There are also some small uranium deposits and several sites of uranium and thorium mineralization in these areas. The only Chernobyl-related doses are those measured in the western part of the Opole region. In the

Kaczawa Mts. and Sowie Mts., the gamma radiation rate ranges between 50 and 70 nGy/h (almost twice the average value for Poland).

Another massive area, where the doses are relatively high and exceed 40 nGy/h, is the Carpathian Mts. The elevated values reflect the occurrence of flysch formations at the surface, represented predominantly by clay shales and fine-grained sandstones. They are characterised by increased contents of uranium and potassium due to their petrographic composition. Monotonous lithology of flysch deposits over the entire Carpathian area is the reason why the relatively uniform values, ranging from 40 to 60 nGy/h, dominate over large areas.

In the Lublin region and Holy Cross Mts. the gamma rays doses commonly vary between 40 and 70 nGy/h. In the Lublin region, they are associated with the occurrence of Cretaceous rocks and the Quaternary loess cover. Especially interesting are the elevated gamma ray doses of the loess cover that, due to its mineral composition, should exhibit low gamma radiation values. High radiation rates in the Holy Cross Mts. concentrate along outcrops of Palaeozoic rocks that are overlain by a thin loess cover in the eastern part of the region.

The Upper Silesian area is characterized by values ranging between 40 and 50 nGy/h.

The lowest gamma dose values (20–30 nGy/h) in pre-Quaternary deposits exposed on the ground surface were recorded in the Cracow-Częstochowa Upland composed of limestones.

Relatively low dose rates (20–40 nGy/h) dominate in central and northern Poland covered with post-glacial deposits. A mosaic pattern of gamma radiation dose rates is, in general, consistent with variable lithology. Due to the small map scale, only large lithological units have been shown on the map. The lowest gamma radiation values (20–30 nGy/h) were recorded in areas covered with sands. These areas include the Lower Silesian Wilderness and the Warsaw-Berlin and Toruń-Eberswalde ice-marginal valleys filled with fluvial and aeolian deposits, as well as the Kurpie Forest, Biebrza Valley and Augustów Forest covered with outwash plain sands, and fluvial and aeolian deposits. Very low gamma dose rates were also detected in areas covered with fluvial deposits of the Tanew River and the lower San River. Among fluvial deposits, the highest doses were measured in over-flood terrace deposits of the Vistula River. This is due to pollution of the Vistula waters by Upper Silesian coal mine waters discharged to the river, which contain significant concentrations of radium.

Moraine uplands, composed of glacial tills, are characterised by the gamma dose rates in the range of 30–40 nGy/h, locally over 40 nGy/h. The highest values reaching 60 nGy/h are typical of glacial tills of the Vistulian Glaciation covering the area of the Masurian Lake

District (near Kętrzyn) and the Suwałki region. These deposits contain considerable amounts of granitoid erratics.

CONCLUSIONS

The contemporary geochemical condition of surface environments in Poland (soils, sediments of inland water bodies and surface waters) has developed as a result of natural factors and economic human activities that continued for centuries.

The geological structure, and particularly the chemical composition of rocks outcropping on the surface or occurring at shallow depths, is the main natural factor responsible for the chemistry of these environments. Due to exogenic (surface) processes, the rocks are subject to physical and chemical weathering, and the products of weathering are transported in the form of solid (sediments) and liquid phases in the stream and river channels to lakes and seas, giving rise to other sedimentary rocks. The biosphere is of great importance for these processes, as soils develop from weathering mantles due to the action of living organisms and water.

Elements mobilized as the result of exogenic processes take part in biogeochemical cycles of the outer geospheres of the Earth (air, soils, both ground and surface waters). The content of chemical elements in these environments depends on the type and chemical composition of basement rocks, chemical properties of individual elements, and hydrogeological and climatic conditions. However, the geological structure is the most important factor.

Economic human activity has caused essential changes in the course of natural processes, particularly over the last 200 years due to an industrial and technical revolution and development of highly efficient agriculture.

Changes in the original geochemical relations demonstrate themselves mostly in the largest and densely populated areas of urban agglomerations being also the areas of specific concentration of industry. Environmental contamination with chemicals is a combined effect of industrial emissions, road and railway transport, and municipal and industrial sewage discharges. It is common that pollution is restricted to the immediate vicinity of the pollution sources; however, it sometimes extends far away from the emission sources.

Excessive or incompetent application of agrochemical treatments results in soil acidification and pollution of both ground and surface waters by phosphorus, potassium and sulphates. Lime recovered from mining wastes of zinc-lead ores or sulphur deposits was used for deacidification of soils. It caused contamination of soils with zinc, lead, cadmium or strontium.

The distribution patterns of elements in soils, sediments and surface waters, presented in the maps, demonstrate a complex geochemical landscape of Poland. Two well-marked geochemical provinces have been distinguished with respect to the natural geochemical background of individual elements, resulting from the geological structure of the country. These are the northern province and the southern province. The provinces have been distinguished based on a proposal of the classification applied in environmental studies (Xie, Binchuan 1993; Danrley et al., 1995). The amount of information (sampling density) used for the preparation of the geochemical maps is insufficient to make a more detailed division. Both the Sudetes and Upper Silesia are included in the geochemical megaprovince of the Bohemian Block, whereas the Carpathians are included in the Carpathian megaprovince (or optionally the Alpine province).

Increased concentrations of almost all elements in soils, as compared to the remaining area of the country, are the characteristic feature of the southern province that includes the Sudetes, Upper Silesia and the Carpathians. Soils of the Sudetes Mts. developed on magmatic and metamorphic rocks, frequently containing abundant trace elements and numerous signs of ore mineralization. In the Carpathians and Upper Silesia, the flysch and molasse formations containing material of magmatic origin are the immediate basement of soils. The coal-bearing Carboniferous rocks and the Triassic ore-bearing formations of Upper Silesia are additional elements that highly affect the geochemical image of the region. High concentrations of chemical elements in the soils of southern Poland can also be related to their granulometric composition. Most of them are clayey soils of much higher sorption capacity than sandy soils of the Polish Lowlands (in the northern province). The effect of granulometric composition on the content of trace elements is also observed in the soils developed on loess in the Rzeszów and Przemyśl region, Lublin Upland, Wrocław Lowland, and in alluvial soils of the Vistula River delta.

Soils of the northern province, covering the remaining part of Poland, are remarkably poorer with respect to majority of chemical elements. The soils are developed mostly on Quaternary glacial and interglacial deposits that originated chiefly from the area of Scandinavia composed of dominant magmatic and metamorphic rocks. The soils that developed on glacial deposits of the youngest glaciation contain slightly increased concentrations of some elements (chromium, mercury, magnesium, nickel, phosphorus, titanium, vanadium and yttrium). Higher concentrations of the elements are the result of the lowest degree of leaching and increased proportion of crystalline rocks in post-glacial material.

Holocene alluvial sediments and fluvial clays also play an important role in the geochemical pattern of the country.

Geochemical image of sediments of inland water bodies also reflects the division into the two geochemical provinces of Poland. However, some characteristic differences appear between the Carpathians and both the Sudetes and Upper Silesia. An assemblage of cobalt-chromium-copper-iron-magnesium-nickel-vanadium, likely related to a considerable proportion of the products of basic volcanism in the flysch formations, is a characteristic feature of the Carpathians. In the Sudetes and Upper Silesia, arsenic, beryllium, lead, titanium and zinc are additional elements that reflect the metallogenetic peculiarity of these areas.

It has been impossible to determine variability of the natural geochemical background of surface waters with respect to many elements: arsenic, cadmium, cobalt, chromium, lithium, nickel, lead, titanium, vanadium and yttrium due to low detectability of the analytical procedures applied. As to other elements, the effect of anthropogenic factors has significantly smoothed the original relations. However, it has been possible to identify regional and local anomalies of some elements. They are of both natural and anthropogenic origin; combined anthropogenic-natural anomalies are also common.

Among interesting regional geochemical anomalies in surface waters are strontium anomalies of the Nida Trough, Lublin Upland (near Chełm, Zamość and Tomaszów Lubelski), and in the vicinity of Tarnobrzeg. Natural strontium anomalies of the Tarnobrzeg and Staszów region are overlapped by an anthropogenic anomaly associated with the sulphur mining activity. The strontium anomalies coincide with the areas of high calcium concentrations in soils and surface waters. A strontium anomaly observed in the Lublin Upland, composed of Cretaceous carbonates, requires more detailed investigations. Enrichment in strontium in that area can be related to the admixture of tuffogenic material in Cretaceous deposits, as indicated by considerably increased values of the geochemical background of a number of elements in soils (cobalt, chromium, copper, iron, nickel and titanium). In the Tarnobrzeg region, the occurrence of strontium is related to the native sulphur mining.

The most important regional geochemical anomaly (mostly of zinc, lead and cadmium) occurs in Upper Silesia (Lis, Pasieczna, 1995a). This region is distinctive by its intensity of various processes, the effect of which expands far away from its boundaries. The geological structure is the main factor that controls the geochemical conditions and the occurrence of zinc–lead ores and hard coal deposits (which are among the largest in Europe) over a relatively small area (approximately 5000 km^2). The existence of these deposits gave the impulse to the development of Upper Silesian agglomerations, the largest and most populated in Poland.

Geochemical peculiarity of this region has emerged already in prehistoric times, when no economic activity was carried out by humans or it occurred on a small scale. Undoubtedly, already at that time, the surface environments (soils, sediments, surface and ground waters, vegetation) should have been affected by strong anomalies of elements such as lead, zinc and cadmium. The anomalies developed as the result of hypergenic processes occurring on the outcrops of ore-bearing rocks. At present, little is known on the intensity and extent of those anomalies since their original character has been altered by human activity, particularly during the last two centuries. High intensity of alterations due to anthropopression has been proved by the study of ancient and recent alluvial sediments of the upper Vistula River near Cracow (Klimek, Macklin, 1991), clearly demonstrating that the cadmium, zinc and lead contents in alluvial sediments of this river have increased several hundred times over the last 150–200 years.

The recent geochemistry of the environment, controlled by both natural factors and anthropopression, is characterised by specific associations of chemical elements originating from the two major sources:

1) mining, processing and metallurgy of zinc-lead ores,

2) hard coal mining and coal-dependent energy industry (coke plants, power plants, metallurgy).

Mining and metallurgy are the industries responsible for the pollution of sediments and surface waters, and especially major rivers, primarily by metals (mainly lead, zinc, cadmium, silver and manganese, to a lesser extent by arsenic, copper, barium and strontium) as well as by sulphur. This category of pollution also includes a very strong contamination of soils with lead, zinc and cadmium, locally also with silver in the vicinities of historical and currently active metallurgical plants and mining dumps. However, high concentrations of these elements in the geological basement are responsible for the high geochemical background of metals in soils of the whole region. Surface runoff from the nearest surroundings is the main source of these elements in small water bodies. Point pollution sources cause the contamination of waters and sediments in rivers on a regional scale. As a consequence, waters and sediments of the Vistula and Odra rivers become polluted and the contamination expands into areas situated far away from the source area.

Both hard coal mining and related energy industry are responsible for the pollution of waters with sodium, potassium, sulphates, boron, barium, strontium, manganese and iron. The effect of coal mining upon the composition of sediments seems to be relatively less important, although coal clasts have been reported from these deposits in distant areas.

Elements of this assemblage are also found in the Vistula and Odra river waters far away from the source areas, and the main mass of chlorides transported by these rivers to the Baltic Sea has originated in Upper Silesia.

Other sources of environmental pollution include municipal sewage and non-mining industrial effluents, road and railway transport, and agriculture. The latter seems to be responsible in part for the pollution of surface waters with phosphorus. Municipal and industrial sewage are other point-type sources of increased phosphorus concentrations in waters.

A regional anomaly of the Głogów-Legnica Copper District and the Intra-Sudetic Trough is directly related to the mining, processing and metallurgy of copper ores. This is an anthropogenic anomaly that requires a more detailed study to determine its intensity and extent. The anomaly is well manifested in soils by anomalous concentrations of copper and lead, whereas in sediments, it is evident by anomalous silver, arsenic, copper and lead concentrations.

Local geochemical anomalies are usually of geological origin (mainly in the Sudetes) and anthropogenic origin (mainly in the Polish Lowlands). The Złoty Stok arsenic anomaly, associated with the mining of arsenopyrite ore deposits, is one of such local Sudetic anomalies. The specificity of mining related pollution is that the responsibility for its development often goes to the past generations. Robber exploitation and processing of metallic raw materials resulted in the past in the formation of very strong pollution outbreaks with toxic substances. The area around the Złoty Stok mines is a good example.

Anthropogenic anomalies occur in city areas and are readily detectable due to increased contents of lead, chromium, copper, zinc, and occasionally of mercury and other elements. They are best expressive in sediments.

The degree of pollution of cultivated soils in Poland is relatively low. Only 0.86% of soils collected from cultivated land contained 20–50 mg/kg of arsenic, and 0.19% contained >50 mg/kg. Similarly, only 0.13% of soils contained 100–200 mg/kg of copper, whereas 0.18% contained >200 mg/kg. Excluding Upper Silesia, 2.28% of total number of cultivated soil samples contained 1 to 5 mg/kg of cadmium, 0.43% of soils contained 100–1000 mg/kg (tolerable value), and 0.78% of soils contained >1000 mg/kg of cadmium. As regards zinc, 0.25% of soil samples contained 300 to <=600 mg/kg, and 0.10% of samples contained >600 mg/kg.

More hazardous is the situation of cultivated soils in Upper Silesia with respect to lead, zinc and cadmium. Out of the total soil samples collected from the area of 6,290 km^2, the samples containing tolerable concentrations of metals account for the following percentages: 15.21% for lead, 8.44% for zinc, and 53.60% for cadmium. The figures for toxic concentrations of lead, zinc and cadmium are 0.78%, 5.19% and 8.6%, respectively. To a large extent, the pollution is of surface character and quickly fades out with depth (except in areas of direct outcrops of ore-bearing dolomites or deep pollution near metallurgical plants).

The optimistic assessment of the pollution level of cultivated soils cannot conceal the fact that the geochemical differentiation of sediments and surface waters is the signal of gradual deterioration of environmental conditions. It particularly refers to surface waters.

While the degradation of waters in major rivers is caused mainly by point sources of pollution, high concentrations of some elements or compounds (such as phosphorus, potassium and sulphur) occur mainly due to surface runoff, as evidenced by high contents of these elements also in a significant part of small water bodies. The likely culprit of these pollutants is primarily agriculture. High purity of water lakes in the Masurian and Pomeranian lake districts is probably due to the fact that these lakes are surrounded by forests, where no mineral fertilization is used.

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