# GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS

1:100 000

Józef Lis, Anna Pasieczna



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# PREFACE

The "Geochemical Atlas of Cracow and Environs" scaled 1:100000 is a consecutive cartographic achievement of the Polish Geological Institute in the area of geochemical cartography of large urban and industrial agglomerations. The atlases of Upper Silesia and Warsaw have been published so far; the series of geochemical atlases also includes similar studies for Łódź, Wrocław, and Szczecin, all currently under way.

The current condition of natural environment of Cracow results not only from the effect of local pollution sources. It is also subject to a strong pressure exerted by such powerful mining and metallurgical centre as Upper Silesia; this pressure is supported by other industrial branches existing in the same area. Data contained in the Atlas is a successful attempt of assessment of different pollution emissions including local as well as far - reaching ones. The "Sendzimir" Metallurgical Plant, and such chemical plants as Bonarka and Solvay in addition to other industrial plants are the most important local sources of pollution in Cracow.

The Vistula river with its valley takes a special position in the cartographic representation of Cracow and environs since it is most exposed to pollution by metals; this pollution results from impact exerted by the Upper Silesian deposits of hard coal and metallic ores. Important to note here is the fact that this negative impact has been taking place at present as well as in the past. Accordingly, waters and alluvia of the Vistula and soils within its valley are expected to be in the nearest future subjected to more detailed geochemical study.

Results of the present study make a valuable source of information available to the State Inspectorate for Environmental Protection and other agencies operating in the field of environmental protection, geology, agriculture and forestry, town and country planning, geomedicine, and public health.

The Atlas appears to be the achievement of both the Polish Geological Institute and the Ministry of Environmental Protection, Natural Resources and Forestry as well as the National Fund for Environmental Protection and Water Management which provided necessary funds to cover the cost.

Director General of the Polish Geological Institute Prof. dr. hab. Stanisław Speczik

# INTRODUCTION

Development of geochemical cartography of urbanized areas falls on the end of the 80's and the beginning of the 90's of this century. The geochemical cartography is a modern branch of geochemistry, directed mainly to the purpose of environmental protection. Geochemical atlases and maps of urban agglomerations provide a synthetic display of the hydrosphere condition and the lithosphere surface as well. Also, they provide a basis allowing to determine the extent and reasons of likely pollution of natural or anthropogenic origin and are indispensable element of the lithosphere protection program.

A number of publications were prepared in recent years, which dealt with areal distribution of chemical elements in soils of urban and industrial areas. (K. Czarnowska, 1980; T. Komornicki, 1986; K. Czarnowska, B. Gworek, 1988, 1991; K. Czarnowska, J. Walczak, 1988; T. Komornicki, K. Oleksynowa, 1989; Z. Czerwiński, J. Pracz, 1990; W.K. Łukaszew, Ł.W. Okuń, 1991; M. Birke et al., 1992; F. Gambuś, 1993; W. Lux, 1993; M.E. Paterson, M. Sanka, 1994). However, these publications have not been prepared in a cartographic form.

So far, there are some scarce cartographic publications that, in general, focus on soil environment (M. Birke, U. Rauch, 1994; R. Sajn et al., 1994; R. Taraškevičius, 1994).

Publications comprising studies of several environments (including soils, surface waters, and water sediments) within urban and industrial areas have been prepared by the Polish Geological Institute. They include: the "Geochemical Atlas of Warsaw" (J. Lis, 1991), the "Geochemical Atlas of Warsaw and Environs" (J. Lis, 1992), the "Geochemical Atlas of Kielce" (L. Lenartowicz, 1994), and the "Geochemical Atlas of Upper Silesia" (J. Lis, A. Pasieczna, 1995a).

This "Geochemical Atlas of Cracow and Environs" on the scale of 1:100 000 is a continuation of similar series of cartographic publications prepared by the Polish Geological Institute. It reflects the chemical conditions within the surficial environments of the Earth in large urban agglomeration and its agricultural-and-forest environs. Knowledge of the extent and degree of pollution within environments under study will be helpful in such fields of human activity as geology, agriculture and forestry, town and country planning, geomedicine, and public health.

The project was initiated in 1994; financial support was provided by the National Fund for Environmental Protection and Water Management.

Soils, water sediments, and surface waters were subjected to this study, and sampling was arranged in the grid of  $1\times1$  km.

Laboratory examination of all samples was entirely carried out at the Central Chemical Laboratory of the Polish Geological Institute.

The surface area covered by this project is equal to 1190 km<sup>2</sup>.

The following research team participated in preparation of the Atlas:

- J. Lis, A. Pasieczna: geochemistry conception and project proposal, project leadership and research coordination, compilation of geochemical maps, interpretation of results;
- T. Gliwicz, G. Przeniosło: data bases, data processing;
- D. Poprawa (the Carpathian Branch of the Polish Geological Institute): supervision of field work;
- J. Dacka, R. Kaczmarski, Z. Koziara, K. Wykowski (the Carpathian Branch of PGI): sampling;
- P. Pasławski, K. Jakimowicz-Hnatyszak: analytical work task leadership and co-ordination;
- H. Bellok, A. Bellok, E. Górecka, I. Jaroń, A. Jaklewicz, J. Kucharzyk, B. Kudowska, D. Lech, M. Liszewska, E. Maciołek: chemical analyses;
- B. Budzicka, B. Karolak, I. Witowska, D. Woźnica: chemical preparation of samples;
- T. Sztyrak, M. Cichorski, J. Duszyński, Z. Prasol: preparation of samples for analyses;
- · W. Ryłko: geology;
- · S. Przeniosło: mineral deposits in the Cracow area.

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The authors appreciate the assistance of all those whose high attitude made it possible to accomplish the project and edit this Atlas.

#### FIELD WORK

The field work was accomplished during the summer season of 1994; field teams were selected from among the employees of the Carpathian Branch of the PGI. Each field team was equipped with topographic maps, equipment and materials suitable for sampling, and a instruction of the field work procedure. A special training was offered to each member of the field team before moving to the field.

Topographic maps of the 1965 State Coordinate System on the scale of 1:25 000 were used to locate sampling points. Each map covering a surface area of 160 km<sup>2</sup> was subdivided into 160 squares of the area of 1 km<sup>2</sup> each. A soil samples, water sediment samples and surface water samples were collected from each of the square. Sampling covered the area of Cracow within its administrative boun-

daries along with its agricultural-and-forestry surroundings including the Niepołomice Woods. Information collected in the field and dealing with the area development, the way of the land use, type of the water body, and petrographic character of sampled material was recorded in special data form sheets; the information was supported with a sampling point location sketch. All locations of sampling points have been presented in the Atlas in Tables 1, 2, 3, 28–69.

Soil samples were collected using an 80-mm hand penetrometer; depth of sampling was 0.0-0.2 m below ground surface. Each soil sample, approx. 1,000 g in

weight, was packed in a cloth sack for protection.

Possibly finest grain-size distribution governed the quality of samples to be collected from water sediments. Different type water bodies were sampled including rivers, streams, and stagnant water reservoirs of variable sizes. Again, the samples were packed in the cloth sacks.

Surface water samples were collected from the very same sites from which water sediments were also sampled. Each water sample was filtered out through a hard filter, then it was placed in a small container of 20 ml capacity and treated with HCl.

# PREPARATION AND FILING OF SAMPLES

Soil and water sediment samples were preliminarily dried in the field, then they were transported to a sample storage house; in this storage house the samples were finally dried at a room temperature. Then, the samples were subjected to screening through nylon sieves (with 1 mm openings in the case of soil samples and 0.2 mm openings in the case of water sediments). After quartering, a 100 g sample was stored in a polyethylene container.

As regards the surface water samples, they were exposed to ultraviolet radiation after transportation from the field; this was aimed at ceasing the microorganism growth.

All samples have been stored in adequately adopted room equipped with suitable shelving and small trays. The containers with the samples were placed on the trays in an order depending on the material type and the map sheet. Each sample was designated with an analytical number.

# LABORATORY STUDY

#### LEACHING OF SAMPLES

Many different leaching procedures of soil and water sediment samples have been used for the purposes of geochemical mapping in various countries.

In the case of this Atlas the acid treatment was selected to extract the samples. Such selection was made due to possibility of determining that mobile portions of the elements, which take the main part in migration through surficial environments of the Earth. The mobile portions of the elements are also most readily assimilated by living organisms.

The sample extraction was carried out by the acid treatment using the hydrochloric acid (HCl 1:4), at a temperature of 90°C for 1 hour. Variable amounts of elements are being released in the process of extraction to the solution; passing amounts can be in the range of several to 100% depending on the form of elements' occurrences. Most resistant to extraction are such main elements being components of primary minerals as: silicon, aluminium, potassium, and sodium contained in feldspars; iron, magnesium, and calcium contained in amphiboles and pyroxenes, and zirconium, titanium, yttrium, and thorium - contained in heavy minerals of soils and water sediments. Most ready to pass to the solution are the elements making structures of carbonate minerals or those occurring in sorptive forms of weak bounds. The sorptive forms of the elements' occurrences are the most characteristic features of soils and water sediments subjected to pollution by anthropogenic processes. A question of susceptibility of different elements to acid extraction has been discussed in a more detailed way in the "Geochemical Atlas of Poland" (J. Lis, A. Pasieczna, 1995b).

#### DETERMINATION OF ELEMENTS AND ACIDITY

The following elements: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V, and Zn in soils and water sediments were determined using the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) method. A PV 8060 type Philips spectrometer was used to analyse the soil samples; and JY 70 Plus Geoplasma type Jobin-Yvon spectrometer was employed to analyse the water sediment samples. Detectability limits of the elements have been compiled in Tables I and II.

A Cold Vapour Atomic Absorption Spectrometry (CV-AAS) method was employed to measure a mercury content. A Perkin-Elmer 4100 ZL with a FIAS-100 flow-through system was additional instrumentation.

A soil standard applied in soil science practice (A chemical-and-agricultural analysis of soil. Determination of pH, BN-75 9180-83) was followed in pH determination of soils in aquatic environment. A total carbon content in soil samples was determined using a coulometric analysis with the use of an analyser of Coulomat 702 C/S Stroehlain type.

Analyses of surface waters with respect to Al, As, B, Ba, Ca, Cd, Co, Cr, Fe, K, Li, Mg, Mn, Na, Ni, P, SO<sub>4</sub>, SiO<sub>2</sub>, Ti, V, and Zn were carried out using the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES); also, the spectrometers of PV 8060 Philips type and JY 70 Plus Geoplasma Jobin-Yvon type were used. As refers to Pb, determinations were made with the use of the Atomic Absorption Spectrometry (AAS) method with supplementary graphite cuvette. Table III was compiled to present the detectability limits of the elements.

# **DATA BASES**

Using a dBase III-plus software package, three independent computer bases were created.

#### SAMPLING POINT COORDINATE BASE

Coordinates of sampling points were determined from the map of sampling points on the scale of 1:25 000 using a Houston Instrument's digitizer and a Sinus software package. Obtained coordinates followed the 1965 State Coordinate System; they were transformed into the 1942 State Coordinate System, then the angular coordinates were calculated. Thus, the sampling point coordinate base comprises the source data (the coordinates of 1965 system) and transformed (those of 1942 system and the geographic ones). The coordinate base provided the basis for construction of all generations of geochemical maps.

#### FIELD DATA BASE

The field data recorded in sampling data forms was entered in the field data base; particular elements of field data were numerically coded. The field data base makes a basis for consecutive subvision aimed at separation of sub-files required for statistical calculations arranged according to different environmental criteria (such as elements' concentration in cultivated soils, forest soils, urban soils, etc.).

#### LABORATORY DATA BASE

Results of chemical analyses provided by the laboratory were entered into the chemical data base. The base comprises 48 945 determinations of elements contained in 2028 samples.

# CONSTRUCTION OF GEOCHEMICAL MAPS

#### TOPOGRAPHIC BASE-MAP

The 1:100 000 topographic map of the 1942 State Coordinate System made the base-map required for construction of geochemical maps. An order for suitable matrices was placed at the Topographic Division of the General Staff of the Polish Army.

#### STATISTICAL CALCULATIONS

Calculation of statistical parameters for entire data sets and sub-files representing different soil, water sediment, and surface water environments was made with the use of STATGRAPHICS software package. The calculation included arithmetic and geometric means along with minimum and maximum values and median as well. Calculated factors were compiled in Tables IV–VI with respect to particular environments. They provided basis for determining suitable parameters applicable to generation of geochemical maps. The geometric mean occurred to be the most common since it characterized any given data population in a better way and remained less affected by the extreme values. Other parameters, such as variance or standard deviation, occurred to be unsuitable to fit undeterminable natural distributions.

#### GENERATION OF GEOCHEMICAL MAPS

A computer of PC 486, HD 330 MB, 16 MB RAM type was employed to generate geochemical maps.

A SURFER for Windows program was applied to generate geochemical maps of soils; this task was carried out utilizing an inverse distance method. A close discussion of this method is contained in explanation to the "Geochemical Atlas of Poland, 1:2500000" (J. Lis, A. Pasieczna, 1995b). An isoline method was selected to produce the maps. Most often, levels of element contents were selected in such a way that the lowest level reflected the mean geometric value representing the data set for particular element. As regards the pH map of soils, the acidity ranges follow the division commonly applied in soil sciences (strongly acidic, acidic, slightly acidic, neutral, and alkaline soils). All generated geochemical maps have been entered into HPGL format.

A circular diagrams method was applied to present the geochemical maps of water sediments and surface waters as well. Area of each circle on any map is directly related to concentration of a given element; the element concentrations were divided into groups defined by the following expressions:  $\leq \bar{x}$ ,  $\bar{x}+s$ ,  $\bar{x}+2s$ ,  $\bar{x}+3s$ , and  $>\bar{x}+3s$ .

#### PLOTTING OF GEOCHEMICAL MAPS

The maps were plotted with the use of an ink plotter of type NOVAJET II. Plates with geochemical maps of particular elements have been supplemented with suitable statistical parameters and bar charts.

# **GEOLOGY**

The area covered by this Atlas is made up of platform formations composed of the Mesozoic and Tertiary (on a local scale) substratum and covered with the Miocene molasse that fills up the foredeep of the Carpathian orogene; there are also the flysch Carpathian rock series occurring (the Sub-Silesian and Silesian units) and the Quaternary formations as well. Plate A is the geological map of the area.

# STRATIGRAPHY PLATFORM-TYPE FORMATIONS

#### Jurassic

Oxford. The upper sequence of middle Oxford and entire upper Oxford are represented by massive limestones, flaglike limestones, and platy limestones, the latter with intercalations of marls and massive limestones.

The massive limestones are hard and tight, light in colour, their fracture is uneven; in principle bedding is missing, cherts are absent. The massive limestones can appear as the dense limestones or as the lumpy ones. It happens that the massive limestones have diversified forms of their shape, less than 1 m to scores of metres thick, which can pass in a continous way in the flaglike limestones. As the result of weathering, they are subjected to preparation and form picturesque klippes.

The flaglike limestones are white, grey or cream-coloured; this rock type is considerably hard and light. Thickness of layers ranges from scores of centimetres to 2.5 m. Cherts of dark colour and diameter up to dozen centimetres or so are common.

Similar types of microfacies occur in both massive and flaglike limestones. The massive limestones are the carbonate structures with rigid skeleton of cyanide and sponge origin; as regards the flagstone limestones, they originated from the deposit which filled up depressions among carbonate structures.

There are some dolomites occurring in the upper section of the Oxford profile. They are light yellow in colour; when weathered they became brownish, sugary grained and crumbly. They form irregular lenses and aggregations with diversified top and bottom, size of which can be from dozen centimetres or so to several metres.

Platy limestones (in both granular and micrite forms), with intercalations of marls and massive limestones occur in the preserved topmost part of deposits of Oxford profile. They fill up depressions in the massive limestones, and their visible thickness does not exceed 20 m. The platy limestones are yellow-creamy coloured; they have shell-like fracture, indistinct bedding, and cuboidal joint. Their top is uneven, covered at places with a marly layer several centimetres thick; a clumpy massive limestone occurs at the top of marl. Some flat flint beds are observed to occur in the platy limestones, their length can reach several metres.

#### Cretaceous

Turonian. It occurs as limestones of variable degree of sand content, with quartzic pea gravel (2 cm in diameter); there are also occurring platy and lumpy limestones and grey or light yellow or brown conglomerates as well. A substratum of Turonian sediments is formed by truncated abrasion surface that developed on Jurassic limestones. The lower Turonian up to 2 m thick is fauna rich (a horizon with *Inoceramus labiatus*). The upper Turonian lies unconformably on the lower Turonian sediments truncated by abrasion surface or on the Jurassic. Locally, a stromatolite enriched in phosphorus compounds appears at the top of the Turonian. Fauna observed here indicate the lower part of upper Turonian (a horizon with *Inoceramus costellatus*).

Senonian includes glauconitic marls deposited on uneven abrasion surface of the Jurassic and Turonian sediments. Their thickness can rich 3 m. Grey marls cover the glauconitic ones; their thickness is in the range of 2–10 m. A contact between Santonian and Campanian appears within the grey marls. Upper part of the lower Campanian is composed of marly limestones and gaizes with cherts; they lie on the grey marls and occasionally on the Jurassic. The upper Campanian is known to occur on a local scale only.

The glauconitic marls are composed of soft clayey marls containing numerous glauconite grains (up to 14%). There are organic remains included that are represented by

foraminifera and fibres of crushed shells of *Inoceramus* sp. The rock matrix is made up of carbonate-marly substance.

The upper part of the profile is represented by marly limestones and gaizes with cherts, irregularly interbedded with greyish marls. Foraminifera and sponge spicules are the organic remains. Some gaize fragments are silica rich; the silica forms white or white-greyish cherts. Intercalations of light-greenish bentonites are found in places; their thickness is of the order of several centimetres.

#### Tertiary

Palaeogene occurs in two facies. The first one is a flint debris which mainly developed on the Jurassic limestones and in karstic funnels.

The flint debits is composed of flint blocks being up to 30 cm in diameter, prepared out by weathering from limestones of the upper Oxford. They are both broken and of original shape; they can occur self-dependently or are embedded in clays. The flint debris formation is widely distributed at Rączna where it overlies the Jurassic limestones, and in Bielany and Mydlniki suburbs of Cracow where its substratum is formed by the Senonian sediments. It is also possible that the sediments considered here to be of Palaeogene age may, in fact, be Pliocene in part.

The second facies is predominantly composed of white fine-grained sands, sometimes clayey, in places intercalated with clay and gravel; they formed from delimed gaizes of the lower Campanian, and quartz and cherts as well. Sometimes sands are on a local scale cemented with silica. These sediments make up an overlying cover of both the Jurassic and Cretaceous formations, and their thickness can rich 16 m. They are also met as the filling of karstic funnels, where sometimes they contain blocks of Senonian rocks. They are equivalent of the Rudawa Beds.

Neogene, Carpatian (?). Limestone and marls (caliche) are predominantly hard and dense, light-blue or grey-yelowish in colour. Sometimes their character is marly or they pass into marls. There are oysters of thick shell type dominating among organic remains; in places, rock is almost entirely composed of broken shells. Substratum is formed by Jurassic limestones, the Badenian clays usually occur in the overlying bed. In non-existing outcrop in the bed of the Vistula river at Zwierzyniec, also at Bodzów, an abrasion surface was developed beneath the oyster limestone, that has been punched out by rock-boring organisms.

#### MOLASSE FORMATIONS OF THE CARPATHIAN FOREDEEP

#### Tertiary

Miocene, Badenian. The Skawina Beds have been found to occur in local outcrops. They are lying discordantly on the upper Jurassic deposits. The Skawina Beds developed in the form of clays and mudstones with interbeddings of coarse-grained sands and gravels. Thickness of the Skawina Beds is about 150 m.

The Wieliczka Beds have been found in the Soboniowice and Wieliczka area. They developed as grey marly clays with rock salts, gypsums, and anhydrites as well. Intercalations of gypsum-like claystones are also present. They overlie the Skawina Beds and are covered by the Chodenice Beds. Fauna is missing in the Wieliczka Beds. Grey and dark-grey claystones with intercalations of laminated gypsums and anhydrites were found to occur in the Sidzina area between Borek Fałęcki and Skotniki-Wola Buchacka.

Sulphur-bearing limestones and marls that occur in the

Swoszowice area rich a thickness of 0.5–3.0 m. They contain bands and gypsum-related limestone modules (originated from transformation of gypsum into sulphur and limestones). It should be noted that the formation under discussion in actually weakly exposed and their dominant occurrence is connected with waste rock banks. As concluded from A. Garlicki's work (1964), sulphur was present in marls in the form of irregular nests, balls, and layers of variable thickness.

The Chodenice Beds within area under consideration lie on the Wieliczka Beds and are covered at their top with the Grabowiec Beds. Their lithology is limited to clays and marly clay-slates, slightly sandy in places. It was been recognized in the areas of Wieliczka and Bochnia that this complex contain tuffites. They contain microfauna; and their thickness is less than 100 m.

A complex of clays and mudstones distinguished on the maps as the Grabowiec Substage is represented by silty clays interbedded with silty sands. Individual layers of grey mudstones are clearly visible. The complex is known to occur on a local scale. Its thickness is 50 m at least.

The Bogucice Sands overlying the Grabowiec Beds are the youngest Miocene deposits within the surveyed area shown on the map. They developed as fine- and medium-grained sands locally interbedded with bands of clays. The Bogucice Sands reach a thickness of about 50 m.

The Pliocene gravels are composed of quartz and Jurassic flints, and Jurassic siliceous limestones and gaizes. They occur as a thin (up to 1 m) cover of different horizons of Badenian clays at Pasternik, that have been truncated by a base-level surface. They originated as the effect of weathering of Mezozoic rocks during the Pliocene washing out of Palaeogene sediments.

#### FORMATIONS OF FLYSCH CARPATHIANS

#### Cretaceous

Valanginian-Hauterivian. The Upper Cieszyn Beds occur on the surface in outcrops of both the Sub-Silesian and Silesian units. They developed as thin-bedded sandstones that are dark, sometimes shell-like, and interbedded with dark shales. The entire complex is strongly calcareous. Red and yellow siliceous-clayey shales with abundant fauna are frequent here. This complex has a thickness of about 150 m. It is sandwiched between the underlying Cieszyn limestones and the overlying Grodzisk Beds.

Hauterivian—Barremian. The Grodzisk Beds are cropping out on the surface in profiles of the Silesian unit and Sub-Silesian one as well. The Grodzisk Beds developed in the form of medium-and thick-bedded coarse- grained sandstones that are interlayered with fine-grained sandstones and conglomerates along with thin beds of black, grey-blue, and grey shales. Shales are hard, and desintegrate in a leaf-shaped way. Apart from variable coloured quartz grains, the conglomerates comprise organogenic limestones and remains of pelecypods, aptychuses, and belemnites, and bigger and smaller chips of hard coals. It is difficult to define a contact of these Beds with the Cieszyn Beds, therefore, both are frequently combined together. The Grodzisk Beds are covered with the Wierzów Shales; they contain fauna and the thickness is about 150 m.

Barremian-Aptian. The Wierzów Shales are exposed on the surface in profile of the Sub-Silesian unit. They are composed of black and dark-gray shales, weakly calcareous or siliceous in their character, chapping in a leaf-shaped way. Their bedding surfaces are covered with micaceous

dust. Thin-bedded sandstones occurring here are friable, dark coloured; sometimes they are shelly, calcareous, micaceous. The Wierzów Shales are known to contain microfauna. In the frame of the Sub-Silesian unit, the Wierzów Shales are covered with the Gaize Beds, while in the Silesian unit – by the Lgota Beds. Thickness of the Wierzów Beds is about 150 m.

Albian—Cenomanien. The Gaize Beds appear in profile of the Sub-Silesian unit in isolated outcrops only. They overlie the Wierzów Shales, and at their top they are covered with variegated shales or the Węglówka Beds. Almost entirely they are formed as sandstones composed of quartz and spiculas of silicic sponges. The sandstones are interbedded with grey or greenish or black shales; locally intercalations of pure montmorillonite can be seen. Variable thickness characterizes the Gaize Beds; it is in the range of dozen metres or so to scores of metres.

Albian. The Lgota Beds is a member of the Silesian unit's profile. They developed as the green mottled shales, occasionally interbedded with thin-bedded sandstones of siliceous cement. They directly overlie the Wierzów Shales or the thick bedded sandstones and shales of lower section of the Lgota Beds. This link reaches the thickness in the range of 100–150 m. There is a layer of the Mikuszowice hornstones that developed at the top of shales and sandstones.

Cenomanien. Jaspers and gaizes have been found in profile of the Silesian unit. Their position is above the Mikuszowice hornstones and below variegated shales. The Gaize Beds occurring in the area under consideration have been described in detail by J. Burtan and M. Turnau-Morawska (1978).

Variegated shales occurring in profiles of the Sub-Silesian unit take the form of red and green shales with secondary intercalations of thin-bedded sandstones of Godula type.

The Żegocin Marls, distinguished in profile of the Sub-Silesian unit, are composed of hard platy marls; they are darker in their bottom section, lighter and mottled in the upper one, intercalated with black shales. Thickness of the Żegocin Marls does not exceed dozen metres or so.

Turonian-Senonian. The Węglówka variegated Marls have been proved in profile of the Sub-Silesian unit within the margin part of the Carpathians, where they occur in the form of disjunctive belt. Marls are soft, red in colour, sometimes they are green. In the top part of this complex, soft grey and dark grey marls are occurring; they appearance is of the Frydek Marls' type. The Węglówka Marls reach a thickness of around 150 m.

Senonian. The Lower Istebna Beds have been distinguished in profile of the Silesian Unit. They appear as the thick-bedded, coarse-grained, arkosic sandstones; they are not very hard and are interbedded with dark-coloured shales. Quartzic conglomerates are frequent here; they are composed of exotic material, sometimes containing large amount of different exotic limestones. Intercalation of variegated shales also appear within this horizon. A phenomenon of kaolinization, sometimes affecting entire sandstone beds, is due to weathering of feldspar-rich sandstones. As refers to thickness, the Lower Istebna sandstones and conglomerates reach around 450 m.

The Tomaszowice Beds occur within the margin of the Carpathians, in profile of the Sub-Silesian unit. They occur in the form of light-coloured, thick-bedded, fine-grained friable sandstones containing muscovites; occasionally, grains of glauconite can also be found. The Beds under consideration are interbedded with dark sandy shales con-

taining floral detritus. Conglomerates can also be met in this horizon; they are built up of vari-coloured quartz, limestones, and sandstones. The said horizon can rich a thickness of about 150 m.

#### Tertiary

Palaeocene. Thick-bedded sandstones and not too hard conglomerates, both interbedded with dark-grey and black clayey and sand-laden shales make up the Upper Istebna Beds. Their thickness does not exceed 300 m.

Palaeocene-Eocene. Variegated shales, occurring in profile of the Sub-Silesian unit, developed as red and green clayey shales, stratified, of leaf-like break. Thin-layered sandstones that appear within the shales are glauconitic, glassy, and flinty. The variegated shales are up to around 150 m thick.

Eocene. The Ciężkowice Sandstones occur in profile of the Silesian unit. They are thick-bedded and fine grained in appearance, with irregular fractional bedding. The sandstones contain large lenses of conglomerates composed of quartz, grey chips of metamorphic rocks and, occasionally, of limestones. Sandstones and conglomerates are interlayered with mudstones and greenish shales that are strongly sand-laden. In places, the Ciężkowice Sandstones are calcium rich; they show a tendency to weathering of spheric type and create picturesque morphologic forms. Their thickness is around 70 m. Sandstones contain fauna that is mostly represented by large foraminiferans.

Oligocene. The Menilite Beds are the components of the Sub-Silesian unit's profiles. They are represented by shales, chocolate- or black-coloured, with alum incrustation; they interlay with thin-bedded glauconitic sandstones. Sometimes, a horizon of black and brown hornstones can be distinguished within the Menilite Beds' complex; the hornstones are usually interbedded with black strongly silicified shales. Thickness of this complex is around 150 m. Fauna is present in the Menilite Beds. Above the Menilite Beds the overlying Krosno Beds have been distinguished.

The Krosno Beds occur in profile of both the Silesian and Sub-Silesian units. They form platy and crustal sandstones that are thin-bedded, friable, muscovite-rich, and calcareous. They are intercalated with grey calcareous shales. Thikcness of the Krosno Beds is difficult to determine; however, it does not exceed 300 m.

#### Quaternary

The Quaternary deposits overlie an erosional surface of variable origin and age, that cuts sediments ranging in age from upper Jurassic to Pliocene (inclusive).

Deposits of the South-Polish Glaciation include fluvial gravels and sands, glacial tills and sands with gravels of fluvial and fluvio-glacial origin occurring south of the Vistula river valley. Deposits mentioned here occupy the area in a form of narrow belt extending from Cracow up to

the area of Targowiska near Bochnia. They are the oldest Ouaternary deposits within the surveyed area.

The Middle-Polish Glaciation has left sands of fluvialperiglacial accumulation and loesses that occur on a local scale in the Cracow area. The fluvial periglacial sands contain beds of gravels and silts.

Sands and gravels of fluvial-periglacial accumulation, gravels, sometimes limestones and loesses make up deposits of the North-Polish Glaciation. All of them occur in two, more or less disjunctive belts to the north of the Vistula valley. Loesses occur in the northern belt where they form a uniform cover the thickness of which is often in excess of 10 m.

Loesses and loess-like clays also occur southwards of the area mentioned here, in the land belt extending from Skawina to Bochnia. From lithological point of view they are clays and dusty clays, yellow and light-yellow in colour, locally they are light-grey and grey. Also, loess-like clay known as so called "Carpathian loess" occurs here (T. Gerlach et al., 1992).

Aeolian sands (also those in a form of dunes) have been found to occur in area located between Niepołomice and the Raba river valley. Sands are mostly coarse-grained, with grains visibly mat in appearance. On a local scale, sands in this area form not large dunes that in part have been worked-out.

Holocene. It is represented by deposits that built up low flood plains and high terraces, sedimentation of which started at the turn of the North-Polish-Glaciation. Muds, clays, and alluvial sands of the flood type and channel-type accumulation, that make up the topmost part of fluvial terraces are also of Holocene age.

Fen peats have been found in the area of Dąbrowa near Niepołomice (K. Lipka, 1973, 1989) and south-eastwards of Wola Zabierzowska; their origin is connected with frequent all-year flooding and long-lasting flow of surface waters. Peatbogs occupy a number of depressions occurring within the aeolian sands in the Dąbrowa area; in the Wola Zabierzowska area the peatbogs appear within fluvio-periglacial sands and gravels.

#### **TECTONICS**

Four structural elements meet in the surveyed area. They are: the Silesian-Cracow Monocline, the Nida Depression, the Carpathian Foredeep, and the Flysch Carpathians.

The Silesian-Cracow Monocline includes outcrops of Mesozoic and locally Tertiary rocks occurring in Cracow and environs. The Nida Depression is represented by outcrops of the Cretaceous rocks, that appear north-westwardly of the line connecting Witkowice and Garliczka (J. Rutkowski, 1993). The Carpathian Foredeep is filled up with Miocene molasse. The Flysch Carpathians occurring southwardly of aforenamed structural elements are represented by rock series belonging to the Sub-Silesian and Silesian units.

# MINERAL DEPOSITS IN THE CRACOW AREA

Deposits of mineral raw materials occurring in the area of this geochemical survey include: chemical raw materials (rock salt and native sulphur), natural gas and abundant raw rock materials (limestones and marls, natural crushed stones and clay raw materials applicable to building industry. Deposits of chemical raw materials, particularly those min-

ed, can have an important bearing on areal distribution of elements under study in surface waters, water sediments, and soils. Deposits of rock raw materials are less important with this respect. In this chapter attention is drawn to the occurrence of abandoned and mined deposits, mainly because of workings left as the result of mining works. Not all excavations have been reclaimed so far. Some of them are utilized as water reservoirs, others are used as waste dumping sites being non-indifferent to the environment.

#### **ROCK SALT DEPOSITS**

Rock salt deposits in the Carpathian Foreland belong to Miocene salt-bearing formation extending from Upper Silesia through the Cracow environs to Przemyśl and farther eastwards through western Ukraine up to Romania. In the Cracow environs and eastwards up to Tarnów, this formation developed as the chloride facies in the form of rock salt deposits with interbeddings of gypsum and anhydrites and claystones as well (A. Garlicki, 1968).

Rock salt deposits of economic value occur in a parallel belt extending from Barycz through Wieliczka, Łężkowice, Siedlec-Moszczenica-Łapczyca to Bochnia. Deposits at Wieliczka and Bochnia were the most important; a dry method of extraction was employed here from the XII century; however, in the last period it was replaced by underground leaching. Leaching through wells was the method employed to exploit salt from remaining deposits. At present, mining was ceased in deposits at Bochnia and Łężkowice; other mines are actually in the stage of liquidation.

The Wieliczka deposits occupies an area of several square kilometres. The deposits is of elongated shape along W-E axis (appr. 6 km.), and depth of workability is more than 300 m. The salt beds are of folded shape; the lower part of the deposit developed in the form of overturned folds and scales whereas the upper part forms disorderly mass of clays with salt blocks. Thus, a bipartite nature of the Wieliczka deposit is clearly exposed in its vertical profile (A. Garlicki, 1970a). A dry chamber system was employed to mine the upper dry salts while a leaching method was applied to exploit stratified salts. In 1994, approx. 59 thousand tons of salt were mined as a brine (S. Przeniosło, ed., 1995) A decision was taken on mine abandonment, and resources left unmined have been qualified for uneconomic category.

The deposit at Barycz occurs within administrative boundaries of Cracow west of Wieliczka. Salt and clay-anhydryte beds of a thickness in the range of 30–50 m are strongly folded. The deposit occurs at a depth of 200–300 m, and it covers a surface area of 1×2 km. Approx. 56 thousand tons of salt were mined in a form of brine in 1994. Resources are assessed to be equal to 2,5 millions tons.

The deposit at Łężkowice has been exploited by leaching method through wells since 1968. It creates a natural western part of the Siedlec-Moszczenica-Łapczyca deposit (A. Garlicki, 1970b; A. Szybist, T. Toboła, 1995). The latter was made available to mining in 1989; however, three year later a decision was taken on mine abandonment due to economic reasons. In 1994, a final extraction was equal to 11 thousand tons of salt. Resources that have been left untouched in the deposit have been evaluated to the almost 190 millions tons (the most abundant in the area under consideration).

At Bochnia, the rock salt deposits extending approx. 4 km along W-E direction is strongly disturbed with respect to its tectonics. There are two anticlinal forms, namely the Bochnia fold and the Uzbornia one, that have an important bearing on the geological structure of the salt deposit. Rock beds situated within the limb of the Bochnia fold, also those situated near-the-surface zone are arranged

almost vertically (A. Garlicki, 1970a). The deposit had been mined from 1251 up to 1991.

Łapczyca is the location where therapeutic waters occur; they are of chloride-sodium type with significant content of iodine and bromine. Resources were evaluated at almost 33 million m³ of brine. The 1994 production of brine was 5.13 thousand m³; the brine was used for production of the Bochnia's iodine-bromine therapeutic salt.

#### SULPHUR DEPOSITS

The area of Swoszowice is known from the occurrence of gypsum and sulphur-bearing marls belonging to the Miocene salt series. The sulphur-bearing rocks were subjected to mining for centuries. It is estimated that approx. 100 thousand tons of sulphur had been extracted between years 1415 and 1884 (T. Osmólski, 1969). A method consisting in underground mining was employed to exploit a sulphur bed 0,5 to 2 m thick, occurring at a depth not exceeding 60 m. At present, the former mine area is occupied by the Swoszowice Spa, the existence of which is based on a mineral spring. Apart from Swoszowice, similar sulphate type waters occur at Lusina and Wrząsowice.

#### NATURAL GAS DEPOSITS

Deposits of natural gas occur in the eastern part of the area of Grobla (commune of Drwinia) and Raciborsko (commune of Wieliczka); a deposit at Grabina-Nieznanowice (commune of Gdów) is practically situated outside the south-eastern border of the area under present study.

#### DEPOSITS OF ROCK RAW MATERIALS

There are numerous limestone deposits in the area under this study; all are utilized by chemical and lime-producing industries. Majority of deposits have already been exhausted or mining has been ceased. The following is a list of limestone deposits situated within the administrative boundaries of Cracow: Pychowice, Tyniec, Zakrzówek, Kryspinów, and Zabiedzin (all in commune of Liszki), and Rząska, Rząska II, and Zabierzów (all in commune of Zabierzów).

Gravels and sands occurring in numerous deposits have been used for building purposes (mainly for industrial needs) of Cracow and Nowa Huta. Mine workings of remaining deposits form water reservoirs that not always are adequately managed. In the Cracow area the uneconomic or abandoned deposits include: Branice, Przylasek Rusiecki, Cholerzyn (all in commune of Liszki), Przybysławice (commune of Zielonki), Zabierzów Bocheński (commune of Niepołomice) and deposit of back-filling sands at Psia Górka near Wieliczka.

Active deposits of gravels and sands include: Branice-Przylasek Rusiecki, Wolica, Budzyń, Złotniki-Łaźnia, Brzegi (I, II, III), Grabie, Grabie-Węgrzce Wielkie, Dumienice-Zakole Raby.

Deposits of clay raw materials for building industry appear mainly within administrative boundaries of Cracow and in the eastern sector of the mapped area. Abandoned clay raw materials are those located at: Rybitwy (commune of Cracow), Wola Zabierzowska (commune of Niepołomice), and Stradomka (commune of Bochnia). Operational are following deposits: Bonarka—Łagiewniki and Zasławice (commune of Cracow), Zielonki (commune of Zielonki), Sułków (commune of Wieliczka), Wawrzeńczyce (commune of Igołomia), Bochnia and Gerczyce (commune of Bochnia).

# MAIN POLLUTION SOURCES

Both natural and anthropogenic factors are responsible for changes in geochemical conditions of investigated environment. Visible impact of man on geological processes taking place in the Cracow environs commenced approx. 6000 years BP (J. Rutkowski, L. Starkel, 1993) when deforestation and soil erosion were initiated. Exploitation of mineral raw materials has lasted since the XI century; from the XIX century it has been arranged on a large scale. A lot of quarries, gravel pits, clay pits, brick-yards, lime kilns, cement mills, and a native sulphur mine of Swoszowice were operational in this area (T. Osmólski 1969; A. Paulo, 1993). Exploitation was followed by land development, extension of communication lines, and construction of industrial plants.

Up to now, it is the industry utilizing both local and imported mineral raw materials which is a perpetrator of the most important damage to the natural environment. The most important plants in the urban-industrial agglomeration of Cracow include:

the ''T. Sendzimir'' Metallurgical Plant (the former Iron Plant)

- the "Solvay" Cracow's Soda Processing Plant,

 the Cracow's Plant of Inorganic Industry at Bonarka (the former Phosphatic Fertilizers Plant),

the "Skawina" Metallurgical Plant (the former Aluminium Plant),

- thermal-electric power station at Skawina,

 rock salt mines at Wieliczka, Barycz, and Łężkowice, and brine extraction plant at Łapczyca,

- thermal-electric power station at Leg.

Operation of the industry is always followed by production of wastes that are deposited on dumping sites. They are sources of surface and ground waters' pollution and of dusting the environs; besides, they occupy significant ground areas.

Dumping sites belonging to the "Sendzimir" Metallurgical Plant occupy an area of approx. 270 ha. They cause pollution of ground waters with sulphates, phenols, man-

ganese, and lead (B. Kamiński et al., 1987).

Production sludges from the "Solvay" Plant are deposited in the settling ponds situated on the right side of the Wilga river valley (where they occupy approx. 70 ha). They mainly contain calcium carbonate and calcium chloride, anhydrite, and silica. Such dumping sites pollute ground waters with chlorides, sulphates, nitrogen compounds; in addition, they cause inundation of adjacent grounds.

Production wastes from the "Bonarka" Plant are deposited in inactive limestone quarry. They are rich in calcium fluoride, calcium carbonate, phosphorus pentoxide, and silica (A. Ślęzak, 1993). Despite sealing and drainage of effluent, infiltration of waters through wastes enhance pollution of ground waters will fluorides, chlorides, and

organic substances.

Wastes from the "Skawina" Metallurgical Plant containing approx. 12% fluorine (B. Kamiński et al., 1987), are dumped in sand-pit excavation. A study of ground waters around this dumping sites revealed their pollution with fluorine compounds, increase of total mineralisation, and high content of alkalies. Maximum fluorine concentrations can be as high as 311 mg/l.

Municipal waste dumping sites along with sewage and industrial effluents exert a heavy impact on the environment. Apart from municipal wastes, other wastes are also dumped here; they are produced at small industrial plants

and craftsman's workshops. The "Barycz" municipal dumping site is the pollution source for waters of the Malinówka, Serafa, and Vistula rivers due to leakage from drainage ditches. Effluents from non-operational municipal dumping site at Zielonki are the pollution sources with respect to sulphates, chlorides, ammonia; cyanides, lead, zinc, and fluorine have also been found here (B. Kamiński et. al., 1987). All of them cause pollution of the Prądnik river.

Municipal sewage, almost untreated, reaches the Drwina Długa river, effluents from thermal-electric power station are flowing down directly to the Vistula, the Suchy Jar canal is a receiver of municipal sewage from Nowa Huta and of industrial effluents of the "Sendzimir" Metallurgical Plant (J. Woyciechowska, P. Morawiec, 1994).

A southern part of the map sheet covers the area where mining damage occurs; the damage is related to exploita-

tion of rock salt (at Barycz and Łężkowice).

Pollution of atmospheric air with dust and gases mainly due to industrial activities and communication as well is a particular problem. Those components of atmospheric dust that are readily soluble exert specific effect on geochemical variations of natural environment. With prevailing western orientations of winds, a significant portion of dusty and gaseous emissions directly affect the area of the Niepołomice Woods. A phase analysis of atmospheric dust (A. Manecki et. al., 1981; W. Wilczyńska-Michalik, 1981; A. Manecki, 1993) revealed their very rich mineral composition. As refers to fall-out of metals, the most significant one deals with Fe, Zn, and Mn; the lower rate deals with Pb, Cu, and Ni, while the cadmium fall-out is the weakest. A study of rain waters from the Cracow area (K.P. Turzański, 1991) made it clear that among anions under study the sulphate ion (28 mg/l/month) dominates over chlorides and nitrates. When alkaline ions are concerned, calcium (up to 6 mg/l/month) can be pointed out as dominating over ammonium (1.8 mg/l/month).

As concluded from monitoring of air pollution over the Cracow province, application of filters contributed much to the decrease of dust fall-out. The annual average of dust fall-out for the period of 1985–87 was ranging from 67 g/m²/yr at Myślenice to 707 g/m²/yr in the vicinity of the "Sendzimir" Metallurgical Plant (F. Gambuś, 1993). In the second half of the 80's, the annual average of dust fall-out was equal to 129 g/m²/yr, whereas in 1990 – 80 g/m²/yr only. Following the increase of wheeled traffic, concentration of carbon oxide has also increased. T. Gawrecki (1993) discusses some cases where the CO concentration is 25 times greater than permissible concentration.

The air pollution is also affected by emissions of such gaseous substances as sulphur dioxide, and nitrogen oxides and fluorine as well (A. Manecki et. al., 1982; B. Godzik et. al., 1994). The thermoelectric power station at Skawina and the "Sendzimir" Metallurgical Plant are the principal emitters, with 50% and 40% emissions, respectively. The CO<sub>2</sub> emissions are generated by power plants, motor vehicle exhausts, industrial exhaust gases, and municipal heating system. Both the "Sendzimir" Metallurgical Plant and the "Skawina" one are responsible for emissions of fluorine.

Transport has significantly contributed to pollution of environment (mainly lead-related pollution). Wearing of tires and other parts of vehicles results in accumulation of Cd, Zn, Cr, and Ni near the road system (Z. Czerwiński, 1987; J. Curzydło, 1988; H.O. Wilfried et. al., 1991; I.

Bojakowska, 1994).

# GEOCHEMICAL MAPS

Sets of sampling points with known coordinates and attributed element concentrations make the basis for generation of geochemical maps. An areal (isoline type) way of element's presentation with respect to its concentration in soils was employed to prepare mono-element maps, whereas point (circular) diagrams were applied to present element contents in water sediments and surface waters.

Selection of classes to be distinguished on isoline maps was made according to results of statistical analysis of element's content distribution. A log-normal distribution was found in majority of incidents; accordingly the selection was followed according to the principle of geometric progression. As refers to generation of soil acidity (pH) maps, division of classes along with their limits were adopted from the soil sciences.

Other method of presentation (with circular diagrams) were used for maps of water sediments and surface waters.

Apart from geochemical contents, all the maps contain additional information which allows better assessment of chemical conditions in environments under study. Histograms and basic statistical parameters for soils are supported by concentration limits.

With respect to suitable standards of permissible concentrations, red contours have been used on some soil maps to mark the concentration limits. Canadian standards (8)\* European Community's standards (18), and available literature (20, 43) were suitable references. The background values were given to those elements for which the permissible concentrations occurred to be unavailable. The background values amount to threefold value of geometric mean for 10 840 samples of Polish soils (54).

Standards for permissible element concentrations in water sediments have not yet been established. Description of cartographic images for particular elements (Plates 28-49) is supported by comparison of such statistical parameters as minimum, maximum, and mean values calculated in the same way as for soils; the calculation has been based on the analyses of 12 778 water sediment samples (54). The geochemical maps of water sediments are of prime importance for assessment of natural environmental conditions. Their contents can frequently be considered the element of "early warning"; this is due to specific properties of water sediments containing substances of high ability to absorb the elements. These substances absorb significant amounts of elements (though yet undetectable in routine analyses) from waters of increased element concentrations. The maps are frequently used to locate the point sources of pollution.

Criteria applicable to permissible concentrations of some elements in surface waters of Poland, divided into three classes (73), have been placed near the map characteristics (Plates 50–69). If a given element has not been included in suitable standard, then its background in surface waters has been shown; the background values for particular elements have been based on analyses of 12 995 samples (54).

It should be remembered, when making use of the Atlas, that it presents a generalized image only. Each geochemical map is the result of mathematical operations carried out in the frame of accepted interpretation model; particulars on the map are not necessarily consistent with actual element concentration in given sampling point. Pre-

cision of representation of actual element concentrations is strongly dependent on density of observations (sampling), and consequently on the map scale. In this Atlas the sampling density was 1 sample per 1 km2 on the average. No conclusion should be drawn on degree of environmental pollution for objects, the surface area of which is inadequate with respect to map scale and density of sampling. The geochemical image as presented in the Atlas should only be considered as the signal for undertaking more detailed study and for determination of actual extent of natural or anthropogenic pollution anomalies. Detailed investigation to be conducted on a suitable scale may reveal that geochemical image is more complicated. It may happen that strongly polluted sites occur next to regions that can be placed within limits of local natural geochemical background.

# pH ACIDITY

Soils: Plate 4, Table IV

Limits of soil acidity (pH - H<sub>2</sub>O), (61):

- very acidic soils  $\leq 5$ - acidic soils > 5 -  $\leq 6$ - slightly acidic soils > 6 -  $\leq 6.7$ - neutral soils > 6.7 -  $\leq 7.4$ - alkaline soils > 7.4

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

3.2-9.5; average 6.5\*\*
4.9-9.5; average 7.2
2.1-9.7; average 5.9
2.2-9.7; average 6.2

Acidity of soils under agricultural use are under influence of both natural (geological) factors and agricultural chemistry.

The way how soil is used is the most significant factor which differentiates acidity of soils in area under study (Table 1). Very acidic soils (pH<5) occur in the entire Niepołomice Woods where they developed on highly permeable sands of aeolian origin and on peats as well. Acidic and slightly acidic soils (pH 5-6.7) occur also in the western sector of the map area. They developed on fluvial periglacial sands.

Anthropogenic factors are of decisive character for alkaline nature (pH>7.4) of majority of urban soils, and particularly – those occurring in town cities and industrial centres. Alkalization of soils is probably connected with fall-out of industrial dust which has originated at such emitters as the "Sendzimir" Metallurgical Plant, other Metallurgical Plant and the thermoelectric power station at Skawina, and the thermoelectric power station at Łeg. As concluded from mineralogic analysis of dust emission over the Cracow agglomeration, dust contains significant concentrations of calcium and magnesium compounds (W. Wilczyńska-Michalik, 1981, A. Manecki, 1993).

Studies of air pollution with dust clearly indicate that the actual dust concentration is many times higher than the permissible concentration (T.Z. Dworak et. al., 1990) despite serious limitations of dust emissions as compared with the situation in the 80's.

<sup>\*</sup> Reference number (see: References at the end of the text).

<sup>\*\*</sup> All average values are geometric mean values

|                        | Soils           |                      |                |                                |   |
|------------------------|-----------------|----------------------|----------------|--------------------------------|---|
| Degree of soil acidity | cultivated land | grassland<br>n = 197 | forest n = 124 | urban areas (total)<br>n = 183 | city areas<br>with compact<br>development<br>n = 86 |
| Very acidic            | 3.15            | 3.05                 | 76.61          | 0.55                           | 0.00  |
| Acidic                 | 18.65           | 36.04                | 14.52          | 10.93                          | 8.14  |
| Slightly acidic        | 23.15           | 17.76                | 4.84           | 9.29                           | 9.30  |
| Neutral                | 13.03           | 13.20                | 1.61           | 13.11                          | 11.63   |
| Alkaline               | 42.02           | 29.95                | 2.42           | 66.12                          | 70.93   |

# Ag SILVER

Soils: Plate 5, Table IV; ppm = mg/kg = g/t

Approximate limit values (8):

| - cultivated soils   | ≤20 |  |
|--|-----|--|
| <ul> <li>soils in city parks, recreation ares,<br/>and house building areas</li> </ul> | ≤20 |  |
| - soils in industrial and commercial building areas                                    | ≤40 |  |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow and environs     | <1- 3; average <1      |
|------------------------------------|------------------------|
| - soils in urban area of Cracow    | <1- 2; average <1      |
| - soils of Poland                  | <1-41; average <1      |
| - soils of Upper Silesia           | <1-13; average <1      |
| - cultivated soils of Upper Silesi | a < 1 - 3: average < 1 |

Content of HCl-extractable silver in soils under study is less than 1 ppm. Increased Ag concentrations (>1 ppm) are of point character and can be found in alluvial soils within the Vistula valley in the north-western sector of the map sheet.

Water sediments: Plate 28, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - water sediments of Cracow and environs | <1-13; average $<1$ |
|--|---------------------|
| - alluvium of Vistula in Cracow          | <1- 4; average 1    |
| - alluvium of Vistula                    | <1- 5; average <1   |
| - water sediments of Poland              | <1-117; average <1  |
| - water sediments of Upper Silesia       | <1-117; average <1  |

Unlikely to soils, water sediments show a visible increase of silver concentrations. Alluvia of the Vistula river within the surveyed area contain average concentrations of slightly more that 1 ppm Ag (up to 4 ppm). The highest concentrations reaching 13 ppm have been found in alluvium of the Drwina Długa which at present takes a role of canal disposing effluents from a complex of plants of building, repair, electrical, mechanical and plastic-producing types that are located at the S. Dąbek Street (northwards of the loading station on the railway line Cracow-Prokocim). There is also a Podgórze waste water treatment plant located in this area.

# AI ALUMINIUM

Soils: Plate 6, Table IV; %

Basic values for investigated area:

- soils of Cracow and environs 0.02-1.58; average 0.41 osoils in urban area of Cracow 0.10-1.41; average 0.38

Concentrations of HCl-extractable aluminium in soils are weakly differentiated and the average figure is around 0,4%. Upper Al content, in excess of 0,8%, is observed in soils of the Vistula river valley, particularly between Zabierzów and Podlesie. Minimum concentration of this element (0,2%) is found to occur in the area of the Niepołomice Woods.

Water sediments: Plate 29, Table V; %

Basic values for investigated area:

| - water sediments of Cracow     |                         |
|---------------------------------|-------------------------|
| and environs                    | 0.08-4.12; average 0.43 |
| - alluvium of Vistula in Cracow | 0.11-1.03; average 0.39 |

Average aluminium concentration (that HCl-extractable) in alluvia and other water sediments within area under study are close to each other and ranging around 0,4%, however, some regional differentiation can be observed. The highest Al content, in excess of 1%, appears mainly in water sediments of eastern sector of the map, in the Vistula valley, and in the Niepołomice Woods. In the latter there is some inverse situation with respect to soils that in this area contain the smallest Al concentrations. It is likely that the presence of increased Al concentration should be connected with conditions of acidity of the environment. Aluminium, when mobile in strongly acidic environment is in part redeposited on the water reservoir bottom in a form of hydroaluminosilicates, and in part it migrates as a delicate matter suspended in waters.

Surface waters: Plate 50, Table VI; ppm = mg/l

Approximate limit values (43, 73):

| - river waters  |          | <0.06-0.30; average 0.20 |
|-----------------|----------|--------------------------|
| - polluted rive | r waters | >2.00                    |
| - drinking wat  |          | 0.05-0.30                |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - surface waters of Cracow        |                           |
|-----------------------------------|---------------------------|
| and environs                      | <0.05-6.44; average 0.06  |
| - Vistula river in Cracow         | <0.05-0.40; average <0.05 |
| - Vistula river                   | <0.1 -0.7; average 0.1    |
| - surface waters of Poland        | <0.1 -1.2; average 0.1    |
| - surface waters of Upper Silesia | <0.1 -1.2; average 0.2    |

Very low figures characterize aluminium concentrations in surface waters of Cracow and environs (0.06 mg/l, on the average). Similarly to water sediments, only surface waters in the Niepołomice Woods contain slightly increased Al content, sometimes in excess of 1 mg/l. Most likely, aluminium originated from very fine colloidal particles of hydroaluminosilicates that are present in waters in a form of suspension (which pass through applied filter).

# As ARSENIC

Soils: Plate 7, Table IV; ppm = mg/kg = g/t

Approximate limit values (20, 43):

| - cultivated soils                   | ≤20; toxic ≥50  |
|--------------------------------------|-----------------|
| - soils in children,s play parks     | ≤20; toxic ≥50  |
| - soils in city parks and            |                 |
| recreation areas                     | ≤40; toxic ≥80  |
| - soils in house building areas      | ≤40; toxic ≥80  |
| - soils in industrial building areas | ≤50; toxic ≥200 |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow and environs      | <5- 29; average <5  |
|-------------------------------------|---------------------|
| - soils in urban area of Cracow     | <5- 29; average <5  |
| - soils of Poland                   | <5-3444; average <5 |
| - soils of Upper Silesia            | <5- 238; average <5 |
| - cultivated soils of Upper Silesia | <5- 95; average <5  |

On the average, arsenic content in soils of Cracow and environs is low and only occasionally exceeds 5 ppm. In the cartographic representation the Vistula valley with its soils and the "Sendzimir" Metallurgical Plant are clearly exposed as the areas with increased As concentrations (>10 ppm).

Water sediments: Plate 30, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - water sediments of Cracow        |                     |
|------------------------------------|---------------------|
| and environs                       | <5- 119; average <5 |
| - alluvium of Vistula in Cracow    | <5- 67; average 5   |
| - alluvium of Vistula              | <5- 43; average <5  |
| - water sediments of Poland        | <5-6215; average <5 |
| - water sediments of Upper Silesia | <5- 915; average 6  |

Arsenic content in water sediments in the study area is very poor (av. <5 ppm). Higher concentrations are only observed in alluvia of small water-courses in the Niepolomice Woods area (up to 119 ppm). It is clearly visible that increased As content is well correlated with increased concentrations of Al, Be, and V, and very high iron concentration (frequently exceeding 10%). Paragenesis of these elements results from very acidic environment that leads to accumulation of iron and aluminium hydroxides of high ability to absorb some elements from surrounding environment.

Surface waters: Table VI; ppb = µg/l

Classes of surface waters purity (73):

Basic values for investigated area:

| - s | surface waters of Cracow and environs | 1-44; average 1.4 |
|-----|---------------------------------------|-------------------|
| - 1 | Vistula river in Cracow               | 1- 4: average 1.4 |

Arsenic in surface waters occurs in low concentrations that relatively occasionally exceed 2  $\mu$ g/l. Increased As content (20 and 36  $\mu$ g/l) was found in waters of two small reservoirs near the Plant of Inorganic Industry at Bonarka. As in water sediments, also waters of water-courses in the Niepolomice Woods area show increased arsenic content (up to 44  $\mu$ g/l).

# **B BORON**

Surface waters: Plate 52, Table VI; ppm = mg/l

Classes of surface waters purity (73):

#### I-III ≤1

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - surface waters of Cracow        |                           |
|-----------------------------------|---------------------------|
| and environs                      | <0.03- 6.73; average 0.10 |
| - Vistula river in Cracow         | 0.05- 0.63; average 0.26  |
| - Vistula river                   | <0.02- 0.80; average 0.17 |
| - surface waters of Poland        | <0.02-12.87; average 0.04 |
| - surface waters of Upper Silesia | <0.02- 7.92; average 0.09 |

Geochemical background of boron in the area under study is low (av. 0.10 mg/l). Only three samples occurred to contain boron in amount exceeding the limit of first purity class applicable to surface waters (1 mg/l). Waters of the Vistula river in the study area exhibit slightly increased concentrations of this element. Some regions are noted here due to increased boron concentrations: the area of metallurgical plant at Skawina (up to 6,73 mg/l), small ponds near chemical plant at Łagiewniki (up to 1.20 mg/l), small unnamed water-course near poultry farm at Bronowice (up to 1.91 mg/l), and small water-courses in the Bochnia area (up to 0.61 mg/l)

# Ba BARIUM

Soils; Plate 8, Table IV; ppm = mg/kg = g/t

Approximate limit values (8):

| The first of the second | P.111 |
|--|-------|
| - cultivated soils   | ≤750  |
| - soils in city parks and  |       |
| in house building areas  | ≤500  |
| - soils in industrial building areas   | ≤2000 |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| _ | soils of Cracow and environs  | 3- 426; average 50  |
|---|-------------------------------|---------------------|
| - | soils in urban area of Cracow | 10- 426; average 57 |
| _ | soils of Poland               | <1-1777; average 32 |
| _ | soils of Upper Silesia        | 2-1777; average 54  |

There is weak differentiation in cartographic representation of barium content in soils (from 3 to 70 ppm); however, two distinct environments can be distinguished. Soils that development on Holocene alluvia of the Vistula river make the first environment with markedly increased barium concentrations; the second environment is formed on acid and very acid soils of the Niepołomice Woods, with very poor Ba content (av. 22 ppm). The average barium concentration in cultivated soils in the vicinity of Cracow (47 ppm) is slightly increased in comparison to the average for soils in the entire area of Poland (32 ppm). The increase of Ba content is soils under study results from dominant position of clayey soils.

Water sediments: Plate 31, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - | water sediments of Cracow        |                    |     |
|---|----------------------------------|--------------------|-----|
|   | and environs                     | 10- 553; average   | 75  |
|   | alluvium of Vistula in Cracow    | 33- 287; average 1 | 102 |
| _ | alluvium of Vistula              | 9- 437; average    | 76  |
| _ | water sediments of Poland        | <1-1794; average   | 52  |
| _ | water sediments of Upper Silesia | 3-1794; average    | 93  |

The average barium content in water sediments in area covered by this study is poorly differentiated. Increased Ba content is a characteristic feature of alluvia in the Vistula river (av. 102 ppm) and the Drwinka river as well (av. 97 ppm), while the lowest content characterizes alluvia of the Wilga (av. 31 ppm) and the Raba rivers (av. 35 ppm). Frequently, small water-courses and small interior reservoirs exhibit differences in Ba content. The cartographic representation displays, similarly to soils, increased barium concentrations in alluvia of those water-courses that drain washes of the Vistula valley.

Surface waters; Plate 53, Table VI; ppb = µg/l

Approximate limit values (8, 43):

| - | river waters          | 10- 100  |
|---|-----------------------|----------|
| - | polluted river waters | ≤450     |
| - | drinking water        | 500-1500 |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| surface waters of Cracow     and environs | 8- 559; average  | 59  |
|---|------------------|-----|
| - Vistula river in Cracow                 | 60- 151; average | 104 |
| - Vistula river                           | 32-1254; average | 90  |
| - surface waters of Poland                | ≤1-3470; average | 55  |
| - surface waters of Upper Silesia         | 2-3470; average  | 87  |

Barium concentrations in waters of Cracow and environs are representative for surface waters (around 50  $\mu$ g/l). In general, there is poor differentiation of Ba background in surface waters; however, waters of the Vistula and some water-courses that drain its valley can be distinguished due to increased Ba concentrations. Maximum Ba content has been found in water of small pond situated near the aluminium metallurgical plant at Skawina (554  $\mu$ g/l).

A comparison can be made here with some foreign data. As reported by I. Rejniewicz (1994), surface waters in the Netherlands contain barium in the range of 48–121 μg/l which is considered natural concentration. A survey of surface waters in Great Britain (P.R. Simpson et al., 1993) revealed barium concentration between 8 and 50 μg/l. Increased concentrations were confined only to such areas where a significant role in substratum was played by carbonate rocks.

#### Be BERYLLIUM

Soils: Plate 9, Table IV; ppm = mg/kg = g/t

Basic values for investigated area:

- soils of Cracow and environs <0.5-17.0; average <0.5
- soils in urban area of Cracow <0.5-17.0; average <0.5

Beryllium in soils of investigated area occurs in very low concentrations (av. 0.5 ppm); in addition, its appearance is connected with poor differentiation. Only two small anomalies (>4.0 ppm) have been recorded: in the centre of the city of Cracow and in Wieliczka.

Water sediments: Plate 32, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - water sediments of Cracow        |                         |
|------------------------------------|-------------------------|
| and environs                       | <0.5-11.4; average 0.5  |
| - alluvium of Vistula in Cracow    | <0.5- 0.9; average <0.5 |
| - alluvium of Vistula              | <0.5- 1.1; average <0.5 |
| - water sediments of Poland        | <0.5-21.0; average <0.5 |
| - water sediments of Upper Silesia | <0.5-19.9; average 0.6  |

The cartographic representation shows increased Be content (up to 11.4 ppm) in water sediments in the Nie-połomice Woods area. Increased concentrations frequently >1 ppm can also be found in alluvia of the Drwinka river which collects water from a large part of the Woods. It is likely that strongly acid environment in this area is conductive to setting Be in motion first, then to its sorption by clay minerals. Such situation is indicated by distinct correlation of beryllium with aluminium extractable in HCl.

Dust produced by coal burning at the metallurgical, energetic, and chemical plants of the urban-industrial Cracow agglomeration is an additional source of beryllium. As concluded from data quoted by A. Kabata-Pendias and H. Pendias (1979), beryllium concentration in hard coal is ranging from 0.1 to 31.0 ppm whereas flue dust from a power plant can contain Be in as high concentration as 45.0 ppm.

# C ORGANIC CARBON

Soils: Plate 10, Table IV, %

Basic values for investigated area:

| - soils of Cracow and environs  | <0.01-40.19; average | 1.77 |
|---------------------------------|----------------------|------|
| - soils in urban area of Cracow | <0.21- 8.27; average | 1.53 |
| - forest soils                  | 0.48-40.19; average  |      |

Abundance of organic carbon in soils of investigated area is visibly diversified. Content of this element over large area does not exceed 2%. This figure is consistent with amount of organic carbon in soil samples collected from the Planty green belt in Cracow; it is ranging from 0.2 to 4.5% (T. Komornicki, 1986; T. Komornicki, K. Oleksynowa, 1989).

Higher concentrations (>2%) occur above all in soils that have developed on Holocene alluvial formations occurring mainly in the Vistula valley and forest soils of the Niepolomice Woods. In the latter, organic carbon concentrations frequently exceed 8%. High organic carbon content is also observed in soils occupying the "Sendzimir" Metallurgical Plant area.

#### Ca CALCIUM

Soils: Plate 11; Table IV; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow and environs  | 0.01-11.40; average 0.32  |
|---------------------------------|---------------------------|
| - soils in urban area of Cracow | 0.01- 9.85; average 0.56  |
| - soils of Poland               | <0.01-25.45; average 0.17 |
| - soils of Upper Silesia        | <0.01-13.47; average 0.23 |

0.01-11.40% is the range of average calcium content in soils under present study. Distribution of this element is governed by two factors: a geological one and an economic activity.

Above all, Ca content in excess of 1% is observed in soils that have developed on Jurassic carbonate formations occurring near Zabierzów, Wola Justowska, Bielany, Podgórki, and Dębniki in the western sector of the map. Also, soils on loesses in the north part of the surveyed area contain calcium in higher concentrations.

High Ca content (>1%) in urban soils in Cracow, Wieliczka, and Bochnia should be connected with anthropogenic factor. This is particularly visible in the "Sendzimir" Metallurgical Plant area where Ca content fre-

quently exceeds 4%. This anthropogenic factor is also expressed by twofold increase of calcium content in urban soils (lawns, parks, allotment gardens, fallows) as compared with Ca content in cultivated soils. Enrichment of urban soils with calcium is likely connected with the fall-out of industrial dust mostly originated from coal burning. It is estimated that annual emission of calcium in industrial dust over Cracow agglomeration is around 4780 t (E. Garścia, K.P. Zając, 1982).

Particularly low Ca content is that in the forest soils (av. 0.07%).

#### Water sediments: Plate 33, Table V, %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
alluvium of Vistula in Cracow
alluvium of Vistula
water sediments of Poland
water sediments of Upper Silesia
0.04-16.75; average 0.93
0.34- 1.92; average 0.83
0.09-31.95; average 1.38
<0.01-43.15; average 0.84</li>
0.02-26.55; average 0.71

The Niepołomice Woods area is that one which, in the calcium distribution pattern, shows particularly low Ca content (<0.75%). Alluvia of the Vistula river are also of low Ca content (av. 0.83%). The maximum values, exceeding average content of 2%, have been found in alluvia of the Pradnik and Dłubnia rivers. It is generally observed that alluvia of bigger rivers and streams contain more calcium than alluvia and sediments of both small water-courses and water reservoirs.

#### Surface waters: Plate 54, Table VI, ppm = mg/l

Approximate limit values (88):

- surface waters as the drinking water supply 100

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- surface waters of Cracow
and environs

- Vistula river in Cracow

- Vistula river

- surface waters of Poland

- surface waters of Upper Silesia

- surface waters of Upper Silesia

- surface waters of Upper Silesia

8- 554; average 95
51- 152; average 96
14- 199; average 87
3-6400; average 83

Surface waters of the area under study contain calcium in poorly differentiated amounts; on the average, calcium content is around 100 mg/l. Higher concentrations have been found only in the area with outcrops of Jurassic limestones (between Kobierzyn and Dębniki) and in waters of the Kościelnicki Stream.

#### Cd CADMIUM

Soils: Plate 12, Table IV; ppm = mg/kg = g/t

Approximate limit values (18, 20, 43):

- cultivated soils
- soils in children's play parks
- soils in city parks and recreation areas
- soils in house building areas
- soils in industrial building areas

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow and environs  | <0.5- 68.4; average 0.7  |
|---------------------------------|--------------------------|
| - soils in urban area of Cracow | <0.5- 27.3; average 0.6  |
| - soils of Poland               | <0.5-253.3; average <0.5 |
| - soils of Upper Silesia        | <0.5-253.3; average 1.4  |

The average cadmium content (0.7 ppm) in soils of the area covered by this project is slightly higher than that dealing with soils of the remaining part of Poland. Results of investigation carried out on cultivated soils (H. Terelak et al., 1995) have shown identical average cadmium concentration (0.74 ppm) in soils of the Cracow province. Slightly increased concentration (1.05 ppm) for soils in the cultivated land areas has been reported by F. Gambuś (1993).

Against low cadmium background, distinct soil anomalies with respect to cadmium have been distinguished in the city of Cracow and in Nowa Huta, with their maximum in the Podgórze region and in soils within the "Sendzimir" Metallurgical Plant. These anomalies are of anthropogenic character, representative for areas strongly urbanized and industrialized. Unfavourable is the fact that soils in the Cracow region have large potential to accumulate cadmium; this negative feature of soils emerges from their origin since they have developed from loesses and loess-like formations and contain large amount of free calcium carbonate. As concluded from F. Gambuś and E. Gorlach's work (1995), over 60% of soils in Cracow region exhibit very high ability to absorb cadmium.

A serious problem exists which deals with cadmium-related pollution (and of other elements too) of alluvial soils in the Vistula valley, in particular along its tract between Niepołomice and Nowe Brzesko. As shown on the cartographic representation, areal extent of soils with increased cadmium content coincides with the occurrence of Holocene alluvial formations (Plate A). Maximum concentrations, in excess of permissible content in cultivated soils, are observed to occur in soils between flood banks. Waters flowing from the area of Zn-Pb ore deposits in Upper Silesia and their alluvia are the sources of pollution mentioned above. Considerable participation of soils with tolerable Cd content (in the range of 1-5 ppm) and toxic concentrations (>5 ppm) in the case of grassland soils (Table 2) results from the fact that grasslands in the Vistula valley occupy the most polluted alluvial soils. Pollution of soils in the Vistula valley is of prime importance and requires that a detailed study by conducted.

Table 2
Amount of soil samples under study with respect to degree of pollution and land use; for cadmium (in %)

|                                |                               | Soils                |                   |  |
|--------------------------------|-------------------------------|----------------------|-------------------|--|
| Degree<br>of soil<br>pollution | cultivated<br>land<br>n = 445 | grassland<br>n = 197 | forest<br>n = 124 |  |
| Permissible                    | 87.87                         | 71.57                | 82.26             |  |
| Tolerable                      | 11.91                         | 20.82                | 17.74             |  |
| Toxic                          | 0.22                          | 7.61                 | 0.00              |  |

Water sediments: Plate 34, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - water sediments of Cracow        |           |                 |     |
|------------------------------------|-----------|-----------------|-----|
| and environs                       | < 0.5-    | 47.1; average   | 1.1 |
| - alluvium of Vistula in Cracow    |           | 47.1; average   |     |
| - alluvium of Vistula              | < 0.5-    | 109.5; average  | 2.5 |
| - water sediments of Poland        | <0.5-8    | 3736.0; average | 0.6 |
| - water sediments of Upper Silesia | < 0.5 - 8 | 3736.0; average | 2.8 |

Water sediments in investigated area contain cadmium in concentrations ranging from <0.5 to 47.1 ppm (av. 1.1 ppm.). Alluvia of the Vistula river are distinguished from among other water sediments due to high Cd content reaching 47.1 ppm. Undoubtedly, cadmium-related pollution of alluvia of this river originates in Upper Silesia. Cadmium-related pollution of the Vistula's sediments was a subject of E. Helios-Rybicka's (1993, 1994) and E. Helios-Rybicka and M. Wardas' studies (1989, 1993). Particularly interesting in this studies was a valley tract between confluence of Przemsza and Cracow. Both authoresses focussed on a sediment fraction less than 63 μm, in which cadmium concentration could be as high as 115 ppm.

The presence of increased cadmium concentrations is also noted in a number of small water-courses (usually unnamed); however, cadmium origin is difficult to determine. It is not excluded that cadmium in these water-courses originate in small plants (such as galvanizing plants, for example). Alluvia of bigger rivers contain not large amounts of cadmium. The Raba river can be given here as the example, as cadmium content in its alluvia is of the order of 0.5–0.6 ppm. Explanation is required why alluvia of small water-courses in the area of the Niepołomice Woods are cadmium enriched (up to several ppm).

Surface waters: Plate 55, Table VI; ppb = µg/l

Classes of surface waters purity (73):

I ≤5 II >5 - ≤30 III >30 - ≤100

Basic values for investigated area, Poland (54) and Upper Silesia (53):

surface waters of Cracow and environs
Vistula river in Cracow
Vistula river
Vistula river
surface waters of Poland
surface waters of Upper Silesia
3-238; average <3</li>
3-238; average <3</li>

It is a very rare case that cadmium content in surface waters is in excess of 3  $\mu$ g/l (detectability limit). Individual water samples with slightly higher concentrations have been collected from small water-courses in the area of the Niepołomice Woods.

# Co COBALT

Soils: Plate 13, Table IV; ppm = mg/kg = g/t

Approximate limit values (8, 43):

- cultivated soils ≤30
- soils in city parks and in house building areas ≤50
- soils in industrial and commercial building areas ≤300

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia
- soils of Cracow and environs
- <1-36; average 3.4

A mobile portion of cobalt, that HCl-extractable, exists in low concentrations in soils of the surveyed area; the range of concentration is between <1 and 36 ppm. However, some regional differentiation can be observed. Increased Co content has been found in soils that developed in alluvial sediments of the Vistula and the Raba valleys and in soils covering the area of the "Sendzimir" Metallurgical

Plant. A compact area with very low Co concentrations in forest soils occurs in the Niepołomice Woods.

Water sediments: Plate 35, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
alluvium of Vistula in Cracow
alluvium of Vistula
water sediments of Poland
water sediments of Upper Silesia
41- 64; average 4
2- 12; average 6
1- 14; average 5
<1-357; average 3</li>
<1-164; average 4</li>

Differentiation of cobalt in water sediments is poor. Scarce points with increased Co content (>16 ppm) have been grouped mainly within the left drainage basin of the Drwinka river and the drainage basin of the Raba river as well. Frequently, increased Co content is associated with increased or high content of iron, phosphorus, and manganese. This may indicate that in acid environment these elements can concentrate in natural way. Undoubtedly, two cases of high Co content (64 ppm) in alluvium of the Malinówka river near waste dumping site at Barycz and in alluvium of small water-course near to a marshalling station Cracow—Batowice (36 ppm) are of anthropogenic origin.

Surface waters: Table VI; ppb =  $\mu g/l$ ).

Approximate limit values (43):

- river waters 0.04-8.00 - drinking water 0.01-0.13

Basic values for investigated area, Poland (54) and Upper Silesia (53):

surface waters of Cracow and environs
 Vistula river in Cracow
 Vistula river
 Vistula river
 surface waters of Poland
 surface waters of Upper Silesia
 surface waters of Upper Silesia

The majority of surface water samples contained cobalt in concentrations less than detectability limit of adopted analytical method (5  $\mu$ g/l). Only four water samples contained cobalt in higher concentrations, from 8 to 33  $\mu$ g/l; all were collected in the Drwinka river drainage basin. Maximum concentration was noted for a small pond in the forest. Origin of cobalt is considered to be of similar nature as in the case of alluvia.

# Cr CHROMIUM

Soils: Plate 14, Table IV; ppm = mg/kg = g/t

Approximate limit values (20, 43):

cultivated soils
soils in children's play parks
soils in city parks and recreation areas
soils in house building areas
soils in industrial building areas
≤100; toxic ≥250
≤150; toxic ≥600
≤100; toxic ≥350
≤200; toxic ≥800

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

- soils of Cracow and environs
- 198; average 8
- 1- 1873; average 4
- 95; average 5

Content of HCl-extractable chromium in soils of investigated area is low and usually does not exceed 10 ppm: similar situation deals with entire Poland's territory. Higher Cr concentrations (sometimes >80 ppm) occur in alluvial soils of the Vistula valley (mainly eastwards of Cracow) and in the Raba river valley. In part, chromium originates from erosion of those rocks in southern Poland that are chromium-rich (J. Lis, A. Pasieczna, 1995b). More abundant in chromium are also urban soils in the suburb of Podgórze and in the area of the "Sendzimir" Metallurgical Plant. Origin of these high concentrations is undoubtedly anthropogenic. Cr concentrations in dusts emitted by the metallurgical plant usually reach a rate of several hundred ppm; dust from some divisions of the same plant can contain as much as 1630 ppm Cr (W. Wilczyńska-Michalik, 1981).

Water sediments: Plate 36, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
alluvium of Vistula in Cracow
alluvium of Vistula
water sediments of Poland
water sediments of Upper Silesia
water sediments of Upper Silesia

Areal distribution of chromium in water sediments in the study area is similar to that in soils. Increased Cr concentrations, mostly of natural origin, occur in alluvia of the Vistula river as well as alluvia of streams that drain alluvial sediments of both the Vistula and the Raba rivers. It is quite sure that of anthropogenic origin are high Cr concentrations in sediments of water-courses draining areas of the "Sendzimir" Metallurgical Plant, chemical Plant at Bonarka, and a complex of industrial plants located to the north of railway Station Cracow-Prokocim (the Drwina Długa river). The maximum Cr content was noted in alluvia of the upper Drwinka (up to >300 ppm) near a tannery at Niepołomice. As concluded from E. Helios-Rybicka and M. Wardas' work (1989), increased chromium concentrations in sediments of the upper Vistula (in fraction <63 µm) are almost entirely connected with a ferruginous phases of the sediment.

Surface waters: Plate 56, Table VI; ppb = µg/l

Classes of surface waters purity (73):

I ≤50 II >50 -≤100

Basic values for investigated area, Poland (54) and Upper Silesia (53):

With respect to chromium concentration, almost all waters of the area under consideration fall in the first purity class (4  $\mu$ g/l). Only individual water samples may contain slight increased concentrations of this element.

# Cu COPPER

Soils: Plate 15, Table IV; ppm = mg/kg = g/t

Approximate limit values (20, 43):

| - cultivated soils                                     | 50-150; toxic ≥200 |
|--|--------------------|
| - soils in children's play parks                       | ≤50; toxic ≥250    |
| - soils in city parks and recreation areas             | ≤200; toxic ≥600   |
| <ul> <li>soils in house building areas</li> </ul>      | ≤50; toxic ≥200    |
| <ul> <li>soils in industrial building areas</li> </ul> | ≤200; toxic ≥2000  |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

Geochemical background of copper falls in the range of 1-20 ppm. As refers to soils with poor Cu content, they mainly occur in the western sector of the map where carbonate rocks of Jurassic age outcrop between Bielany and Zabierzów. Forest soils of the Niepołomice Woods make another region of low Cu concentrations. Soils with increased copper concentrations, sometimes in excess of permissible limit for soils (>80 ppm), are observed in urban soils of Cracow (at Borek Fałęcki, Podgórze) as well as in soils in industrial area of the "Sendzimir" Metallurgical Plant. Results of studies carried out by other authors are close to present observations. Analysis of soils from the immediate vicinity of the "Sendzimir" Plant revealed copper concentration to be in the range of 11.2-20.7 ppm (J. Curzydło, 1995). Average copper content in soils of cultivated land has been defined around 12.0 ppm, with its range from 2.2 to 44.5 ppm (F. Gambuś, 1993). Distribution of copper in soil profiles of the Cracow region (E. Gorlach et. al., 1993) indicate a substratum as the source of this element. Soil samples collected from depth interval 0.0-1.5 m revealed that copper content increased with depth. These results did not appear to be dependent on type of soils.

Soils of grassland in the Vistula valley are also of increased copper content. They constitute around 4% of samples under study (Table 3).

Table 3
Amount of soil samples under study with respect to degree of pollution and way of land use; for cooper (in %)

|                                | Soils                         |                      |                   |  |
|--------------------------------|-------------------------------|----------------------|-------------------|--|
| Degree<br>of soil<br>pollution | cultivated<br>land<br>n = 445 | grassland<br>n = 197 | forest<br>n = 124 |  |
| Permissible                    | 100.00                        | 95.54                | 100.00            |  |
| Tolerable                      | 0.00                          | 4.46                 | 0.00              |  |
| Toxic                          | 0.00                          | 0.00                 | 0.00              |  |

Worthy of comparing are the results of soils survey in agglomeration of Hamburg, conducted by W. Lux (1993). Applying similar method of sample extraction (using HCl), the author found that surficial soil layer (0–5 cm) contained copper in the range of 2–3688 ppm (av. 103 ppm). The average of copper content in urban soils of Warsaw was found to be 17 ppm (J. Lis, 1991, 1992). This element in urban soils in Belorussia appears, on the average, in following concentrations: 9.5 ppm in Brest, 16 ppm in Grodno and Vitjabsk, and 15 ppm at Gomel (W.K. Łukaszew, Ł. Okuń, 1991).

Water sediments: Plate 37, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
 alluvium of Vistula in Cracow
 alluvium of Vistula
 water sediments of Poland
 water sediments of Upper Silesia
 2- 1231; average 18
 14- 126; average 23
 1- 419; average 23
 1- 15 460; average 8
 water sediments of Upper Silesia

The geochemical background of copper in water sediments of investigated area is relatively low (av. 18 ppm). Alluvia of the Vistula river make the area where copper occurs at higher and equalized level of concentrations (av. 53 ppm). Such equalized concentrations may prove that copper in alluvia of the Vistula river originates in part from local sources, but its main source is related to erosion of rocks in southern Poland and Upper Silesia area of high industrial development. Undoubtedly, numerous point anomalies of Cu, situated in industrial plants, are of anthropogenic origin. The most characteristic is an anomaly in alluvia of the Drwina Długa; at present this river is utilized as a canal through which waste waters are disposed from a complex of industrial plants located northwards of the railway station Cracow-Prokocim. Copper content reaches a rate of up to 402 ppm here. The highest Cu concentration (1231 ppm) was also noted here, namely in sediments of a canal flowing into the Drwina Długa (the canal runs in an immediate vicinity of the "Podgórze" sewage treatment plant). A ditch near settling ponds belonging to former "Solvay" soda processing plant is the place where copper was noted at the rate of 282 ppm. Concentrations of up to 161 ppm were recorded in sediments of canals in the vicinity of the "Sendzimir" Metallurgical Plant. Outside Cracow, abnormal Cu content (in the range of 61-108 ppm) was noted in alluvia of the upper Drwinka near Niepołomice. Copper in alluvia is associated here with a high chromium concentration which suggests that a tannery has to be a pollution source.

## Fe IRON

Soils: Plate 16, Table IV; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

- soils of Upper Silesia

0.02-9.13; average 0.77
0.18-3.48; average 0.74
<0.01-9.57; average 0.50
<0.01-5.06; average 0.56

The geochemical background of iron in soils is ranging between 0.5 and 1.5%. As shown on the histogram, popula-

tion of small iron content deals mainly with forest soils where average Fe content is of the order of 0.35%. Fe concentrations in alluvial soils in the Vistula valley and in soils covering the "Sendzimir" Metallurgical Plant are higher than the average values. Such situation is reflected by average Fe content in soils of industrial areas, which is equal to 1.17% (Table IV). Clearly visible increased iron concentrations (1.09–3.63%) in soils around Nowa Huta have also been noted in the K. Tymińska-Zawora and M. Trafas' work (1982). Both authoresses are of the opinion that the increase of iron concentrations is most visible in soils occurring to the south of Nowa Huta (on low terraces of the Vistula).

High Fe concentrations, in excess of 2%, have also been noted in soils occurring in extended peatbog near locality of Błoto in the western part of the Niepołomice Woods. This anomaly may be connected with accumulation of iron in the form of bog iron ore.

Water sediments: Plate 38, Table V; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
alluvium of Vistula in Cracow
alluvium of Vistula
water sediments of Poland
water sediments of Upper Silesia
0.15-27.38; average 1.34
0.76- 2.92; average 1.51
0.22- 3.18; average 1.11
<0.01-31.14; average 0.75</li>
0.03-26.43; average 1.01

Average Fe content in water sediments approximates to 1%. Higher concentrations (3%) are related to alluvia of small water-courses in the area of the Niepołomice Woods; this fact is connected with very acid character of the environment in this region. Maximum concentrations in alluvia are frequently in excess of 10% or even 20% Fe. High iron concentrations are frequently followed by high manganese content.

Surface water: Plate 57, Table VI; ppm = mg/l

Classes of surface waters purity (73):

 $\begin{array}{ccc} I & \leq 1.0 \\ II & > 1.0 - \leq 1.5 \\ III & > 1.5 - \leq 2.0 \\ \end{array}$ 

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- surface waters of Cracow and environs

- Vistula river in Cracow

- Vistula river

- Vistula river

- Surface waters of Poland

- Surface waters of Upper Silesia

- Surface waters of Surface waters in the study area contain

Table 4 Amount of surface water samples under study in particular classes of water purity with respect to iron (in %)

| Purity<br>class     | The Vistula river n = 49 | Rivers* and bigger streams n = 92 | Streams<br>n = 75 | Small water<br>courses<br>(streams, ditches)<br>n = 196 | Small closed<br>water bodies<br>(ponds, ditches)<br>n = 44 |
|---------------------|--------------------------|-----------------------------------|-------------------|---|--|
|                     | 98.00                    | 93.48                             | 88.00             | 75.51   | 88.63  |
| 11                  | 2.00                     | 4.35                              | 5.33              | 7.14  | 2.27   |
| III                 | 0.00                     | 0.00                              | 2.67              | 2.04  | 4.55   |
| Below all standards | 0.00                     | 2.17                              | 4.00              | 15.31   | 4.55   |

<sup>\*</sup> without the Vistula river

iron in concentrations consistent with criteria applicable to the first purity class (<1 mg/l - Table 4). The main region where strongly ferruginous waters occur is the Niepołomice Woods. A frequent fact is that waters in this area (belonging to drainage basins of the Raba and the Drwinka rivers) contain excessive iron concentrations which classifies them among waters below standards. Apart from numerous samples with iron content >10 ppm, maximum concentration (of 213.5 mg/l) was recorded for a small water-course in the drainage basin of the Raba river.

Outside this region, increased Fe concentrations have been found in individual points only; some of these points sometimes contain iron in concentrations in excess of criteria applicable to first and second water purity classes.

# Hg MERCURY

Soils: Plate 17, Table IV; ppm = mg/kg = g/t

Approximate limit values (18, 20, 43):

| - cultivated soils                         | 1-2; toxic ≥10  |
|--|-----------------|
| - soils in children's play parks           | ≤0.5; toxic ≥10 |
| - soils in city parks and recreation areas | ≤5; toxic ≥15   |
| - soils in house building areas            | ≤2; toxic ≥20   |
| - soils in industrial building areas       | ≤10; toxic ≥50  |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow and environs  | <0.05-3.13; average | 0.05   |
|---------------------------------|---------------------|--------|
| - soils in urban area of Cracow | <0.05-1.38; average | 0.06   |
| - soils of Poland               | <0.05-7.55; average | < 0.05 |
| - soils of Upper Silesia        | <0.05-4.00; average | 0.08   |

Average mercury content in soils of Cracow and environs is in the low range of <0.05 to 3.13 ppm; on the average it is equal to 0.05 ppm. Urbanization is of insignificant influence on the mercury content. Slight increased Hg concentration is a characteristic feature of soils in street lawns (av. 0.09 ppm). Soils in the Vistula river, particularly those occurring in the eastern sector of the map, clearly deviate the cartographic pattern of mercury distribution. Alluvial soils occurring between the flood banks are the most mercury-rich soils; frequently, mercury content is in excess of 2 ppm here. These soils are used mainly as a grassland area (Table 5). The origin of mercury is of anthropogenic nature, and contemporary waters of the Vistula river make the source of this pollution.

Table 5

Amount of soil samples under study with respect to degree of pollution and way of land use; for mercury (in %)

|                                | Soils                         |                      |                   |  |
|--------------------------------|-------------------------------|----------------------|-------------------|--|
| Degree<br>of soil<br>pollution | cultivated<br>land<br>n = 445 | grassland<br>n = 197 | forest<br>n = 124 |  |
| Permissible                    | 99.78                         | 95.43                | 100.00            |  |
| Tolerable                      | 0.22                          | 4.57                 | 0.00              |  |
| Toxic                          | 0.00                          | 0.00                 | 0.00              |  |

Some data related to the area of Warsaw and its anomaly with respect to mercury is given here for comparison; the Warsaw anomaly has been distinguished due to Hg concentration of 2 ppm. Occassionally, some points are recorded here with as high Hg concentration as 10.78 ppm (J. Lis; 1992).

Soils in industrial quarters and parks of Berlin are cha-

racterized by average Hg content of the order of 0.17 ppm whereas the Berlin's agricultural surrounding – by average Hg content of 0.06 ppm (M. Birke, U. Rauch, 1994).

Water sediments: Plate 39, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - water sediments of Cracow        |            |       |         |        |
|------------------------------------|------------|-------|---------|--------|
| and environs                       | < 0.05 -   | 3.60; | average | 0.10   |
| - alluvium of Vistula in Cracow    | 0.23-      | 1.79; | average | 0.77   |
| - alluvium of Vistula              | < 0.05 -   | 2.15; | average | 0.14   |
| - water sediments of Poland        | < 0.05 - 1 | 1.00; | average | < 0.05 |
| - water sediments of Unper Silesia | <0.05-1    | 0 50  | average | -0.05  |

Alluvia of the Vistula distinguished themselves among other water sediments of the surveyed area due to high Hg concentrations (from 0.23 to 2.15 ppm; av. 0.77 ppm). As much as 17 samples out of 43 contain mercury in concentrations exceeding 1 ppm. Visibly high Hg concentrations are noted in alluvia of the Vistula river eastwards of Cracow. It seems likely that to some extent the increased mercury concentrations are under influence of sewage and industrial effluents of the city and those industrial effluents that are produced at the "Sendzimir" Metallurgical Plant. Effect of effluent disposal is reflected by high Hg concentrations (from 1.57 to 2.21 ppm) in the sediments of the Drwina Długa river which disposes effluents from industrial area situated to the north of a railway station Cracow-Prokocim; similarly high concentrations are noted in sediments in canals running down from the "Sendzimir" Plant and flowing into the Dłubnia river (concentrations of up to 1.28 ppm) and the Vistula (concentrations of up to 3.60 ppm). Explanation is needed of high mercury concentration (3.31 ppm) in a ditch at Bieda Duża (to the north of Bochnia, at the margin of the Niepołomice Woods). Alluvia of the Raba river are known among bigger rivers of the area due to the smallest concentrations (av. <0.05 ppm).

A monitoring survey was conducted from 1991 to 1993 (I. Bojakowska, G. Sokołowska, 1994) on alluvia of bigger rivers of the Cracow region; the survey allowed to determine Hg content ranging from 0.01 to 1.94 ppm. Observations concluded from monitoring of similar alluvia of the Elbe river revealed that sediment fraction <60 µm can contain mercury up to the rate of 15.5 ppm (J. Vesely, 1991).

# K POTASSIUM

Surface waters: Plate 58, Table VI; ppm = mg/l

Classes of surface waters purity (73):

$$\begin{array}{ccc} I & \leq 10 \\ II & > 10 - \leq 12 \\ III & > 12 - \leq 15 \end{array}$$

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - surface waters of Cracow        |                     |    |
|-----------------------------------|---------------------|----|
| and environs                      | <0.5-178.1; average | 7  |
| - Vistula river in Cracow         | 5.3- 28.5; average  | 12 |
| - Vistula river                   | 2- 92; average      | 11 |
| - surface waters of Poland        | <1-473; average     | 5  |
| - surface waters of Upper Silesia | <1-473; average     | 8  |

Surface runoff is the main factor which controls potassium content in surface waters of the surveyed area. This is evidenced by varied participation of samples that have been

Amount of surface water samples under study in particular classes of water purity with respect to potassium (in %)

| Purity<br>class     | The Vistula river n = 49 | Rivers*<br>and bigger<br>streams<br>n = 92 | Streams<br>n = 75 | Small water<br>courses<br>(streams, ditches)<br>n = 196 | Small closed<br>water bodies<br>(ponds, ditches)<br>n = 44 |
|---------------------|--------------------------|--|-------------------|---|--|
|                     | 24.49                    | 86,16                                      | 72.00             | 63.27   | 52.28  |
| II                  | 10.21                    | 4.63                                       | 5.33              | 5.10  | 11.36  |
| III                 | 36.73                    | 2.46                                       | 1.33              | 6.63  | 2.27   |
| Below all standards | 28.57                    | 6.75                                       | 21.34             | 25.00   | 34.09  |

<sup>\*</sup> without the Vistula river

classified among suitable water quality classes (Table 6) with respect to type of water reservoir. River waters (the Vistula river excluded) are mostly of I purity class; share of waters below standards in river waters approximates 6.75%. High share of waters below standards is a characterisation feature of waters below streams and small interior water reservoirs. The latter can contain potassium-rich water as the result of evaporation; potassium fertilizers applied in agriculture are likely the source of potassium.

Significantly polluted with potassium are waters of the Vistula river; only 24.49% of samples fall into I quality class while as much as 28.57% – into waters below standards. Waters flowing down from the Upper Silesian area are likely a source of such high concentrations, as they are enriched with potassium due to brine disposal (J. Lis, A. Pasieczna, 1995a).

Local point sources of potassium-related pollution are the reason why very high K concentrations have been noted in a pond situated close to fattening farm at Kobierzyn (143.2 mg/l), a pond near aluminium smelter at Skawina (178.1 mg/l), and a setting pond near the Cracow Plant of Inorganic Industry at Bonarka (104.8 mg/l).

In the cartographic image an attention should be directed to increased K content (>40 mg/l) in the Skawina area, and to very low concentration (<5 mg/l) in the area of the Niepołomice Woods.

# Li LITHIUM

Surface waters: Plate 59, Table VI; ppm = mg/l

Approximate limit values (8, 43, 57):

| ***                      |            |
|--------------------------|------------|
| - waters used in irrigat | ion ≤2.50  |
| - river waters           | < 0.02     |
| - underground waters     | 0.002-0.04 |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - surface waters of Cracow        |                           |
|-----------------------------------|---------------------------|
| and environs                      | <0.02-0.13; average <0.02 |
| - Vistula river in Cracow         | <0.02-0.11; average 0.04  |
| - Vistula river                   | <0.02-0.15; average 0.02  |
| - surface waters of Poland        | <0.02-2.78; average <0.02 |
| - surface waters of Upper Silesia | <0.02-2.78; average <0.02 |

Average lithium content in surface waters of the area covered by this project is below sensitivity applied method (<0.02 mg/l). Against a poor background of lithium, waters of the Vistula river distinguish themselves due to lithium concentrations at a rate of up to 0.11 mg/l. Enrichment of the Vistula waters with lithium, similar to the cases of potassium and sodium, is closely connected with migration of brines from the Upper Silesian mines.

A highest lithium concentration of 0.13 mg/l has been noted in waters of small stream at Pleszew (southwards of the "Sendzimir" Metallurgical Plant).

# Mg MAGNESIUM

Soils: Plate 18, Table IV; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow and environs  | 0.01-1.45; average 0.10  |
|---------------------------------|--------------------------|
| - soils in urban area of Cracow | 0.02-1.45; average 0.11  |
| - soils of Poland               | <0.01-4.90; average 0.06 |
| - soils of Upper Silesia        | <0.01-4.90; average 0.06 |

The content of magnesium in soils of investigated area is higher than the average value for all Poland. The geochemical image displays increased magnesium concentrations in soils in the vicinity of the "Sendzimir" Plant and particularly in those soils that occur within the Planty green belt in the city of Cracow (>0.4% Mg). Also, soils on alluvial formations in the eastern part of the Vistula valley and the Raba valley are more magnesium-rich.

0.10% is the average magnesium content in soils of cultivated land; 0.14% is respective figure for soils within grassland. Forest soils are the poorest with respect to magnesium concentration (av. 0.02%); this deals with the Niepołomice Woods and forests situated in western sector of the map area (Podgórki near Tyniec for example).

Water sediments: Plate 40, Table V; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - water sediments of Cracow        |                           |
|------------------------------------|---------------------------|
| and environs                       | 0.02- 2.77; average 0.15  |
| - alluvium of Vistula in Cracow    | 0.12- 0.57; average 0.26  |
| - alluvium of Vistula              | 0.04- 2.04; average 0.22  |
| - water sediments of Poland        | <0.01-10.62; average 0.11 |
| - water sediments of Upper Silesia | 0.01- 5.87: average 0.13  |

A poor differentiation is observed in distribution pattern of magnesium in water sediments. In addition, no effect of water reservoir type is observed on magnesium concentration in water sediments.

Within the mapped area only alluvia of both the Vistula and Raba rivers exhibit concentrations equal to almost twice (0.26%) the average figure for the entire surveyed area.

The cartographic image draws attention to particularly small Mg concentrations in alluvia of small water-courses in the Niepołomice Woods.

# Surface waters: Plate 60, Table VI; ppm = mg/l

Approximate limit values (88):

- surface waters used as the source

of public water supply recommended 30; permissible 50

Basic values for investigated area, Poland (54) and Upper Silesia (53):

surface waters of Cracow and environs
Vistula river in Cracow
Vistula river
Vistula river
surface waters of Poland
surface waters of Upper Silesia
1.6-194.0; average 15.4
14.6-91.8; average 38.6
2.6-224.3; average 24.7
0.2-833.8; average 11.5
0.2-833.8; average 14.1

Waters of the Vistula river differ from other surface waters of the area because of their average magnesium concentration being of the order of 38.6 mg/l. Mine waters flowing down from Upper Silesia to the Vistula are the source of magnesium enrichment. As reported by Z. Płochniewski and H. Ważny (1971), brines discharged from some mines contain even as much magnesium as 4000 ppm.

Increased Mg concentration (up to 43.15 mg/l) occurs in small water courses and closed reservoires in the drainage basin of the Kościelnicki Stream. Maximum Mg values (193 mg/l) have been found in a pond near aluminium smelter at Skawina.

# Mn MANGANESE

Soils: Plate 19, Table IV; ppm = mg/kg = g/t

Approximate limits (43):

- permissible in cultivated soils 1500-3000

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

1 - 6440; average 257
46 - 3156; average 300
<1-24270; average 173
2 - 7000; average 186

The geochemical manganese background in the area is less than 500 ppm. The geochemical image displays increased Mn content in alluvial beds in the Vistula valley (to the east of Cracow); a valley of the Raba river is similar in this respect. Maximum Mn concentrations, in excess of 2000 ppm, have been recorded in the area of the "Sendzimir" Metallurgical Plant. Areas with low Mn content (250 ppm) include soils in the Niepołomice Woods.

A comparison of manganese concentrations in soils of Cracow and other cities indicates higher concentrations in the project area. Observations by K. Czarnowska et al. (1992) revealed Mn content in soils of Pabianice in the range of 17–460 ppm (av. 177). The average for soils in Warsaw is 119 ppm Mn (J. Lis, 1992). On the average, respective figure for soils in Łódź is 189 ppm (K. Czar-

nowska, J. Walczak, 1988). The authors are of the opinion that this value is low.

Water sediments: Plate 41, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- water sediments of Cracow
and environs

- alluvium of Vistula in Cracow
- alluvium of Vistula
- water sediments of Poland
- water sediments of Upper Silesia

10-39 031; average 313
145- 1 628; average 345
72- 2 648; average 401
<1-63 719; average 255
4-21 295; average 280

The manganese content in water sediments in the surveyed area is subject to considerable differentiation (from 10 to 39 031 ppm); however, no regularity has been found in its spatial distribution pattern. Despite considerable differentiation, the average Mn concentrations in sediments of particular rivers and water environments are of similar value (Table V). Maximum Mn content deals with alluvium of the Malinówka Stream in the vicinity of a rubbish dump at Barycz.

Surface waters: Plate 61, Table VI; ppb = µg/l

Classes of surface waters purity (73):

I ≤100 II >100 - ≤300 III >300 - ≤800

Basic values for investigated area, Poland (54) and Upper Silesia (53):

surface waters of Cracow and environs
Vistula river in Cracow
Vistula river
Vistula river
surface waters of Poland
surface waters of Upper Silesia
7-10 333; average 199
127- 892; average 303
17- 1 087; average 122
41-34 500; average 107
1-16 829; average 186

There is large variation of manganese content in the project area; this deals with both the regional and local scale (the latter with respect to particular types of water reservoirs). The Vistula is the carrier of waters of the II and III quality classes with respect to Mn content (Table 7), and share of water below standards is relatively insignificant (2.04%). Rivers with the smallest Mn concentrations include: the Prądnik (av. 30 µg/l), the Dłubnia (47 µg/l), and the Raba (av. 63 µg/l). The main occurrences of manganese-rich waters are connected with the Niepołomice Woods. Waters in this area (belonging to drainage basins of the Raba and Drwinka rivers) most often contain manganese in concentrations below standards (>800 µg/l). Similarly to the case of iron, a high manganese concentration in this water remains under the influence of strongly acid character of the environment.

Table 7

Amount of surface water samples under study in particular classes of water purity with respect to manganese (in %)

| Purity<br>class     | The Vistula river n = 49 | Rivers*<br>and bigger<br>streams<br>n = 92 | Streams<br>n = 75 | Small water<br>courses<br>(streams, ditches)<br>n = 196 | Small closed<br>water bodies<br>(ponds, ditches)<br>n = 44 |
|---------------------|--------------------------|--|-------------------|---|--|
| I                   | 0.00                     | 46.74                                      | 32.00             | 23.46   | 43.18  |
| 11                  | 40.82                    | 29.35                                      | 38.67             | 37.76   | 29.55  |
|                     | 57.14                    | 13.04                                      | 24.00             | 19.39   | 18.18  |
| Below all standards | 2.04                     | 10.87                                      | 5.33              | 19.39   | 9.09   |

<sup>\*</sup> without the Vistula river

Amount of surface water samples under study in particular classes of water purity with respect to sodium (in %)

| Purity<br>class     | The Vistula river n = 49 | Rivers*<br>and bigger<br>streams<br>n = 92 | Streams<br>n = 75 | Small water<br>courses<br>(streams, ditches)<br>n = 196 | Small closed<br>water bodies<br>(ponds, ditches)<br>n = 44 |
|---------------------|--------------------------|--|-------------------|---|--|
| 1                   | 0.00                     | 93.48                                      | 78.66             | 92.35   | 77.27  |
| II                  | 0.00                     | 0.00                                       | 0.00              | 1.02  | 9.09   |
| III                 | 4.10                     | 0.00                                       | 2.67              | 0.51  | 0.00   |
| Below all standards | 95.90                    | 6.52                                       | 18.67             | 6.12  | 13.64  |

<sup>\*</sup> without the Vistula river

# Na SODIUM

Surface waters: Plate 62, Table VI; ppm = mg/l

Classes of surface waters purity (73):

 $\begin{array}{ccc} I & \leq & 100 \\ II & > & 100 - \leq & 120 \\ III & > & 120 - \leq & 150 \end{array}$ 

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- surface waters of Cracow
and environs

- Vistula river in Cracow

- Vistula river

- surface waters of Poland

- surface waters of Upper Silesia

2-2478; average 39

129 - 982; average 368

4-1817; average 156

<1-5723; average 28

Very low sodium concentration is a characteristic feature of surface waters (the Vistula excluded) in the mapped area; with respect to sodium, the majority of waters belong to I quality class. As refers to Na content in the Vistula waters, almost all of them should be qualified below standards (Table 8). The range of Na content is relatively equalized (from 129 to 982 ppm, av. 368 mg/l) which evidences a strong but distant source of pollution. Saline waters and brines discharged from the coal mine region in Upper Silesia and disposed to the Vistula river make the sources of this pollution.

Strong sodium anomalies occurring within restricted areas have local pollution sources. This includes the anomaly in waters and drainage basin of the Serafa river (with maximum concentration reaching 1881.9 mg/l); important to note here is the fact that the anomaly is situated in the region of outcrops of salt-bearing rocks and of salt mines at Wieliczka and Barycz. Similar anomaly (up to 2478.0 mg/l) occurs near location of Łapczyca (close to Bochnia), where a brine is extracted. An anomaly in the vicinity of Bodzanów (up to 1804.7 mg/l) is connected with outcrops of salt-bearing formations of the Miocene age.

# Ni NICKEL

Soils: Plate 20, Table IV; ppm = mg/kg = g/t

Approximate limit values (20, 43):

- cultivated soils
- soils in children's play parks
- soils in city parks and recreation areas
- soils in house building areas
- soils in industrial building areas

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

A mobile portion of nickel, that HCl-extractable, appears in soils under present study in small concentrations (less than 10 ppm). Soils with abnormal Ni content (>20 ppm) with respect to geochemical background occur in the Vistula and the Raba valleys. Weathering rocks of the Carpathian flysch make Ni sources. It is likely that bounding through sorption in hydrated iron and manganese oxides is the main form of the Ni occurrence; such idea is supported by almost identical areal distribution patterns of afore--named elements. From G.G.S. Holmgren's and co-authors an idea can be concluded that chemical composition of substratum is the main factor decisive for enrichment of soils with nickel; it should be noted that this team of authors has investigated nickel distribution in soils in the USA. Analyses have revealed the average Ni content ranging from 10 to 94 ppm in particular states (the latter figure has dealt with soils that developed on serpentinites).

Water sediments: Plate 42, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- water sediments of Cracow and environs 2- 150; average 13
- alluvium of Vistula in Cracow 310- 47; average 22
- alluvium of Vistula 2- 282; average 17
- water sediments of Poland 4-1298; average 6
- water sediments of Upper Silesia 4- 795; average 10

As refers to nickel in water sediments, its content in water sediments is weakly differentiated. Increased concentrations are noted in alluvia of the Drwinka (up to 150 ppm) and left part of the drainage basin of this river. It is likely that nickel originates from alluvial soils of the Vistula valley, subjected to drainage. There are increased nickel concentrations in water sediments of the Drwina Długa (up to 70 ppm) and in alluvia of the Malinówka (up to 106 ppm) near a rubbish dump at Barycz; their origin should be considered anthropogenic.

Surface waters: Plate 63, Table VI; ppb =  $\mu g/l$ 

Classes of surface waters purity (73):

I-III <=1000

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- water sediments of Cracow and environs <10- 46; average <10 - alluvium of Vistula in Cracow <10- 32; average 11

Amount of surface water samples under study in particular classes of water purity with respect to phosphorus (in %)

| Purity class        | The Vistula river n = 49 | Rivers*<br>and bigger<br>streams<br>n = 92 | Streams<br>n = 75 | Small water<br>courses<br>(streams, ditches)<br>n = 196 | Small closed<br>water bodies<br>(ponds, ditches)<br>n = 44 |
|---------------------|--------------------------|--|-------------------|---|--|
| I and II            | 49.00                    | 84.78                                      | 66.67             | 59.19   | 70.45  |
| III                 | 46.90                    | 3.26                                       | 5.33              | 7.65  | 4.55   |
| Below all standards | 4.10                     | 11.96                                      | 28.00             | 33.16   | 25.00  |

<sup>\*</sup> without the Vistula river

| - alluvium of Vistula              | <8- 30; average  | <8 |
|------------------------------------|------------------|----|
| - water sediments of Poland        | <8-1326; average | <8 |
| - water sediments of Upper Silesia | <8- 194; average | <8 |

Nickel in surface waters occurs within limits of its geochemical background (<10  $\mu$ g/l). Due to too high detectability limit for nickel (8  $\mu$ g/l), more precise determination of geochemical background is impossible.

Its content in waters of pure rivers is in the range of  $1-5 \mu g/l$ , but in many rivers of western Europe it appears in concentrations reaching almost 75  $\mu g/l$  (A. Kabata-Pendias, H. Pendias, 1993).

Scarce points with abnormal Ni concentration with respect to the background have been noted in the Vistula river near Tyniec, in water of a small pool near Skawina, and in the Kościelnicki stream at Węgrzynowice.

# P PHOSPHORUS

Soils: Plate 21, Table IV; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow               |                             |
|---------------------------------|-----------------------------|
| and environs                    | <0.005-0.410; average 0.036 |
| - soils in urban area of Cracow | 0.008-0.183; average 0.036  |
| - soils of Poland               | <0.005-1.613; average 0.033 |
| - soils of Upper Silesia        | <0.005-0.476; average 0.027 |

Phosphorus in soils of the study area is characterized by poor differentiation. Only forest soils contain smaller P concentrations (av. 0.020%); therefore, they can be included in soils with scanty phosphorus content. In other soils, independently of the way of land use, average phosphorus content is in the range of 0.027% (soils of city parks) to 0.042% (soils in allotment gardens). Areal distribution of phosphorus as displayed on the cartographic representation is of mosaic character. Distinctly higher P concentrations occur in the Vistula river valley within the eastern sector of the mapped area.

#### Water sediments: Plate 43, Table V; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - water sediments of Cracow     |                             |
|---------------------------------|-----------------------------|
| and environs                    | <0.005-1.751; average 0.090 |
| - alluvium of Vistula in Cracow | 0.037-0.483; average 0.175  |
| - alluvium of Vistula           | <0.023-5.866; average 0.094 |
| - water sediments of Poland     | <0.005-5.866; average 0.064 |
| - water sediments of Upper      |                             |
| Silesia                         | <0.005-3.961; average 0.067 |

Water sediments of the surveyed area are poor with respect to phosphorus content (0.5%). However, some area can be distinguished due to increased concentrations reaching 1.75%; these areas include alluvia of water-courses

draining alluvial sediments of the Vistula and the Raba rivers.

Surface waters: Plate 64, Table VI; ppm = mg/l

Classes of surface waters purity (73):

 $\begin{array}{ccc} I & \leq 0.10 \\ II & > 0.10 - \leq 0.25 \\ III & > 0.25 - \leq 0.40 \end{array}$ 

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| <0.16-12.60; average 0.20 |
|---------------------------|
| <0.16- 0.45; average 0.21 |
| <0.04- 2.80; average 0.24 |
| <0.04-45.12; average 0.19 |
| <0.04-45.12; average 0.31 |
|                           |

Data compiled in Table 9 indicates that the surface runoff (erosion of rocks, phosphorus fertilization) is the main source of phosphorus concentration in surface waters. It is evidenced by considerable share of waters below standards in small water-courses and interior water reservoirs as well. Water of bigger streams and rivers (the Vistula excluded) belong mainly to I quality class. As refers to the Vistula, her waters are substantially polluted (almost half of her waters represent the III quality class). The point sources are of secondary importance in contributing to the pollution of water. A literature search (R. Taylor at al., 1992) leads to the conclusion that in 90–98% the phosphorus-related pollution of surface waters arise from surface runoff.

#### Pb LEAD

Soils: Plate 22, Table IV; ppm = mg/kg = g/t

Approximate limit values (20, 43):

| - cultivated soils                                | ≤100;  | toxic ≥1000 |
|---|--------|-------------|
| - soils in children's play parks                  | ≤200;  | toxic ≥1000 |
| - soils in city parks and                         |        |             |
| recreation areas                                  | ≤500;  | toxic ≥2000 |
| <ul> <li>soils in house building areas</li> </ul> | ≤300;  | toxic ≥1000 |
| - soils in industrial building areas              | ≤1000; | toxic ≥2000 |

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - soils of Cracow and environs      | <3- 705; average 23   |
|-------------------------------------|-----------------------|
| - soils in urban area of Cracow     | <3- 705; average 29   |
| <ul> <li>soils of Poland</li> </ul> | <3-16 972; average 16 |
| - soils of Upper Silesia            | <3-16 972; average 53 |

A range of 5 to approx. 50 ppm is the geochemical background of lead in soils of Cracow and environs. Average concentrations of this element in the study area are almost twice the average concentrations for soils in remaining part of Poland (23 and 16 ppm, respectively). Higher

Pb concentrations are the effect of geological structure and of soil character (predominance of clayey soils). Data compiled in Table IV points out that concentration of lead in soils is under the influence of urbanization. Maximum values are observed in soils of street lawns (av. 36 ppm Pb) and soils in industrial grounds (av. 41 ppm Pb).

The geochemical image shows that Pb anomalies (>50 ppm) occur within the city of Cracow, in the "Sendzimir" Metallurgical Plant, at Wieliczka and Swoszowice, and in alluvial soils in the Vistula valley to the east of Cracow (which is evidenced by increased Pb concentration in soils of some meadows; Table 10). Similar increase in lead concentration in soils of the Planty green belt in the city of Cracow (up to 330 ppm) was reported by T. Komornicki and K. Oleksynowa (1985).

Table 10

Amount of soil samples under study with respect to degree of pollution and way of land use; for lead (in %)

|                                | Soils                         |                      |                   |  |
|--------------------------------|-------------------------------|----------------------|-------------------|--|
| Degree<br>of soil<br>pollution | cultivated<br>land<br>n = 445 | grassland<br>n = 197 | forest<br>n = 124 |  |
| Permissible                    | 100.00                        | 95.94                | 100.00            |  |
| Tolerable                      | 0.00                          | 4.06                 | 0.00              |  |
| Toxic                          | 0.00                          | 0.00                 | 0.00              |  |

Pb concentrations in excess of 200 ppm occur in the soils of the "Sendzimir" Metallurgical Plant; also in the Podgórze suburb. Transport and industrial activities are the source of these anomalies. Abnormal Pb content in soils of the Vistula valley is to some extent connected with translocation of this element and sediments from Upper Silesian Pb-Zn deposits.

Results of soil study in Warsaw and environs (J. Lis, 1992) are quoted here for comparison; the concentration of 14 ppm Pb is the average for the entire study area whereas the cartographic representation of the city centre exposes anomalies along the traffic route to be higher than 60 ppm Pb. Similar trend in the occurrence of lead anomalies along the main streets has also been found in Łódź (K. Czarnowska, J. Walczak, 1988). Analysis of soils in Berlin and environs (M. Birke et al., 1992) revealed much serious lead-related pollution of urban and suburban soils (av. 178 ppm). The authors are of the opinion that this pollution is exclusively of anthropogenic origin. This is concluded from the same authors' other study (conducted parallel) in which the geochemical backround of lead has been revealed at the rate of 7.7 ppm, on the average. Contrary to situation in Berlin, soils in Belorussian cities of Brest, Grodno, Vityabsk, Gomel and others (W.K. Łukaszow, Ł.W. Okuń, 1991) contain 8-16 ppm Pb on the average.

Water sediments: Plate 44, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

As in the case of soils, the geochemical background of lead in water sediments in the vicinity of Cracow is upper than that in the Polish Lawlands. Among rivers, alluvia of the Raba (av. 8 ppm) are noted due to the smallest Pb concentrations; on the other hand, alluvia of the Vistula are known from the highest Pb concentrations (av. 81 ppm). In the latter, high lead content is followed by high content of both cadmium and zinc. This pollution mainly arises from erosion of rocks contain Zn-Pb ores and exposed on the surface and from washing out of mine dumps and industrial waste produced at the Zn-Pb processing plants.

Although of rather point character, participation of local sources in polluting water sediments with lead is clearly visible. Maximum lead concentration has been found in alluvium of small water-course at Rząska near Bronowice (1783 ppm) and in alluvium of similar water-course near a garage repair shop at Czyżyny (in the vicinity of Nowa Huta).

Surface waters: Plate 65, Table VI; ppb =  $\mu g/l$ 

Classes of surface waters purity (73):

I-III ≤50

Basic values for investigated area:

- surface waters of Cracow and environs 0.2-47.9; average 3.7
- Vistula river in Cracow 0.5-35.1; average 4.3

Average concentrations of lead in waters of the area under present study are low (far below standards applicable to I quality class for surface waters). Higher concentrations (up to 47.9  $\mu$ g/l) were recorded in waters of the Vistula and the Skawinka rivers in the region of Skawina. Lead content equal to 42.8  $\mu$ g/l was found to occur in waters of small water-course near Skotniki, in the place where effluents are being discharged.

# S SULPHUR

Soils: Plate 23, Table IV; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
   soils in urban area of Cracow
   soils of Poland
   soils of Cracow and environs
   <0.005-1.030; average 0.013
   <0.005-1.030; average 0.013
   <0.005-3.263; average 0.012
- soils of Upper Silesia <0.005-0.516; average 0.015

On the average, HCl-extractable sulphur is present in soils under study in concentrations similar to those representative for sulphur content in soils in other regions of Poland. Local anomalies (>0.04% S) are of double character. Increased sulphur concentrations in the area of the Niepolomice Woods are natural for peaty soils with high acidity and high content of organic carbon. In other areas a relationship can be observed between sulphur and calcium, and this relationship is associated with alkaline reaction of soil. The increase of sulphur content, coexisting with higher concentration of calcium and strontium near Kocmyrzów (in the drainage basin of the Kościelnicki Stream), is likely connected with shallow gypsum (or gypsum-related limestones) of the Posądza type.

Water sediments: Plate 45, Table V; %

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- water sediments of Cracow
  - and environs <0.005-2.125; average 0.080
- alluvium of Vistula in Cracow 0.017-0.655; average 0.066

Amount of surface water samples under study in particular classes of water purity with respect to sulphates (in %)

| Purity<br>class  | The Vistula river n = 49 | Rivers*<br>and bigger<br>streams<br>n = 92 | Streams<br>n = 75 | Small water<br>courses<br>(streams, ditches)<br>n = 196 | Small closed<br>water bodies<br>(ponds, ditches)<br>n = 44 |
|--|--------------------------|--|-------------------|---|--|
| i de la companya de l | 42.86                    | 89.13                                      | 81.34             | 61.22   | 63.64  |
| II   | 48.98                    | 6.52                                       | 9.33              | 11.22   | 6.82   |
| 111  | 2.04                     | 0.00                                       | 0.00              | 5.10  | 6.82   |
| Below all standards  | 6.12                     | 4.35                                       | 9.33              | 22.46   | 22.72  |

<sup>\*</sup> without the Vistula river

- alluvium of Vistula 0.005-1.056; average 0.047 vater sediments of Poland <0.005-8.610; average 0.047

 water sediments of Upper Silesia

<0.005-2.193; average 0.064

Sulphur occurs in water sediments of investigated area in concentrations higher than the average sulphur content in entire territory of Poland. Samples with increased sulphur concentrations (>1%) have predominantly been collected from small water courses. It is difficult to explain the origin of these anomalies. A high sulphur content (2.056%) in alluvium of small water-course at Swoszowice is likely connected with sulphate-type waters occurring here. Similarly high S concentrations (1.829%) in alluvium of a canal near Chałupki (which disposes effluents from the "Sendzimir" Metallurgical Plant), and in alluvium of the Drwina Długa (1.288-1.414%) which collects waters from industrial area near a railway station Cracow-Prokocim are undoubtedly of anthropogenic origin. Some points can be met westwards of Cracow (in the areas of Skotniki and Kostrze) where sulphur content is >1%. This may be connected with the occurrence of Badenian gypsums and anhydrites here. The lowest sulphur content was recorded in alluvia of the Wilga (av. 0.019%) and the Raba (av. 0.023%) rivers.

# SO<sub>4</sub> SULPHATES

Surface waters: Plate 67, Table VI; ppm = mg/l

Classes of surface waters purity (73):

I ≤150 II >150 - ≤200 III >200 - ≤250

Basic values for investigated area, Poland (54) and Upper Silesia (53):

surface waters of Cracow and environs
Vistula river in Cracow
Vistula river
Vistula river
surface waters of Poland
surface waters of Upper Silesia

There is significant differentiation of sulphate concentrations in surface waters; it is also close to that of strontium. The lowest values of sulphate concentrations characterize waters in the forest areas of the Niepolomice Woods (<150 mg/l).

Among bigger rivers, waters of the Pradnik river (av. 28 mg/l) occur to be the poorest with respect to sulphate concentration; waters of the Vistula are the most abundant (av. 143 mg/l). Sulphates in waters of the Vistula are likely to originate from the Upper Silesian area. Abnormal area with outcrops of gypsum and anhydrites of Badenian age

between the Vistula to the north and Sidzina to the south is more distinct than the anomaly in water sediments. High sulphate waters are also observed in the vicinity of Swoszowice. These concentrations are most likely of geological origin.

The most interesting is a high sulphate anomaly in waters of the Kościelnicki Stream and its drainage basin. Average SO<sub>4</sub> content is 114 mg/l in the Kościelnicki Stream whereas as high as 193 mg/l for its entire drainage basin. Maximum concentration of 1195 ppm was found to occur in the Kościelnicki Stream's tributary in the vicinity of Kocmyrzów. The same sample also contained maximum (ever found) concentration of strontium equal to 9398 µg/l. Sulphur in these waters shows close relation to strontium and calcium.

High sulphate content (1138 mg/l) in the drainage ditch around a settlement pond of the former "Solvay" Soda Processing Plant in Cracow is of anthropogenic origin.

As concluded from Table 11, surface runoff has an important bearing on sulphate concentration, and the geological substratum along with mineral fertilizers are the sulphur sources.

# SiO<sub>2</sub> SILICA

Surface waters: Plate 66, Table VI; ppm = mg/l

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- surface waters of Cracow

and environs < 0.1-37.1; average 9.9

Vistula river in Cracow 0.6- 9.4; average 5.6

Vistula river 0.4-17.7; average 4.7

surface waters of Poland 0.3-83.1; average 10.2

surface waters of Upper Silesia 0.3-82.5; average 10.2

The content of silica dissolved in surface waters is subjected to considerable variability. Particular attention should be directed to very poor SiO<sub>2</sub> concentration in waters of the Vistula (av. 5.6 mg/l) and the Raba (av. 3.3 mg/l) rivers and small closed reservoirs (av. 4.5 mg/l) as well.

Surface waters in the northern sector of the mapped area are frequently enriched with silica (>20 mg/l). Alkaline reaction of waters flowing through the region covered with soils that have developed on loesses might be a reason why silica concentrations are high here. Despite very low soil pH (<4), also high (>25 mg/l) concentrations of silica have been found in some water samples collected from the Niepołomice Woods area. These increased concentrations can be justified in situations when fluorides enhancing solubility of silicates are also present (A. Macioszczyk, 1987).

# Sr STRONTIUM

Soils: Plate 24, Table IV; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

- soils of Upper Silesia

<1-2712; average 13
1-2712; average 20
<1-1298; average 8
<1-708; average 10

The average Sr content is soils of surveyed area is slightly higher than that dealing with the other regions of Poland. Increased Sr concentrations are characteristic for soils containing a high part of floatable (clayey) particles. The influence of anthropogenic factor is expressed by the increase of strontium content in soils of street lawns and industrial areas (av. 22 and 26 ppm, respectively). The poorest Sr concentrations have been found in forest soils (av. 3 ppm).

The cartographic image clearly demonstrates that soils with increased Sr concentrations mainly occur within the urban (Cracow, Wieliczka) and extensively industrialized (the "Sendzimir" Metallurgical Plant) areas, and in the area between Borek Fałęcki and Skotniki. The latter area can be connected with the presence of outcrops of gypsum and anhydrites (Badenian in age).

A distinct strontium anomaly has been disclosed east-wards of Kocmyrzów; its maximum Sr concentration is as high as 1032 ppm. It is also present in both alluvia and waters of the Kościelnicki Stream which drains the area. Origin of this anomaly seems to be natural, caused by occurrence of Miocene gypseous rocks or gypsum-related limestones under the loess cover. Geological structure of substratum is similar here to that occurring at Posadza (several kilometres to the north-east) which is known from the occurrence of gypsum-related limestones along with sulphur deposits (T. Osmólski, 1962).

The nature of other anomaly (with maximum Sr concentration at the rate of 497 ppm) seems to be similar to that aforementioned; however, its anthropogenic origin is more probable due to relation to strontium emission from very big brick-yard at Zesławice. This anomaly is weakly marked in water sediments in the Zesławice area. Other anomalies occurring near Bronowice and Nowe Brzesko, also of lesser intensity, are waiting for careful recognition.

Water sediments: Plate 46, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
alluvium of Vistula in Cracow
alluvium of Vistula
water sediments of Poland
water sediments of Upper Silesia

Differentiation of strontium content in water sediments is relatively poor. Against the background of average Sr content (2–100 ppm), alluvia in the area of the occurrence of Badenian gypsums and anhydrites are distinctly exposed between Sidzina, Borek Fałęcki, and Płaszów.

An anomaly in alluvia of small water-course near Kobierzyn is marked with maximum concentration of 461 ppm. The anomaly is consistent with increased strontium concentrations in soils and surface waters.

Also distinct is an anomaly (up to 169 ppm Sr) in alluvia of the Kościelnicki Stream; it is associated with

increased strontium and sulphur concentrations both in soils and surface waters. Strontium is likely to occur mostly in a sulphate form through isomorphic substitution of calcium

High strontium concentrations in sediments (up to 377 ppm) have been noted in small closed reservoirs in the vicinity of chemical plant at Bonarka. Their origin is likely anthropogenic.

Surface waters: Plate 68, Table VI; ppb = µg/l

Approximate limit values (70):

- sea water 8000 - river waters 200

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- surface waters of Cracow
and environs

- Vistula river in Cracow
- Vistula river
- surface waters of Poland
- surface waters of Upper Silesia

31 - 9 398; average 417
345 - 2 045; average 919
4-26 078; average 263
4-26 078; average 310

On a regional scale, differentiation of strontium pattern in surface waters is considerable. The smallest Sr concentrations are characteristic features of forest area in the Niepolomice Woods (<200  $\mu$ g/l). Among bigger rivers of the region, the smallest strontium content appears in waters of the Pradnik (av. 108  $\mu$ g/l), and the maximum – in waters of the Vistula (av. 919  $\mu$ g/l). Strontium in the Vistula's water probably comes from the Upper Silesian area; this is concluded from the fact that local sources, being in principle of considerably lesser concentrations, could not lead to such high and even Sr concentrations in waters of this big river.

Similarly to soil and water sediment anomalies, an area with outcrops of Badenian gypsums and anhydrites also makes an anomaly between the Vistula to the north and Sidzina to the south. High strontium waters are also observed in the vicinity of Swoszowice and Wieliczka, and Łapczyca near Bochnia as well. All anomalies mentioned here are likely of geological origin.

The most interesting anomalies also include a high strontium anomaly in waters of the Kościelnicki Stream and its drainage basin; it is though to be of geological origin. Average Sr concentrations are 953  $\mu$ g/l for waters in the Kościelnicki Stream while 940  $\mu$ g/l for the entire drainage basin. Maximum concentration of 9398  $\mu$ g/l was recorded in the Kościelnicki Stream's tributary in the vicinity of Kocmyrzów. Similarly high Sr content (up to 9305  $\mu$ g/l was found in 1992 in waters of this stream drainage basin (J. Lis, A. Pasieczna, 1995b). These figures are comparable with Sr concentrations in surface waters in the area of sulphur occurrence and exploitation (Staszów and Tarnobrzeg), where concentration as high as 12 982  $\mu$ g/l was recorded. Strontium in this waters remains in close relation to sulphates and calcium.

A high strontium concentration (6590  $\mu$ g/l) in water appearing in a drainage ditch of settling pond near the former "Solvay" Soda Processing Plant is most likely connected with leachate percolating from the pond.

# Ti TITANIUM

Soils: Plate 25, Table IV; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

2- 382; average 25
8- 382; average 32
<1-1542; average 26
1- 396; average 27

Titanium content (that HCl-extractable) in soils in the Cracow region is similar to that in other regions of Poland. An insignificant increase of Ti concentration is observed in urban soils in Cracow and Wieliczka, in the "Sendzimir" Metallurgical Plant ground, and in area of Skawina. A distinct area with very poor Ti concentrations includes the Niepołomice Woods.

The presence of this element in soils is much more dependent on the chemistry of rocks in substratum than on soil-forming processes (B. Gworek, 1990). Thus, Ti content in majority of soils that developed on rocks with poor titanium content is also weak.

Water sediments: Plate 47, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
alluvium of Vistula in Cracow
alluvium of Vistula
water sediments of Poland
water sediments of Upper Silesia
5 - 268; average 30
7 - 426; average 27
<1-5345; average 31</li>
3 - 3439; average 40

The occurrence of titanium (HCl-extractable) in water sediments in the study area is of poor variability. Scarce points of increased Ti concentrations (>85 ppm) are observed in water sediments situated in urbanized areas and in the vicinity of the "Sendzimir" Metallurgical Plant.

#### Surface waters: Table VI, ppb = $\mu g/l$

Basic values for investigated area, Poland (54) and Upper Silesia (53):

| - surface waters of Cracow and environs | <5-30; average <5 |
|---|-------------------|
| - Vistula river in Cracow               | <5- 9; average <5 |
| - Vistula river                         | <5-13; average <5 |
| - surface waters of Poland              | <5-89; average <5 |
| - surface waters of Upper Silesia       | <5-76; average 5  |

Titanium was found to occur in surface waters under present study in quantities below detectability of this element. In several samples, titanium was detected in amount between 8 and 30  $\mu g/l.$  Accordingly, no map of titanium distribution was prepared.

# V VANADIUM

Soils: Plate 26, Table IV; ppm = mg/kg = g/t

Approximate limit values (8,43):

- cultivated soils ≤200

 soils in city parks, recreation areas and house building areas ≤200

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

The content of vanadium in soils is poor, in the range of <1 to 25 ppm. On the average, slightly increased V concentrations (>25 ppm) are noted in soils of the Vistula valley near Drwina and in the ground occupied by the "Sen-

dzimir'' Metallurgical Plant; maximum concentrations here are in excess of 40 ppm.

Water sediments: Plate 48, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- water sediments of Cracow
and environs
- alluvium of Vistula in Cracow
- alluvium of Vistula
- water sediments of Poland
- water sediments of Upper Silesia

Vanadium in water sediments appear in small concentrations; as in the case of soils, its appearance in water sediments is also related to geological substratum.

On the average, vanadium content in water sediments is around 12 ppm. Higher concentrations (40 ppm) are detectable in alluvia of small water-courses flowing cross the Niepolomice Woods area. They are visibly correlated with high concentrations of iron which can appear in excess of 10 or even 20%.

Surface waters: Table VI; ppb = µg/l

Classes of surface waters purity (73):

I-III ≤1000

Basic values for investigated area, Poland (54) and Upper Silesia (53):

surface waters of Cracow and environs
 Vistula river in Cracow
 Vistula river
 Vistula river
 surface waters of Poland
 surface waters of Upper Silesia
 46-84; average <6</li>
 average <8</li>
 average <8</li>
 28-243; average <8</li>
 72; average <8</li>

The majority of water samples occurred to contain vanadium in concentrations below detection limit (6  $\mu$ g/l) of analytical method employed in this study; only individual samples contained vanadium above this limit. Maximum concentration of 84  $\mu$ g/l was detected in waters of water reservoir near chemical plant at Bonarka. Frequently, increased vanadium content appears in waters of small water-courses flowing cross the Niepołomice Woods; similarly to situation in alluvia, increased vanadium concentrations in this environment also coexist with iron.

# Zn ZINC

Soils: Plate 27, Table IV; ppm = mg/kg = g/t

Approximate limit values (20, 43):

- cultivated soils ≤300; toxic ≥600
- soils in children's play parks ≤300; toxic ≥2000
- soils in city parks and recreation areas ≤1000; toxic ≥3000
- soils in house building areas ≤300; toxic ≥600
- soils in industrial building areas ≤1000; toxic ≥3000

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- soils of Cracow and environs
- soils in urban area of Cracow
- soils of Poland
- soils of Upper Silesia

- soils of Upper Silesia

6- 3 664; average 73
15- 3 663; average 107
<1-91 110; average 40
5-87 500; average 121

The distribution of zinc in soils of the surveyed area is similar to distribution pattern of cadmium, copper, and lead – all being elements subjected to clearly visible effect of anthropogenic factor on their concentration.

The geochemical background of zinc is contained between 6 to around 200 ppm. The average zinc content in soils in the surveyed area is almost twice as high as the average in soils of entire Poland (73 and 40 ppm, respectively). Higher Zn concentrations in soils of the surveyed area result from its geological structure and character of soils (clayey soils are predominant here). Similar Zn content in soils within cultivated areas of the Cracow region (87.5, on the average) was recorded by F. Gambuś (1994).

Data compiled in Table IV suggests that urbanization has an important bearing on Zn concentrations in soils. The highest concentrations have been observed in soils of industrial areas (av. 175 ppm Zn), street lawns (av. 129 ppm), and city parks (av. 143 ppm). A study conducted by E. Gorlach et. al. (1994) pointed out the anthropogenic factor to be the main source of zinc-related pollution. Soil profiles analysed by these authors allowed observations of repeated decrease of zinc concentrations with increasing distance from emission source (the "Sendzimir" Metallurgical Plant); similar observation was made in relation to deeper soil horizons.

The least zinc content appear in sandy forest soils of the Niepolomice Woods.

The geochemical representation exposes Zn anomalies (>200 ppm) within the city of Cracow, in the "Sendzimir" Metallurgical Plant ground, at Wieliczka, and in soils of the Vistula valley to the east of Cracow. Frequently, the latter can be of such heavy pollution that Zn concentration can be in excess of 1000 ppm. Transport and industrial activity are the zinc sources. It is likely that abnormal increase of Zn concentrations in soils of the Vistula valley originates, in considerable portion, in the Upper Silesian Pb-Zn ores. This is reflected by increased content of zinc and meadow soils (Table 12).

Table 12
Amount of soil samples under study with respect to degree of pollution and land use; for zinc (in %)

|                                | Soils                         |                      |                   |  |
|--------------------------------|-------------------------------|----------------------|-------------------|--|
| Degree<br>of soil<br>pollution | cultivated<br>land<br>n = 445 | grassland<br>n = 197 | forest<br>n = 124 |  |
| Permissible                    | 99.55                         | 92.38                | 100.00            |  |
| Tolerable                      | 0.00                          | 2.54                 | 0.00              |  |
| Toxic                          | 0.45                          | 5.08                 | 0.00              |  |

Water sediments: Plate 49, Table V; ppm = mg/kg = g/t

Basic values for investigated area, Poland (54) and Upper Silesia (53):

water sediments of Cracow and environs
alluvium of Vistula in Cracow
alluvium of Vistula
alluvium of Vistula
water sediments of Poland
water sediments of Upper Silesia

23- 4852; average 168
97- 3060; average 968
10- 2759; average 235
21-407 500; average 73
11-407 500; average 300

Among water sediments of the study area, alluvia of the Vistula are known from high Zn concentrations (from 297

to 3060 ppm, av. 968 ppm). Up to 20 samples out of 49 contain Zn concentrations in excess of 1000 ppm. High Zn concentrations in alluvia of the Vistula river are associated with high cadmium content (from 9.7 to 47.1 ppm). Zincand cadmium-related pollution originates, to some extent, from Upper Silesia. Municipal sewage and industrial effluents as well as wastes disposed from the "Sendzimir" Metallurgical Plant make additional source of zinc-related pollution. This is evidenced by high Zn concentrations (from 1168 to 1340 ppm) in sediments of the Drwina Długa disposing effluents from industrialized area to the north of the railway station Cracow-Prokocim, in canals flowing from the "Sendzimir" Metallurgical Plant and discharging into the Dłubnia (up to 1225 ppm), and in the Vistula itself (up to 1651 ppm). Zinc occurring in water sediments is chemically bound with clay minerals, carbonates, and iron and manganese oxides (I. Bojakowska, G. Sokołowska, 1992). It is readily set in motion which lead to considerable zinc concentrations in waters (particularly in the Vistula).

Among biggest rivers of the area, the smallest Zn concentrations characterize alluvia of the Raba river (av. 47 ppm).

Surface waters: Plate 69, Table VI; ppb = μg/l

Classes of surface waters purity (73):

I-III ≤200

Basic values for investigated area, Poland (54) and Upper Silesia (53):

- surface waters of Cracow
and environs

- Vistula river in Cracow

- Vistula river

- Surface waters of Poland

- surface waters of Upper Silesia

Zinc-related pollution of surface waters is relatively poor. Maximum load of this element characterizes waters of the Vistula which carries it in concentrations from 13 to 269  $\mu$ g/l (av. 105  $\mu$ g/l). In waters of other river, zinc has been detected in concentrations not exceeding criteria applicable to surface water purity (200  $\mu$ g/l).

Individual points with zinc concentrations 200 µg/l have mostly been noted in small water-courses and small closed reservoirs (Table 13). The most interesting are those in the area of the Niepołomice Woods. In these points, increased or high concentrations of iron, cadmium, arsenic, and beryllium are frequently noted. It is strongly acid environment causing intensive extraction of elements from soils and substratum rocks, which gives rise to the increase of these elements' concentrations. In addition, elements that originated in industrial emissions and entered soils as the result of atmospheric precipitation, cannot be, under such circumstances, retained in soils and pass into surface and ground waters, accordingly. A study of zinc content in rain waters (K.P. Turzański, 1991) revealed that this metal concentration in the area of the Niepołomice Woods is considerable (150 µg/month).

Amount of surface water samples under study in particular classes of water purity with respect to zinc (in %)

| Purity class        | The Vistula river n = 49 | Rivers*<br>and bigger<br>streams<br>n = 92 | Streams<br>n = 75 | Small water<br>courses<br>(streams, ditches)<br>n = 196 | Small closed<br>water bodies<br>(ponds, ditches)<br>n = 44 |
|---------------------|--------------------------|--|-------------------|---|--|
| I, II and III       | 91.80                    | 98.91                                      | 96.00             | 93.88   | 93.18  |
| Below all standards | 8.20                     | 1.09                                       | 4.00              | 6.12  | 6.82   |

<sup>\*</sup> without the Vistula river

# RECAPITULATION

Geochemical landscape of surface environment of the Earth in Cracow and environs is relatively simple.

A short distance to the Upper Silesian Industrial District, with its hard coal and lead-zinc ore mines and associated processing plants, metallurgical plants, power station and other industrial branches, is a decisive element for specific character of the Cracow region. Influence of the industrial and mining district is strongly reflected by geochemical conditions in the Vistula valley. In the cartographic representation of soils it is expressed by increased concentrations of some elements (such as silver, arsenic, cadmium, mercury, lead, zinc), the extent of which is almost exactly consistent with the occurrences of Holocene sediments of the Vistula river. Maximum metals' concentrations occur in soils that developed on the youngest sediments deposited between flood banks. A study of buried and recent alluvia of the Vistula in the Cracow environs (K. Klimek, M. Macklin, 1991) revealed that concentrations of cadmium, zinc, and lead in these alluvia have increased several hundred times for the last 150-200 years.

Local sources, mainly the "Sendzimir" Metallurgical Plant, significantly contribute to the pollution of these soils. It is evidenced by high concentrations of a number of elements in alluvia and waters of canals disposing effluents from the "Sendzimir" Plant to the Vistula and the Dłubnia

A complex of industrial plants, stores, and sewage treatment plants in the area of railway loading station Cracow-Prokocim is other source of pollution, from which effluents are being disposed to the Vistula river through the Drwina Długa canal.

Less hazardous pollution sources include the Cracow's Plant of Inorganic Industry at Bonarka, the "Solvay" Soda Processing Plant at Borek Fałecki in the drainage basin of the lower Wilga river, and the Metallurgical Plant at Skawina in the basin of the Skawinka river.

At this stage, participation of local and far-reaching sources in pollution of soils in the valley of the Vistula river is difficult to determine. However, it seems likely that largest portion of metals mentioned above is carried by waters from the Upper Silesian area. This concept is proved by the fact that the increase of concentrations of metals, though less distinct, is also observed in soils and alluvia outside the flood banks. The said metals entered the Vistula's alluvial soils in the past, when the river bed was frequently changing its course.

A distinct increase of Co, Cr, Fe, Mg, and Ni content is known to occur in soils that developed on the Holocene alluvia in valleys of both the Vistula and Raba rivers. It is likely that the flysch Carpathian's formations subjected to erosion make sources of these metals (J. Lis, A. Pasieczna, 1995b)

Disposal of mine waters from the Upper Silesian Coal Basin in the basic source of sodium, lithium, potassium, and sulphates in the Vistula's waters. Distinct anomalies of these elements are sometimes observed in waters of small water-courses and small closed reservoirs. They are connected with rock salt mining in the areas of Wieliczka and Bochnia, but they cannot markedly affect the overall salinity of the Vistula's waters. Only exceptional situations may happen; such was the case when in 1974, as the result of catastrophic flow out of approx. 100 000 m³ of brine from the salt mine at Barycz, the Vistula's waters reached in a day the NaCl concentration almost equal to the salinity of the Baltic Sea (J. Poborski et al., 1995). Other bigger rivers of the area under study are of weak salinity and only

occasionally the concentrations of Na, K, Li, SO<sub>4</sub> may be in excess of criterion applicable to I quality class for surface waters.

Of geological nature are strontium anomalies appearing between Sidzina on the south and the Vistula valley to the north. Their sources are composed of gypsums and anhydrites (Badenian in age) that are exposed in this area.

The most interesting among strontium anomalies is that one which occurs in soils, alluvia, and water in the area of Kocmyrzów in the drainage basin of the Kościelnicki Stream; strontium content is high and origin of this anomaly is of geological type. Strontium in this anomaly remains in close relation to sulphur and calcium. Concentrations of these elements are comparable here with their concentrations in anomalies connected with the occurrence and exploitation of sulphur in the area of Staszów and Tarnobrzeg (J. Lis, A. Pasieczna, 1995b). The origin of this anomalies is likely to be natural, caused by the occurrence of gypseous rocks or gypsum-related limestones (of Miocene age) covered by loesses; similar situation deals with gypsum-related limestones occurring several kilometres to the north, in former sulphur deposit at Posadza.

A specific character distinguishes the geochemical environment of the Niepołomice Woods. The presence of acid and very acid forest soils that developed on sandy substratum is the characteristic feature of the Woods area. These soils are very poor with respect to all elements under study. Contrary to soils, alluvia and surface waters of this area are frequently enriched in some elements including iron, aluminium, vanadium, arsenic, chromium, zinc, and cadmium. Acid reaction acting in favour of their extraction from eroded rocks is the reason of enrichment of the environment with the said elements. And formations of bog iron ores and alike are most likely their sources. There is no information available so far on the occurrence of bog iron ores in the environs under consideration. On the other hand, an important iron smelting centre existed in prehistoric time at Igołomia, situated on the edge of the Vistula valley, which had to utilize a source of mineral raw material situated relatively not far. The Vistula river or boggy area of the Niepołomice Woods with conditions favourable for forming the bog iron ores were the most probable regions from which the raw material could be extracted. It is also possible that such formations have later been covered by younger deposits.

The geochemical image of soils with respect to the land

use is rather typical.

Some urban soils distinguish themselves due to increased concentrations of a number of elements (Cd, Cu, Hg, Pb, S, Zn). However, cases are exceptional when concentrations of these elements exceed the permissible concentrations for cultivated soils. Interesting is the fact that high lead and zinc concentrations are observed in entire soil profiles (in places to a depth of 150 cm) of the Cracow's Planty green belt (park) located where medieval city walls and moats were situated (T. Komornicki, K. Oleksynowa, 1989). The authors did not found a reliable explanation to this phenomenon. In the light of the present study it is likely that lead and zinc were brought to grounds of the Planty green belt when the old moats were filled up with alluvial soils extracted in the Vistula valley; these alluvial soils occurred to be enriched in the afore-named elements due to erosion of rocks and ores in the Upper Silesian area. To document this concept a suitable study of archival material should be conducted aimed at identification of sites from which an earthy material was extracted to fill up old moats and level the terrain at the beginning of the XIX century.

Soils in the area occupied by the "Sendzimir" Metallurgical Plant are distinctly exposed on the cartographic representation of geochemical situation due to high metals concentrations. It is evident that this type of pollution originates in the Plant itself, therefore its areal extent is restricted. High pH of soils acts in favour of metal stability in soils; high pH is caused by fall-out of alkaline industrial dust which is calcium- and magnesium-rich. The phenomenon under discussion is a type one, also observed in other urbanized and industrial areas such as Warsaw (J.

Lis, 1992) or Upper Silesia for example (J. Lis, A. Pasieczna, 1995a).

Cultivated soils within surveyed area contain metals in concentrations similar to those in clayey soils in other, pollution-free regions of Poland. However, some effect of urbanization on the increase of metals concentrations in soils can be observed also here.

As compared with cultivated soils, increased concentrations of metals are characteristic for soils in grassland and fallows. This mostly results from the fact that meadows most often occur on alluvia of the Vistula valley, and fallows in cities and industrial areas.

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Table I Praktyczne granice oznaczalności pierwiastków i metody analityczne stosowane dla próbek gleb Practical detection limits of elements and analytical methods used for soil testing

| Pierwiastek<br>Element | Metoda analityczna<br>Analytical method | Długość fali<br>(w nm)<br>Wave length<br>(in nm) | Jednostka<br>Unit | Praktyczna granica<br>oznaczalności<br>Practical detection<br>limit |
|------------------------|---|--|-------------------|---|
| рН                     | potencjometryczna<br>potentiometric     |  |                   |   |
| Ag                     | ICP-AES                                 | 328.068  | ppm               | 1   |
| Al                     |   | 308.215  | %                 | 0.01  |
| As                     |   | 193.695  | ppm               | 5   |
| Ва                     |   | 455.403  | ppm               | 1   |
| Ве                     |   | 313.042  | ppm               | 0.5   |
| С                      | kulometryczna<br>culometric             |  | %                 | 0.01  |
| Ca                     | ICP-AES                                 | 315.887  | %                 | 0.01  |
| Cd                     |   | 226.502  | ppm               | 0.5   |
| Со                     |   | 228.616  | ppm               | 1   |
| Cr                     |   | 267.716  | ppm               | 1   |
| Cu                     |   | 324.754  | ppm               | 1   |
| Fe                     |   | 259.940  | %                 | 0.01  |
| Hg                     | CV-AAS                                  |  | ppm               | 0.05  |
| Mg                     | ICP-AES                                 | 383.829  | %                 | 0.01  |
| Mn                     |   | 257.610  | ppm               | 1   |
| Ni                     |   | 231.604  | ppm               | 1   |
| Р                      |   | 178.224  | %                 | 0.005   |
| Pb                     |   | 220.353  | ppm               | 3   |
| S                      |   | 182.000  | %                 | 0.005   |
| Sr                     |   | 407.771  | ppm               | 1   |
| Ti                     |   | 337.279  | ppm               | 1   |
| V                      |   | 290.881  | ppm               | 1   |
| Y                      |   | 371.029  | ppb               | 0.5   |
| Zn                     |   | 213.856  | ppm               | 1   |

ICP-AES – atomowa spektrometria emisyjna ze wzbudzeniem plazmowym Inductively Coupled Plasma Atomic Emission Spectrometry CV-AAS – atomowa spektrometria absorbcyjna z techniką zimnych par Cold Vapour Atomic Absorption Spectrometry

Table II Praktyczne granice oznaczalności pierwiastków i metody analityczne stosowane dla próbek osadów wodnych Practical detection limits of elements and analytical methods used for water sediment testing

| Pierwiastek<br>Element | Metoda analityczna<br>Analytical method | Długość fali<br>(w nm)<br>Wave length<br>(in nm) | Jednostka<br>Unit | Praktyczna granic<br>oznaczalności<br>Practical detection<br>limit |
|------------------------|---|--|-------------------|--|
| Ag                     | ICP-AES                                 | 328.068  | ppm               | 1  |
| Al                     |   | 308.215  | %                 | 0.01   |
| As                     |   | 189.042  | ppm-              | 5  |
| Ва                     |   | 233.527  | ppm               | 1  |
| Ве                     |   | 313.042  | ppm               | 0.5  |
| Ca                     |   | 317.933  | %                 | 0.01   |
| Cd                     |   | 226.502  | ppm               | 0.5  |
| Co                     |   | 228.616  | ppm               | 1  |
| Cr                     |   | 267.716  | ppm               | 1  |
| Cu                     |   | 324.754  | ppm               | 1  |
| Fe                     |   | 259.940  | %                 | 0.01   |
| Hg                     | CV-AAS                                  |  | ppm               | 0.05   |
| Mg                     | ICP-AES                                 | 279.079  | %                 | 0.01   |
| Mn                     |   | 257.610  | ppm               | 1  |
| Ni                     |   | 231.604  | ppm               | 1  |
| Р                      |   | 178.225  | %                 | 0.005  |
| Pb                     |   | 220.353  | ppm               | 5  |
| S                      |   | 181.974  | %                 | 0.005  |
| Sr                     |   | 407.771  | ppm               | 1  |
| Ti                     |   | 337.279  | ppm               | 1  |
| ٧                      |   | 310.230  | ppm               | 1  |
| Zn                     |   | 213.856  | ppm               | 1  |

ICP-AES – atomowa spektrometria emisyjna ze wzbudzeniem plazmowym Inductively Coupled Plasma Atomic Emission Spectrometry

CV-AAS – atomowa spektrometria absorbcyjna z techniką zimnych par Cold Vapour Atomic Absorption Spectrometry

### Praktyczne granice oznaczalności pierwiastków i metody analityczne stosowane dla próbek wód powierzchniowych Practical detection limits of elements and analytical methods used for surface water testing

Długość fali (w nm) Wave length (in nm) Praktyczna granica wykrywalności Practical detection limit Metoda analityczna Analytical method Pierwiastek Jednostka Unit Element ICP-AES 0.05 308.215 Al ppm As 189.042 ppb 2 В 208.893 ppm 0.03 455.403 Ba 1 ppb 315.887 1 Ca ppm 3 226.502 Cd ppb 5 Co 228.616 ppb Cr 267.716 ppb 4 324.754 5 Cu ppb 259.940 0.01 Fe ppm 766.491 0.5 K ppm Li 670.776 0.02 ppm 383.829 0.1 Mg ppm 1 Mn 257.610 ppb Na 589.592 ppm 1 231.604 ppb 10 Ni P 178.224 0.1 ppm 0.1 GF-AAS ppb Pb 0.1 251.611 SiO<sub>2</sub> ICP-AES ppm 1 182.000 SO ppm 1 Sr 407.771 ppb Ti 337.279 ppb 5 ٧ 290.881 ppb 6

Y

Zn

ICP-AES – atomowa spektrometria emisyjna ze wzbudzeniem plazmowym Inductively Coupled Plasma Atomic Emission Spectrometry

GF-AAS – atomowa spektrometria absorbcyjna ze wzbudzeniem elektrotermicznym (kuweta grafitowa) Graphite Furnace Atomic Absorption Spectrometry

371.029

213.856

ppb

ppb

1 5

| Gleby<br>Soils  | Para-<br>metry<br>Parameters | Ag                         | Al                                   | As                           | Ва                             | Be                                   | C <sub>org.</sub>                      | Ca                                     | Cd                                   | Co                      |
|---|------------------------------|----------------------------|--------------------------------------|------------------------------|--------------------------------|--------------------------------------|--|--|--------------------------------------|-------------------------|
| Gleby Krakowa i okolic<br>Soils of Cracow and environs<br>n = 979   | a b c d e                    | <1<br>3<br><1<br><1<br><1  | 0.02<br>1.58<br>0.47<br>0.41<br>0.47 | <5<br>29<br><5<br><5<br><5   | 3<br>426<br>62<br>50<br>52     | <0.5<br>17.0<br><0.5<br><0.5<br><0.5 | <0.01<br>40.19<br>2.35<br>1.77<br>1.68 | 0.01<br>11.40<br>0.61<br>0.32<br>0.32  | <0.5<br>68.4<br>1.2<br>0.7<br>0.7    | <1<br>36<br>4<br>3<br>4 |
| Gleby uprawne<br>Cultivated soils<br>n = 465  | a<br>b<br>c<br>d<br>e        | <1 ° < 1 < 1               | 0.13<br>1.23<br>0.50<br>0.47<br>0.49 | <5<br>22<br><5<br><5<br><5   | 12<br>215<br>57<br>52<br>50    | <0.5<br>1.4<br><0.5<br><0.5<br><0.5  | 0.06<br>6.62<br>1.65<br>1.49<br>1.53   | 0.02<br>6.84<br>0.54<br>0.36<br>0.32   | <0.5<br>14.5<br>0.8<br>0.6<br>0.7    | <1<br>12<br>5<br>4<br>4 |
| Gleby uprawne terenów bez zabudowy<br>Cultivated soils in non-urbanized areas<br>n = 104  | a<br>b<br>c<br>d<br>e        | 7777                       | 0.17<br>1.00<br>0.47<br>0.44<br>0.47 | √5 9 √5 √5<br>√5 √5          | 19<br>183<br>51<br>47<br>47    | <0.5<br>0.9<br><0.5<br><0.5<br><0.5  | 0.47<br>6.62<br>1.49<br>1.37<br>1.40   | 0.03<br>6.84<br>0.47<br>0.27<br>0.24   | <0.5<br>4.6<br>0.7<br>0.6<br>0.7     | 1<br>9<br>4<br>4<br>4   |
| Gleby uprawne terenów podmiejskich<br>Cultivated soils in suburban areas<br>n = 97  | a<br>b<br>c<br>d<br>e        | 7777                       | 0.12<br>1.13<br>0.38<br>0.34<br>0.37 | \$2 \$5 \$5<br>\$5           | 13<br>426<br>62<br>52<br>53    | <0.5<br>7.8<br><0.5<br><0.5<br><0.5  | 0.24<br>6.05<br>1.79<br>1.51<br>1.49   | 0.01<br>5.89<br>0.81<br>0.45<br>0.51   | <0.5<br>7.2<br>0.8<br>0.6<br>0.6     | <1<br>10<br>3<br>3<br>4 |
| Gleby terenów o zabudowie miejskiej zwartej<br>Soils in urban areas with compact development<br>n = 47  | a<br>b<br>c<br>d<br>e        | <1<br>2<br><1<br><1<br><1  | 0.10<br>1.41<br>0.40<br>0.35<br>0.37 | √5<br>1 √ 5<br>√5<br>√5      | 16<br>331<br>66<br>54<br>56    | <0.5<br>17.0<br>1.1<br><0.5<br>0.5   | 0.21<br>8.27<br>1.97<br>1.53<br>1.55   | 0.04<br>5.28<br>1.04<br>0.60<br>0.52   | <0.5<br>27.3<br>1.2<br>0.6<br>0.7    | 1<br>10<br>4<br>3<br>4  |
| Gleby uprawne terenów o zabudowie przemysłowej<br>Cultivated solls in industrial areas<br>n = 38  | a<br>b<br>c<br>d<br>e        | <1<br><1<br><1<br><1<br><1 | 0.20<br>1.28<br>0.57<br>0.52<br>0.48 | <5<br>29<br>6<br><5<br>5     | 10<br>225<br>87<br>76<br>78    | <0.5<br>1.7<br>0.5<br><0.5<br><0.5   | 0.07<br>11.96<br>2.52<br>1.65<br>1.70  | 0.02<br>9.85<br>1.65<br>0.84<br>0.78   | <0.5<br>5.3<br>1.4<br>1.0<br>1.0     | 1<br>36<br>6<br>5<br>4  |
| Gleby lasów<br>Forest soils<br>n = 124  | a<br>b<br>c<br>d<br>e        | <1<br>1<br><1<br><1<br><1  | 0.02<br>1.29<br>0.34<br>0.22<br>0.18 | <5<br>16<br><5<br><5<br><5   | 3<br>268<br>40<br>22<br>18     | <0.5<br>3.5<br><0.5<br><0.5<br><0.5  | 0.48<br>40.19<br>4.98<br>3.30<br>3.08  | 0.01<br>4.45<br>0.22<br>0.07<br>0.05   | <0.5<br>1.9<br>0.6<br><0.5<br><0.5   | <1<br>10<br>2<br>1      |
| Gleby łąk<br>Meadow soils<br>n = 197  | a<br>b<br>c<br>d<br>e        | <1<br>2<br><1<br><1<br><1  | 0.09<br>1.58<br>0.55<br>0.47<br>0.48 | <5<br>17<br><5<br><5<br><5   | 4<br>372<br>80<br>63<br>58     | <0.5<br>1.8<br><0.5<br><0.5<br><0.5  | 0.11<br>25.29<br>2.63<br>2.02<br>2.03  | 0.01<br>11.40<br>0.55<br>0.35<br>0.33  | <0.5<br>63.9<br>2.7<br>0.9<br>0.8    | <1<br>13<br>5<br>4<br>4 |
| Gleby ugorów<br>Fallow soils<br>n = 53  | a<br>b<br>c<br>d             | 1 1 1 1 1 1                | 0.10<br>1.24<br>0.44<br>0.38<br>0.42 | <5<br>25<br><5<br><5<br><5   | 3<br>426<br>76<br>54<br>55     | <0.5<br>8.9<br>0.7<br><0.5<br><0.5   | 0.21<br>8.27<br>1.86<br>1.39<br>1.39   | 0.01<br>5.89<br>1.01<br>0.48<br>0.59   | <0.5<br>2.5<br>0.7<br>0.6<br>0.7     | <1<br>36<br>5<br>4<br>4 |
| Gleby parków miejskich<br>City park soils<br>n = 28   | a<br>b<br>c<br>d             | <1 <1 <1 <1 <1 <1 <1 <1    | 0.10<br>1.15<br>0.41<br>0.36<br>0.44 | <5<br>21<br><5<br><5<br><5   | 18<br>169<br>59<br>51<br>54    | <0.5<br>1.7<br><0.5<br><0.5<br><0.5  | 0.07<br>11.96<br>2.05<br>1.29<br>1.72  | 0.09<br>9.85<br>1.71<br>0.76<br>0.58   | <0.5<br>5.3<br>1.0<br>0.6<br>0.5     | <1<br>14<br>4<br>4<br>4 |
| Gleby trawników<br>Lawn soils<br>n = 47   | a<br>b<br>c<br>d<br>e        | <1<br>2<br><1<br><1<br><1  | 0.15<br>1.41<br>0.40<br>0.37<br>0.38 | <5<br>29<br><5<br><5<br><5   | 16<br>331<br>71<br>61<br>61    | <0.5<br>17.0<br>0.9<br><0.5<br><0.5  | 0.44<br>8.54<br>2.27<br>1.82<br>1.85   | 0.04<br>4.29<br>0.97<br>0.62<br>0.60   | <0.5<br>27.3<br>1.4<br>0.7<br>0.7    | 1<br>10<br>4<br>3<br>4  |
| Gleby ogródków działkowych<br>Allotment soils<br>n = 43   | a<br>b<br>c<br>d             | <1<br>2<br><1<br><1<br><1  | 0.15<br>0.79<br>0.44<br>0.41<br>0.42 | <5<br>7<br><5<br><5<br><5    | 23<br>180<br>64<br>59<br>60    | <0.5<br>5.2<br><0.5<br><0.5<br><0.5  | 0.67<br>6.05<br>1.92<br>1.73<br>1.54   | 0.09<br>4.72<br>0.91<br>0.56<br>0.48   | <0.5<br>7.2<br>0.9<br>0.7<br>0.8     | 1<br>8<br>4<br>4<br>4   |
| Gleby Polski <sup>1)</sup><br>Soils of Poland<br>n = 10840  | a<br>b<br>c<br>d             | <1<br>41<br><1<br><1<br><1 |                                      | <5<br>3444<br><5<br><5<br><5 | <1<br>1777<br>48<br>32<br>32   |                                      |  | <0.01<br>25.45<br>0.47<br>0.17<br>0.18 | <0.5<br>253.3<br>0.8<br><0.5<br><0.5 | <1<br>46<br>3<br>2<br>2 |
| Gleby uprawne Polski <sup>1)</sup> Cultivated soils of Poland n = 4899  | a<br>b<br>c<br>d             | <1<br>12<br><1<br><1<br><1 |                                      | <5<br>168<br><5<br><5<br><5  | <1<br>1404<br>41<br>32<br>32   |                                      |  | <0.01<br>14.96<br>0.43<br>0.20<br>0.19 | <0.5<br>16.7<br><0.5<br><0.5<br><0.5 | <1<br>29<br>3<br>2      |
| Gleby terenów miejskich i przemysłowych<br>Górnego Śląska <sup>2)</sup><br>Soils in urban and industrial<br>areas of Upper Silesia<br>n = 228 | a<br>b<br>c<br>d             | <1<br>13<br><1<br><1<br><1 |                                      | <5<br>238<br>12<br>7<br>7    | 5<br>1777<br>144<br>105<br>116 |                                      |  | 0.03<br>12.40<br>0.96<br>0.54<br>0.59  | <0.5<br>159.5<br>6.9<br>2.7<br>2.8   | <1<br>17<br>4<br>3<br>3 |
| Gleby Warszawy³)<br>Soils in Warsaw<br>n = 188  | a<br>b<br>c<br>d             |                            |                                      | 1<br>18<br>5<br>4<br>4       |                                |                                      |  |  | <0.3<br>5.0<br><0.3<br><0.3<br><0.3  | 1<br>7<br>2<br>2<br>2   |

a - minimum;

b – maksimum; maximum

c – średnia arytmetyczna; arithmetic mean

d – średnia geometryczna; geometric mean

e – mediana; median

n – liczba próbek; number of samples

<sup>&</sup>lt;sup>1)</sup> J. Lis, A. Pasieczna, 1995b; <sup>2)</sup> J. Lis, A. Pasieczna, 1995a; <sup>3)</sup> J. Lis, 1992

i kwasowość w glebach Krakowa i okolic Ti, V, Y, Zn w ppm), (Al,  $C_{\rm org.}$ , Ca, Fe, Mg, P, S w %) and acidity in soils of Cracow and environs Ti, V, Y, Zn in ppm), (Al,  $C_{\rm org.}$ , Ca, Fe, Mg, P, S in ppm)

| Cr                          | Cu                          | Fe                                    | Hg                                      | Mg                                    | Mn                                | Ni                         | Р  | Pb                               | S  | Sr                           | Ti                          | V                          | Zn                                | рН                              |
|-----------------------------|-----------------------------|---------------------------------------|---|---------------------------------------|-----------------------------------|----------------------------|--|----------------------------------|--|------------------------------|-----------------------------|----------------------------|-----------------------------------|---------------------------------|
| <1<br>198<br>10<br>7        | 1<br>403<br>15<br>11<br>11  | 0.02<br>9.13<br>0.95<br>0.77<br>0.85  | <0.05<br>3.13<br>0.09<br>0.05<br>0.05   | 0.01<br>1.45<br>0.14<br>0.10<br>0.13  | 1<br>6 440<br>365<br>257<br>319   | <1<br>59<br>11<br>8<br>9   | <0.005<br>0.410<br>0.043<br>0.036<br>0.037 | <3<br>705<br>30<br>23<br>22      | <0.005<br>1.030<br>0.017<br>0.013<br>0.013 | <1<br>2712<br>22<br>13<br>13 | 2<br>382<br>30<br>25<br>28  | <1<br>85<br>12<br>10<br>12 | 6<br>3664<br>118<br>73<br>70      | 3.2<br>9.5<br>6.6<br>6.5<br>6.8 |
| 8<br>2<br>47<br>9<br>8<br>8 | 3<br>60<br>11<br>11         | 0.17<br>2.92<br>0.96<br>0.87<br>0.87  | <0.05<br>1.38<br>0.05<br>0.05<br>0.05   | 0.02<br>0.72<br>0.15<br>0.13<br>0.13  | 26<br>1 690<br>383<br>346<br>340  | 2<br>47<br>11<br>10<br>10  | 0.014<br>0.291<br>0.045<br>0.041<br>0.041  | 6<br>196<br>21<br>20<br>20       | <0.005<br>0.346<br>0.014<br>0.013<br>0.013 | 136<br>16<br>13<br>13        | 7<br>82<br>32<br>29<br>33   | 2<br>50<br>13<br>12<br>13  | 17<br>1710<br>85<br>70<br>67      | 4.0<br>8.3<br>6.8<br>6.8<br>7.0 |
| 2<br>21<br>8<br>7<br>8      | 3<br>28<br>10<br>9          | 0.26<br>2.10<br>0.87<br>0.80<br>0.82  | <0.05<br>0.42<br>0.05<br><0.05<br><0.05 | 0.03<br>0.40<br>0.13<br>0.11<br>0.12  | 88<br>1 150<br>356<br>328<br>323  | 2<br>34<br>10<br>9<br>8    | 0.014<br>0.291<br>0.043<br>0.038<br>0.037  | 7<br>59<br>21<br>20<br>20        | <0.005<br>0.031<br>0.012<br>0.011<br>0.012 | 136<br>14<br>11<br>11        | 8<br>54<br>31<br>28<br>31   | 3<br>24<br>12<br>11<br>12  | 24<br>299<br>67<br>61<br>58       | 4.6<br>8.0<br>6.6<br>6.5        |
| 2<br>28<br>7<br>6<br>7      | 2<br>164<br>15<br>12<br>11  | 0.18<br>1.70<br>0.71<br>0.64<br>0.71  | <0.05<br>0.59<br>0.06<br>0.05<br>0.05   | 0.02<br>1.45<br>0.14<br>0.10<br>0.10  | 46<br>1 120<br>302<br>267<br>283  | <1<br>29<br>8<br>7<br>8    | 0.015<br>0.183<br>0.042<br>0.037<br>0.036  | <3<br>218<br>31<br>24<br>23      | <0.005<br>1.030<br>0.024<br>0.012<br>0.012 | 1<br>2712<br>56<br>18<br>14  | 8<br>203<br>33<br>28<br>28  | 1<br>33<br>10<br>9<br>10   | 15<br>1710<br>129<br>84<br>75     | 4.9<br>8.3<br>7.3<br>7.7        |
| 2<br>80<br>9<br>7<br>7      | 3<br>251<br>27<br>15<br>13  | 0.23<br>1.91<br>0.75<br>0.67<br>0.76  | <0.05<br>1.38<br>0.19<br>0.09<br>0.06   | 0.02<br>0.79<br>0.13<br>0.10<br>0.12  | 68<br>539<br>287<br>260<br>282    | 1<br>30<br>9<br>7<br>8     | 0.011<br>0.163<br>0.045<br>0.035<br>0.032  | 6<br>670<br>55<br>32<br>31       | <0.005<br>0.209<br>0.016<br>0.011<br>0.011 | 4<br>175<br>28<br>18<br>16   | 11<br>316<br>48<br>38<br>38 | 2<br>47<br>11<br>9<br>9    | 1000<br>170<br>118<br>110         | 6.<br>8.<br>7.<br>7.<br>7.      |
| 3<br>78<br>19<br>14<br>13   | 5<br>403<br>41<br>20<br>17  | 0.48<br>3.48<br>1.42<br>1.25<br>1.17  | <0.05<br>0.58<br>0.08<br>0.06<br>0.06   | 0.02<br>1.21<br>0.26<br>0.19<br>0.19  | 129<br>3 156<br>663<br>492<br>432 | 2<br>28<br>13<br>11<br>11  | 0.008<br>0.126<br>0.040<br>0.034<br>0.032  | <3<br>705<br>87<br>41<br>28      | 0.005<br>0.287<br>0.027<br>0.018<br>0.017  | 2<br>143<br>36<br>27<br>26   | 8<br>382<br>56<br>35<br>43  | 5<br>85<br>22<br>17<br>15  | 25<br>3 664<br>403<br>175<br>127  | 5.<br>9.<br>7.<br>7.<br>7.      |
| <1<br>53<br>6<br>3<br>2     | 1<br>32<br>7<br>5<br>5      | 0.02<br>2.88<br>0.59<br>0.35<br>0.24  | 0.05<br>0.24<br>0.05<br><0.05<br><0.05  | 0.01<br>1.45<br>0.07<br>0.03<br>0.02  | 1<br>1280<br>161<br>42<br>39      | <1<br>30<br>6<br>3<br>2    | <0.005<br>0.243<br>0.029<br>0.021<br>0.020 | <3<br>98<br>28<br>22<br>23       | <0.005<br>1.030<br>0.025<br>0.013<br>0.013 | <1<br>2712<br>28<br>4<br>3   | 2<br>55<br>15<br>12<br>11   | <1<br>69<br>9<br>5<br>4    | 6<br>444<br>53<br>33<br>28        | 3.<br>7.<br>4.<br>4.<br>4.      |
| 1<br>145<br>15<br>10<br>9   | 2<br>133<br>17<br>12<br>12  | 0.12<br>9.13<br>1.22<br>0.98<br>0.97  | <0.05<br>2.73<br>0.16<br>0.06<br>0.05   | 0.01<br>0.53<br>0.16<br>0.12<br>0.14  | 11<br>6440<br>436<br>336<br>347   | <1<br>43<br>14<br>10<br>10 | <0.005<br>0.410<br>0.045<br>0.036<br>0.035 | <3<br>171<br>30<br>25<br>23      | <0.005<br>0.256<br>0.019<br>0.015<br>0.015 | 1<br>1032<br>26<br>16<br>15  | 3<br>259<br>24<br>20<br>21  | 2<br>38<br>14<br>12<br>12  | 8<br>2 480<br>158<br>88<br>77     | 4<br>8<br>6<br>6<br>6           |
| 1<br>52<br>10<br>7<br>7     | 1<br>403<br>28<br>13<br>11  | 0.15<br>3.48<br>0.91<br>0.76<br>0.84  | <0.05<br>0.58<br>0.07<br><0.05<br><0.05 | 0.01<br>0.79<br>0.15<br>0.10<br>0.11  | 33<br>1 440<br>388<br>318<br>296  | <1<br>28<br>10<br>8<br>9   | 0.007<br>0.183<br>0.040<br>0.033<br>0.032  | <3<br>705<br>67<br>28<br>24      | <0.005<br>0.052<br>0.016<br>0.013<br>0.013 | 1<br>497<br>39<br>19<br>17   | 8<br>219<br>39<br>27<br>24  | 1<br>84<br>14<br>10<br>10  | 9<br>710<br>118<br>82<br>90       | 4<br>9<br>7<br>7<br>7           |
| 2<br>78<br>14<br>9          | 4<br>164<br>20<br>12<br>11  | 0.23<br>2.95<br>0.91<br>0.76<br>0.83  | <0.05<br>0.82<br>0.08<br><0.05<br><0.05 | 0.03<br>1.21<br>0.24<br>0.15<br>0.14  | 68<br>2 971<br>510<br>337<br>321  | 1<br>22<br>9<br>7<br>9     | 0.008<br>0.057<br>0.029<br>0.027<br>0.027  | <3<br>260<br>50<br>28<br>26      | <0.005<br>0.040<br>0.013<br>0.011<br>0.011 | 4<br>143<br>30<br>18<br>15   | 11<br>382<br>63<br>44<br>45 | 2<br>75<br>15<br>11<br>12  | 27<br>3 664<br>414<br>143<br>102  | 6<br>9<br>7<br>7<br>7           |
| 2<br>80<br>10<br>8<br>7     | 3<br>251<br>30<br>18<br>14  | 0.27<br>1.91<br>0.80<br>0.71<br>0.67  | <0.05<br>1.38<br>0.16<br>0.09<br>0.07   | 0.02<br>0.28<br>0.12<br>0.10<br>0.11  | 77<br>561<br>288<br>263<br>268    | 2<br>30<br>10<br>8<br>8    | 0.011<br>0.163<br>0.048<br>0.039<br>0.039  | 9<br>240<br>48<br>36<br>32       | <0.005<br>0.287<br>0.023<br>0.013<br>0.012 | 4<br>175<br>29<br>21<br>22   | 10<br>316<br>44<br>36<br>35 | 3<br>47<br>11<br>9<br>10   | 27<br>1 000<br>190<br>129<br>110  | 5 8 7 7 7 7                     |
| 3<br>21<br>9<br>8<br>8      | 6<br>210<br>19<br>14<br>13  | 0.26<br>1.80<br>0.84<br>0.77<br>0.84  | <0.05<br>0.63<br>0.09<br>0.06<br>0.05   | 0.03<br>0.51<br>0.15<br>0.13<br>0.13  | 138<br>792<br>349<br>324<br>318   | 3<br>27<br>10<br>9<br>9    | 0.018<br>0.164<br>0.049<br>0.042<br>0.040  | 12<br>139<br>32<br>28<br>27      | 0.006<br>0.052<br>0.015<br>0.013<br>0.013  | 4<br>79<br>25<br>19<br>16    | 14<br>151<br>36<br>32<br>28 | 3<br>20<br>11<br>10<br>11  | 48<br>608<br>139<br>110<br>96     | 5                               |
| <1<br>1873<br>6<br>4<br>4   | <1<br>6401<br>10<br>5<br>5  | <0.01<br>9.57<br>0.67<br>0.50<br>0.51 | <0.05<br>7.55<br>0.06<br><0.05<br><0.05 | <0.01<br>4.90<br>0.10<br>0.06<br>0.06 | <1<br>24270<br>267<br>173<br>217  | <1<br>146<br>6<br>4<br>4   | <0.005<br>1.613<br>0.042<br>0.033<br>0.034 | <3<br>16972<br>35<br>16<br>13    | <0.005<br>3.263<br>0.017<br>0.012<br>0.012 | <1<br>1298<br>17<br>8<br>8   | 1<br>1542<br>34<br>26<br>26 | 266<br>8<br>6<br>7         | 91 110<br>88<br>40<br>35          | 9                               |
| <1<br>1873<br>6<br>5<br>5   | <1<br>2190<br>8<br>5<br>5   | 0.03<br>5.99<br>0.64<br>0.52<br>0.53  | <0.05<br>4.75<br>0.05<br><0.05<br><0.05 | <0.01<br>1.75<br>0.10<br>0.07<br>0.07 | <1<br>24270<br>286<br>225<br>246  | <1<br>146<br>6<br>4<br>4   | <0.005<br>0.476<br>0.043<br>0.038<br>0.038 | <3<br>2113<br>20<br>13<br>12     | <0.005<br>1.860<br>0.013<br>0.011<br>0.011 | <1<br>1179<br>15<br>9        | <1<br>968<br>34<br>27<br>29 | <1<br>58<br>8<br>7<br>7    | 2 140<br>53<br>37<br>34           |                                 |
| <1<br>95<br>9<br>7<br>7     | <1<br>805<br>30<br>17<br>16 | 0.09<br>3.21<br>0.98<br>0.83<br>0.87  | <0.05<br>4.01<br>0.20<br>0.13<br>0.14   | <0.01<br>3.81<br>0.21<br>0.13<br>0.13 | 6<br>2229<br>440<br>314<br>338    | <1<br>89<br>10<br>7<br>8   | 0.005<br>0.254<br>0.044<br>0.035<br>0.035  | 5<br>16 972<br>320<br>110<br>102 | <0.005<br>0.516<br>0.026<br>0.019<br>0.019 | 708<br>43<br>26<br>27        | 8<br>318<br>63<br>49<br>49  | 1<br>60<br>12<br>10<br>11  | 15<br>11 899<br>719<br>306<br>317 |                                 |
|                             | 1<br>560<br>27<br>17<br>20  | 0.10<br>2.00<br>0.68<br>0.61<br>0.63  | 0.01<br>10.78<br>0.35<br>0.22<br>0.22   |                                       | 9<br>852<br>213<br>185<br>194     | 2<br>26<br>8<br>7<br>7     |  | 5<br>275<br>45<br>33<br>34       |  |                              |                             |                            | 10<br>1300<br>140<br>102<br>104   |                                 |

| Osady wodne<br>Water sediments  | Para-<br>metry<br>Para-<br>meters | Ag              | Al   | As               | Ва               | Ве                   | Ca                     | Cd                    | Со             |
|---|-----------------------------------|-----------------|------|------------------|------------------|----------------------|------------------------|-----------------------|----------------|
| Osady wodne Krakowa i okolic  | a                                 | <1              | 0.08 | <5               | 10               | <0.5                 | 0.04                   | <0.5                  | <1             |
| Water sediments of Cracow and environs                                | b                                 | 13              | 4.12 | 119              | 553              | 11.4                 | 16.75                  | 47.1                  | 64             |
| n = 585   | c                                 | <1              | 0.43 | <5               | 75               | 0.5                  | 0.93                   | 1.1                   | 4              |
| Strumienie z nazwą  | a                                 | <1              | 0.12 | <5               | 17               | <0.5                 | 0.13                   | <0.5                  | 1              |
| Streams (named)   | b                                 | 13              | 0.98 | 24               | 461              | 2.8                  | 4.23                   | 11.7                  | 64             |
| n = 68  | c                                 | <1              | 0.36 | <5               | 62               | <0.5                 | 1.14                   | 0.7                   | 4              |
| Male cieki bez nazwy  | a                                 | <1              | 0.10 | <5               | 12               | <0.5                 | 0.04                   | <0.5                  | <1             |
| Small streams (unnamed)   | b                                 | 7               | 4.12 | 119              | 553              | 11.4                 | 16.75                  | 21.1                  | 51             |
| n = 315   | c                                 | <1              | 0.49 | <5               | 82               | 0.7                  | 0.81                   | 1.1                   | 5              |
| Male zbiorniki bez nazwy  | a                                 | <1              | 0.08 | <5               | 10               | <0.5                 | 0.04                   | <0.5                  | 1              |
| Small reservoires (unnamed)   | b                                 | 1               | 1.34 | 39               | 291              | 2.6                  | 13.21                  | 37.9                  | 19             |
| n = 48  | c                                 | <1              | 0.39 | <5               | 66               | <0.5                 | 0.80                   | 0.7                   | 4              |
| Dłubnia The Dłubnia river n = 8                                       | a                                 | <1              | 0.35 | <5               | 39               | <0.5                 | 1.60                   | <0.5                  | 3              |
|   | b                                 | 1               | 0.72 | <5               | 94               | 0.7                  | 4.52                   | 1.1                   | 5              |
|   | c                                 | <1              | 0.46 | <5               | 66               | <0.5                 | 2.86                   | 0.6                   | 4              |
| Drwinka   | a                                 | <1              | 0.14 | <5               | 15               | <0.5                 | 0.06                   | <0.5                  | 2              |
| The Drwinka river   | b                                 | 3               | 0.79 | 13               | 293              | 1.7                  | 5.74                   | 5.4                   | 27             |
| n = 23  | c                                 | 01 <1           | 0.43 | <5               | 97               | 0.6                  | 0.74                   | 0.6                   | 6              |
| Prądnik   | a                                 | <1              | 0.14 | <5               | 27               | <0.5                 | 1.41                   | <0.5                  | 1              |
| The Prądnik river   | b                                 | 1               | 0.47 | <5               | 67               | 0.5                  | 4.14                   | 1.1                   | 4              |
| n = 12  | c                                 | <1              | 0.29 | <5               | 40               | <0.5                 | 2.30                   | 0.7                   | 2              |
| Raba  | a                                 | <1              | 0.26 | <5               | 20               | <0.5                 | 0.31                   | <0.5                  | 3              |
| The Raba river  | b                                 | 1               | 0.49 | 5                | 54               | <0.5                 | 3.36                   | <0.5                  | 8              |
| n = 11  | c                                 | <1              | 0.33 | <5               | 35               | <0.5                 | 0.96                   | <0.5                  | 5              |
| Rudawa  | a                                 | <1              | 0.11 | <5               | 27               | <0.5                 | 1.10                   | 0.6                   | 1              |
| The Rudawa river  | b                                 | 1               | 0.43 | <5               | 71               | 0.7                  | 2.61                   | 2.2                   | 4              |
| n = 10  | c                                 | <1              | 0.23 | <5               | 46               | <0.5                 | 1.84                   | 1.2                   | 2              |
| Wilga   | a                                 | <1              | 0.11 | <5               | 17               | <0.5                 | 0.39                   | <0.5                  | 2              |
| The Wilga river   | b                                 | 1               | 0.26 | <5               | 83               | <0.5                 | 1.86                   | 1.1                   | 4              |
| n = 9   | c                                 | <1              | 0.19 | <5               | 31               | <0.5                 | 0.94                   | <0.5                  | 3              |
| Wisła   | a                                 | <1              | 0.11 | <5               | 33               | <0.5                 | 0.34                   | 2.7                   | 2              |
| The Vistula river   | b                                 | 4               | 1.03 | 67               | 287              | 0.9                  | 1.92                   | 47.1                  | 12             |
| n = 43  | c                                 | 1               | 0.39 | 5                | 102              | <0.5                 | 0.83                   | 13.8                  | 6              |
| Osady wodne Polski <sup>1)</sup> Water sediments of Poland n = 12 778 | a<br>b<br>c                       | <1<br>117<br><1 |      | <5<br>6215<br><5 | <1<br>1794<br>52 | <0.5<br>21.0<br><0.5 | <0.01<br>43.15<br>0.84 | <0.5<br>8735.9<br>0.6 | <1<br>357<br>3 |
| Osady wodne Górnego Śląska²)  | a                                 | <1              |      | <5               | 3                | <0.5                 | 0.02                   | <0.5                  | <1             |
| Water sediments of Upper Silesia                                      | b                                 | 117             |      | 901              | 1794             | 19.9                 | 26.55                  | 8735.9                | 164            |
| n = 1459  | c                                 | <1              |      | 6                | 93               | 0.6                  | 0.71                   | 2.8                   | 4              |

a – minimum; minimum

b – maksimum; maximum

c – średnia arytmetyczna; arithmetic mean

d – średnia geometryczna; geometric mean

e – mediana; median

n – liczba próbek; number of samples

<sup>&</sup>lt;sup>1)</sup> J. Lis, A. Pasieczna, 1995b; <sup>2)</sup> J. Lis, A. Pasieczna, 1995a

w osadach zbiorników wodnych Krakowa i okolic Ti, V, Zn w ppm), (Al, Ca, Fe, Mg, P, S w %) of water reservoirs of Cracow and environs Ti, V, Zn in ppm), (Al, Ca, Fe, Mg, P, S in ppm)

| Cr            | Cu          | Fe                    | Hg                    | Mg                   | Mn                  | Ni            | Р                       | Pb             | S                       | Sr             | Ti             | ٧              | Zn                 |
|---------------|-------------|-----------------------|-----------------------|----------------------|---------------------|---------------|-------------------------|----------------|-------------------------|----------------|----------------|----------------|--------------------|
| 1             | 2           | 0.15                  | <0.05                 | 0.02                 | 10                  | 2             | <0.005                  | 5              | <0.005                  | 2              | 5              | 1              | 23                 |
| 302           | 1231        | 27.38                 | 3.60                  | 2.77                 | 39 031              | 150           | 1.751                   | 1783           | 2.125                   | 461            | 268            | 113            | 4852               |
| 11            | 18          | 1.34                  | 0.10                  | 0.15                 | 313                 | 13            | 0.090                   | 30             | 0.080                   | 33             | 30             | 12             | 168                |
| 3             | 4           | 0.33                  | <0.05                 | 0.04                 | 52                  | 3             | 0.012                   | 7              | 0.008                   | 6              | 6              | 3              | 33                 |
| 144           | 402         | 4.87                  | 2.21                  | 0.62                 | 39 03 1             | 106           | 0.449                   | 186            | 1.464                   | 425            | 88             | 24             | 1 340              |
| 9             | 17          | 1.07                  | 0.07                  | 0.15                 | 39 0                | 11            | 0.071                   | 25             | 0.064                   | 33             | 33             | 10             | 141                |
| 1<br>95<br>10 | 1 231<br>17 | 0.15<br>27.38<br>1.61 | <0.05<br>3.60<br>0.09 | 0.02<br>2.77<br>0.13 | 10<br>21 303<br>305 | 3<br>71<br>14 | 0.013<br>1.751<br>0.095 | 5<br>540<br>30 | 0.006<br>2.125<br>0.093 | 3<br>461<br>33 | 8<br>104<br>30 | 2<br>113<br>15 | 29<br>4 852<br>162 |
| 2             | 3           | 0.15                  | <0.05                 | 0.02                 | 13                  | 2             | <0.005                  | <5             | 0.005                   | 2              | 5              | 1              | 23                 |
| 161           | 167         | 3.84                  | 1.68                  | 0.42                 | 1 673               | 88            | 0.651                   | 1783           | 0.659                   | 377            | 268            | 42             | 1 467              |
| 9             | 15          | 0.86                  | 0.06                  | 0.12                 | 220                 | 11            | 0.047                   | 25             | 0.066                   | 31             | 27             | 11             | 104                |
| 7             | 8           | 0.62                  | <0.05                 | 0.12                 | 169                 | 8             | 0.035                   | 16             | 0.021                   | 30             | 38             | 7              | 70                 |
| 15            | 44          | 1.30                  | 0.36                  | 0.25                 | 377                 | 18            | 0.094                   | 59             | 0.173                   | 82             | 67             | 14             | 400                |
| 11            | 17          | 0.87                  | 0.09                  | 0.19                 | 253                 | 10            | 0.059                   | 29             | 0.056                   | 53             | 47             | 11             | 153                |
| 3             | 3           | 0.40                  | <0.05                 | 0.04                 | 111                 | 4             | 0.010                   | <5             | <0.005                  | 3              | 9              | 2              | 41                 |
| 302           | 108         | 15.48                 | 0.41                  | 0.44                 | 2400                | 150           | 1.121                   | 140            | 1.188                   | 100            | 90             | 35             | 896                |
| 16            | 18          | 1.95                  | 0.08                  | 0.14                 | 448                 | 19            | 0.104                   | 23             | 0.066                   | 29             | 27             | 14             | 167                |
| 4             | 7           | 0.36                  | <0.05                 | 0.08                 | 74                  | 4             | 0.034                   | 13             | 0.021                   | 12             | 27             | 4              | 73                 |
| 10            | 48          | 0.82                  | 0.47                  | 0.17                 | 340                 | 8             | 0.085                   | 74             | 0.114                   | 34             | 49             | 10             | 279                |
| 7             | 14          | 0.55                  | 0.08                  | 0.12                 | 187                 | 6             | 0.060                   | 28             | 0.038                   | 20             | 40             | 6              | 165                |
| 6             | 6           | 0.82                  | <0.05                 | 0.18                 | 158                 | 12            | 0.018                   | 5              | 0.006                   | 11             | 14             | 6              | 29                 |
| 13            | 17          | 2.52                  | 0.06                  | 0.67                 | 623                 | 26            | 0.048                   | 12             | 0.044                   | 85             | 25             | 13             | 89                 |
| 8             | 9           | 1.19                  | <0.05                 | 0.26                 | 304                 | 16            | 0.033                   | 8              | 0.023                   | 26             | 19             | 8              | 47                 |
| 3             | 5           | 0.30                  | <0.05                 | 0.06                 | 126                 | 3             | 0.035                   | 14             | 0.014                   | 13             | 21             | 3              | 104                |
| 9             | 28          | 0.88                  | 0.14                  | 0.20                 | 368                 | 9             | 0.113                   | 58             | 0.077                   | 29             | 53             | 10             | 347                |
| 5             | 13          | 0.51                  | 0.07                  | 0.15                 | 219                 | 5             | 0.062                   | 33             | 0.034                   | 20             | 36             | 6              | 207                |
| 3             | 6           | 0.42                  | <0.05                 | 0.06                 | 125                 | 5             | 0.016                   | 6              | 0.007                   | 19             | 11             | 4              | 33                 |
| 20            | 73          | 0.99                  | 0.14                  | 0.15                 | 610                 | 11            | 0.137                   | 34             | 0.052                   | 59             | 35             | 9              | 247                |
| 6             | 15          | 0.66                  | <0.05                 | 0.09                 | 251                 | 8             | 0.031                   | 13             | 0.019                   | 31             | 17             | 7              | 64                 |
| 12            | 14          | 0.76                  | 0.23                  | 0.12                 | 145                 | 10            | 0.037                   | 24             | 0.017                   | 12             | 18             | 3              | 297                |
| 125           | 126         | 2.92                  | 1.79                  | 0.57                 | 1 628               | 47            | 0.483                   | 260            | 0.655                   | 93             | 56             | 24             | 3 060              |
| 45            | 53          | 1.51                  | 0.77                  | 0.26                 | 345                 | 22            | 0.175                   | 81             | 0.066                   | 39             | 30             | 10             | 968                |
| <1            | <1          | <0.01                 | <0.05                 | <0.01                | <1                  | 1             | <0.005                  | <5             | <0.005                  | <1             | <1             | <1             | <1                 |
| 12251         | 15460       | 31.14                 | 11.00                 | 10.62                | 63719               | 1298          | 5.866                   | 43878          | 8.610                   | 7628           | 5345           | 427            | 407 501            |
| 6             | 7           | 0.75                  | <0.05                 | 0.11                 | 255                 | 6             | 0.064                   | 15             | 0.047                   | 21             | 31             | 7              | 73                 |
| <1            | 1           | 0.03                  | <0.05                 | 0.01                 | 4                   | <1            | <0.005                  | <5             | <0.005                  | 1              | 3              | <1             | 11                 |
| 12251         | 1 886       | 26.43                 | 10.50                 | 5.87                 | 21 295              | 795           | 3.961                   | 43878          | 2.193                   | 1120           | 3439           | 155            | 407 500            |
| 10            | 16          | 1.01                  | 0.05                  | 0.13                 | 280                 | 10            | 0.067                   | 72             | 0.064                   | 25             | 40             | 11             | 259                |

| Wody powierzchniowe<br>Surface waters                                       | Para-<br>metry<br>Para-<br>meters | Al                 | As | В                      | Ва               | Ca               | Cd              | Со              | Cr               | Fe                      |
|---|-----------------------------------|--------------------|----|------------------------|------------------|------------------|-----------------|-----------------|------------------|-------------------------|
| Wody powierzchniowe Krakowa i okolic  | a                                 | <0.05              | <2 | <0.03                  | 8                | 8                | <3              | <5              | <4               | 0.03                    |
| Surface waters of Cracow and environs                                       | b                                 | 6.44               | 44 | 6.73                   | 559              | 554              | 28              | 33              | 17               | 213.54                  |
| n = 464   | c                                 | 0.06               | 1  | 0.10                   | 59               | 95               | <3              | <5              | <4               | 0.38                    |
| Strumienie z nazwą  | a                                 | <0.05              | <2 | <0.03                  | 22               | 18               | <3              | <5              | <4               | 0.07                    |
| Streams (named)   | b                                 | 0.50               | 7  | 0.70                   | 485              | 238              | 6               | <5              | <4               | 9.31                    |
| n = 75  | c                                 | 0.06               | <2 | 0.10                   | 56               | 96               | <3              | <5              | <4               | 0.38                    |
| Małe cieki bez nazwy  | a                                 | 0.03               | <2 | <0.03                  | 13               | 8                | <3              | <5              | <4               | 0.03                    |
| Small streams (unnamed)   | b                                 | 6.44               | 44 | 1.91                   | 360              | 554              | 28              | 10              | 8                | 213.54                  |
| n = 196   | c                                 | 0.06               | <2 | 0.10                   | 57               | 98               | 2               | <5              | <4               | 0.50                    |
| Małe zbiorniki bez nazwy  | a                                 | <0.05              | <2 | <0.03                  | 8                | 9                | <3              | <5              | <4               | 0.05                    |
| Small reservoires (unnamed)   | b                                 | 2.58               | 36 | 6.73                   | 559              | 242              | 5               | 33              | 17               | 3.93                    |
| n = 44  | c                                 | 0.11               | 2  | 0.12                   | 56               | 68               | <3              | <5              | <4               | 0.29                    |
| Dłubnia The Dłubnia river n = 9   | a                                 | <0.05              | <2 | <0.03                  | 44               | 65               | <3              | <5              | <4               | 0.11                    |
|   | b                                 | 0.23               | <2 | 0.04                   | 58               | 102              | <3              | <5              | <4               | 0.33                    |
|   | c                                 | 0.08               | <2 | <0.03                  | 52               | 90               | <3              | <5              | <4               | 0.19                    |
| Drwinka   | a                                 | <0.05              | <2 | 0.05                   | 20               | 26               | <3              | <5              | <4               | 0.14                    |
| The Drwinka river   | b                                 | 0.14               | 12 | 0.29                   | 177              | 162              | <3              | <5              | <4               | 4.33                    |
| n = 20  | c                                 | <0.05              | 2  | 0.11                   | 54               | 82               | <3              | <5              | <4               | 0.62                    |
| Prądnik   | a                                 | <0.05              | <2 | <0.03                  | 21               | 91               | <3              | <5              | <4               | 0.05                    |
| The Prądnik river   | b                                 | 0.08               | <2 | <0.03                  | 37               | 116              | <3              | <5              | <4               | 0.22                    |
| n = 12  | c                                 | 0.06               | <2 | <0.03                  | 27               | 102              | <3              | <5              | <4               | 0.09                    |
| Raba  | a                                 | <0.05              | <2 | 0.04                   | 37               | 49               | <3              | <5              | <4               | 0.10                    |
| The Raba river  | b                                 | 0.10               | <2 | 0.08                   | 56               | 76               | <3              | <5              | <4               | 0.33                    |
| n = 11  | c                                 | 0.05               | <2 | 0.05                   | 47               | 56               | <3              | <5              | <4               | 0.20                    |
| Rudawa  | a                                 | <0.05              | <2 | <0.03                  | 49               | 100              | <3              | <5              | <4               | 0.13                    |
| The Rudawa river  | b                                 | 0.30               | 2  | <0.03                  | 64               | 113              | <3              | <5              | <4               | 0.51                    |
| n = 10  | c                                 | 0.12               | <2 | <0.03                  | 58               | 106              | <3              | <5              | <4               | 0.24                    |
| Wilga   | a                                 | <0.05              | <2 | 0.08                   | 35               | 65               | <3              | <5              | <4               | 0.11                    |
| The Wilga river   | b                                 | 0.09               | 2  | 0.18                   | 137              | 542              | <3              | <5              | <4               | 0.54                    |
| n = 10  | c                                 | 0.06               | <2 | 0.10                   | 63               | 162              | <3              | <5              | <4               | 0.34                    |
| Wisła   | a                                 | <0.05              | <2 | 0.05                   | 60               | 51               | <3              | <5              | <4               | 0.06                    |
| The Vistula river   | b                                 | 0.40               | 4  | 0.63                   | 151              | 152              | 3               | <5              | <4               | 1.14                    |
| n = 49  | c                                 | <0.05              | <2 | 0.26                   | 104              | 96               | <3              | <5              | <4               | 0.31                    |
| Wody powierzchniowe Polski <sup>1)</sup> Surface waters of Poland n = 12955 | a<br>b<br>c                       | <0.1<br>1.2<br>0.1 |    | <0.02<br>12.87<br>0.04 | <1<br>3470<br>55 | <3<br>6400<br>79 | <3<br>238<br><3 | <5<br>136<br><5 | <5<br>4445<br><5 | <0.02<br>438.72<br>0.52 |
| Wody powierzchniowe Górnego Śląska²)  | a                                 | 0.1                |    | <0.02                  | 2                | 3                | <3              | <5              | <5               | <0.02                   |
| Surface waters of Upper Silesia   | b                                 | 1.2                |    | 7.92                   | 3470             | 6400             | 238             | 136             | 4445             | 93.44                   |
| n = 1188  | c                                 | 0.2                |    | 0.09                   | 87               | 83               | <3              | <5              | <5               | 1.01                    |

a – minimum;

b – maksimum; maximum

c – średnia arytmetyczna; arithmetic mean

d – średnia geometryczna; geometric mean

e – mediana; median

n – liczba próbek; number of samples

<sup>&</sup>lt;sup>1)</sup> J. Lis, A. Pasieczna, 1995b; <sup>2)</sup> J. Lis, A. Pasieczna, 1995a

w wodach powierzchniowych zbiorników wodnych Krakowa i okolic As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, Ti, V, Zn w ppb ( $\mu$ g/I) in surface waters reservoires of Cracow and environs As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, Ti, V, Zn in ppb ( $\mu$ g/I)

| К              | Li                     | Mg                   | Mn                   | Na               | Ni               | Р                        | Pb   | SiO <sub>2</sub>      | SO <sub>4</sub> | Sr                 | Ti              | ٧                | Zn                |
|----------------|------------------------|----------------------|----------------------|------------------|------------------|--------------------------|------|-----------------------|-----------------|--------------------|-----------------|------------------|-------------------|
| <0.5           | <0.02                  | 1.6                  | 7                    | 2                | <10              | <0.1                     | 0.2  | <0.1                  | 4               | 31                 | <5              | <6               | 8                 |
| 178.1          | 0.13                   | 194.0                | 10333                | 2478             | 46               | 12.6                     | 47.9 | 37.1                  | 1195            | 9398               | 30              | 86               | 528               |
| 7.0            | <0.02                  | 15.0                 | 199                  | 39               | <10              | 0.2                      | 3.7  | 9.9                   | 102             | 417                | <5              | <6               | 79                |
| 0.7            | <0.02                  | 3.8                  | 15                   | 2                | <10              | <0.1                     | 0.2  | 0.5                   | 22              | 81                 | <5              | <6               | 30                |
| 51.1           | 0.06                   | 62.3                 | 2674                 | 1882             | 46               | 10.0                     | 16.9 | 28.2                  | 457             | 1 800              | 19              | <6               | 238               |
| 6.9            | 0.01                   | 14.3                 | 177                  | 46               | <10              | 0.2                      | 4.1  | 10.9                  | 94              | 400                | <5              | <6               | 79                |
| <0.5           | <0.02                  | 1.6                  | 7                    | 3                | <10              | <0.1                     | 0.2  | 0.5                   | 4               | 31                 | <5              | <6               | 8                 |
| 91.4           | 0.13                   | 75.3                 | 10333                | 2478             | 46               | 12.6                     | 42.8 | 37.1                  | 1195            | 9 398              | 30              | 32               | 528               |
| 6.8            | <0.02                  | 14.8                 | 240                  | 28               | <10              | 0.2                      | 3.6  | 13.7                  | 112             | 423                | <5              | <6               | 79                |
| 1.6            | <0.02                  | 1.9                  | 17                   | 4                | <10              | <0.1                     | 0.9  | 0.3                   | 12              | 51                 | <5              | <6               | 25                |
| 178.1          | 0.08                   | 194.0                | 1529                 | 1134             | 46               | 8.9                      | 18.1 | 26.5                  | 641             | 2161               | 28              | 84               | 319               |
| 9.4            | <0.02                  | 13.5                 | 134                  | 38               | 10               | 0.2                      | 3.5  | 4.5                   | 112             | 312                | <5              | <6               | 84                |
| 2.4            | <0.02                  | 8.3                  | 21                   | 5                | <10              | <0.1                     | 2.5  | 6.0                   | 22              | 239                | <5              | <6               | 45                |
| 5.8            | <0.02                  | 11.8                 | 142                  | 12               | 15               | 0.3                      | 8.8  | 17.9                  | 55              | 467                | <5              | <6               | 197               |
| 4.1            | <0.02                  | 9.8                  | 47                   | 8                | <10              | <0.1                     | 4.5  | 13.4                  | 36              | 324                | <5              | <6               | 78                |
| 1.6            | <0.02                  | 4.0                  | 104                  | 7                | <10              | <0.1                     | 0.4  | 6.4                   | 26              | 80                 | <5              | <6               | 19                |
| 23.1           | 0.06                   | 41.9                 | 6044                 | 1805             | 24               | 2.9                      | 7.2  | 20.9                  | 187             | 1 043              | <5              | <6               | 204               |
| 4.8            | <0.02                  | 12.1                 | 693                  | 40               | 14               | <0.1                     | 2.3  | 13.0                  | 113             | 325                | <5              | <6               | 76                |
| 2.0            | <0.02                  | 2.4                  | 22                   | 7                | <10              | <0.1                     | 1.2  | 8.1                   | 18              | 63                 | <5              | <6               | 13                |
| 3.9            | <0.02                  | 7.8                  | 55                   | 12               | 11               | 0.2                      | 6.2  | 11.6                  | 49              | 178                | <5              | <6               | 149               |
| 2.7            | <0.02                  | 4.7                  | 30                   | 9                | <10              | <0.1                     | 3.2  | 9.8                   | 28              | 108                | <5              | <6               | 51                |
| 3.3            | <0.02                  | 8.4                  | 24                   | 32               | <10              | <0.1                     | 1.5  | 2.4                   | 27              | 175                | <5              | <6               | 34                |
| 6.6            | <0.02                  | 13.0                 | 166                  | 223              | 14               | 0.1                      | 5.3  | 15.6                  | 86              | 268                | <5              | <6               | 145               |
| 4.4            | <0.02                  | 9.7                  | 63                   | 42               | <10              | <0.1                     | 2.8  | 3.3                   | 56              | 227                | <5              | <6               | 58                |
| 3.5            | <0.02                  | 10.8                 | 52                   | 9                | <10              | <0.1                     | 0.9  | 9.7                   | 61              | 196                | <5              | <6               | 33                |
| 4.6            | <0.02                  | 13.1                 | 279                  | 25               | <10              | 0.2                      | 9.1  | 10.6                  | 97              | 279                | <5              | <6               | 116               |
| 4.0            | <0.02                  | 11.8                 | 95                   | 12               | <10              | <0.1                     | 2.3  | 10.1                  | 71              | 239                | <5              | <6               | 54                |
| 1.4            | <0.02                  | 6.9                  | 30                   | 12               | <10              | <0.1                     | 2.0  | 4.0                   | 71              | 269                | <5              | <6               | 44                |
| 11.0           | <0.02                  | 20.8                 | 768                  | 433              | 20               | 0.5                      | 12.7 | 14.4                  | 267             | 1 669              | <5              | <6               | 170               |
| 5.3            | <0.02                  | 10.8                 | 176                  | 51               | <10              | <0.1                     | 4.3  | 8.5                   | 125             | 695                | <5              | <6               | 87                |
| 5.3            | <0.02                  | 14.6                 | 127                  | 129              | <10              | <0.1                     | 0.5  | 0.6                   | 72              | 345                | <5              | <6               | 13                |
| 28.5           | 0.11                   | 91.8                 | 892                  | 982              | 32               | 0.5                      | 47.9 | 9.4                   | 274             | 2 045              | 9               | <6               | 269               |
| 12.3           | 0.04                   | 38.6                 | 303                  | 368              | 11               | 0.2                      | 4.3  | 5.6                   | 143             | 919                | <5              | <6               | 105               |
| <1<br>473<br>5 | <0.02<br>2.78<br><0.02 | 0.2<br>833.8<br>11.5 | <1<br>120 956<br>107 | <1<br>5723<br>16 | <8<br>1326<br><8 | <0.04<br>4112.01<br>0.19 |      | <0.3<br>549.9<br>10.2 | 2<br>7085<br>58 | 4<br>26 078<br>263 | <5<br>350<br><5 | <8<br>1848<br><8 | <5<br>16414<br>36 |
| <1<br>473<br>8 | <0.02<br>2.78<br><0.02 | 0.2<br>833.8<br>14.1 | 1<br>16829<br>186    | 1<br>5723<br>28  | <8<br>194<br><8  | <0.04<br>45.12<br>0.31   |      | 0.3<br>82.5<br>10.2   | 3<br>7085<br>85 | 4<br>26 078<br>310 | <5<br>76<br>5   | <8<br>72<br><8   |                   |

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| Quaternary                            |         |      |    |    |       |       |                 |       |      |    |     |   |     |              |      |      |     |   |      |       |      |     | 10 |
| Tectonics                             |         |      |    |    |       |       |                 |       |      |    |     |   |     |              |      |      |     |   |      |       |      |     | 10 |
| Mineral deposits in the Cracow area   |         |      | •  |    |       |       |                 |       |      |    |     |   | •   |              |      |      |     |   |      |       | 1    |     | 10 |
| Main pollution sources                |         |      |    |    | 17:00 |       |                 |       |      |    |     |   | •   |              |      |      |     |   |      |       | -    |     | 12 |
| Geochemical maps                      |         |      |    |    |       |       |                 |       |      |    |     |   |     |              |      | . ,  |     |   | •    | •35)• | are: |     | 13 |
| Recapitulation                        |         |      |    |    |       |       |                 |       |      |    |     |   |     |              |      |      |     |   | •833 |       |      |     | 31 |
| References                            |         |      |    |    |       | N. S. | -               |       |      |    |     |   |     |              |      |      |     | • |      |       |      |     | 32 |
| Tables                                |         |      |    |    |       |       |                 |       |      |    |     |   |     |              |      |      |     |   | SEL  | 253   | 100  |     | 35 |
|                                       |         |      |    |    |       |       |                 |       |      |    |     |   |     |              |      |      |     |   |      |       |      |     |    |



# ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC

GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS

1:100 000

Józef Lis, Anna Pasieczna



Sfinansowano ze środków NARODOWEGO FUNDUSZU OCHRONY ŚRODOWISKA I GOSPODARKI WODNEJ



WYDAWNICTWO KARTOGRAFICZNE POLSKIEJ AGENCJI EKOLOGICZNEJ S.A.





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WYDAWNICTWO KARTOGRAFICZNE POLSKIEJ AGENCJI EKOLOGICZNEJ S.A. WARSZAWA 1995

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Akceptował do druku 30.10.1995 r. dyrektor naczelny Państwowego Instytutu Geologicznego prof. dr hab. Stanisław SPECZIK

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|  |                          | Geologi          | тсат тар |            |             |                  |            |            |
|--|--------------------------|------------------|----------|------------|-------------|------------------|------------|------------|
| Gleby  |                          | Osady wodne      |          |            | Wody pow    |                  | niowe      |            |
| Soils  |                          | Water sediments  |          |            | Surface wat | ers              |            |            |
| Tablica 1. Opróbowanie. Zabu   | dowa                     | Tablica 28. Ag   | Srebro   | Silver     | Tablica 50. | Al               | Glin       | Aluminium  |
| Sampling. Land devel   |                          | Tablica 29. Al   | Glin     | Aluminium  | Tablica 51. | As               | Arsen      | Arsenic    |
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| Tablica 3. Opróbowanie. Rodz<br>Sampling. Kinds of so  |                          | Tablica 32. Be   | Beryl    | Beryllium  | Tablica 54. |                  | Wapń       | Calcium    |
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| •  | Silver                   | Tablica 34. Cd   | Kadm     | Cadmium    | Tablica 55. |                  | Kadm       | Cadmium    |
| The state of the s | Aluminium                | Tablica 35. Co   | Kobalt   | Cobalt     | Tablica 56. |                  | Chrom      | Chromium   |
|  | Arsenic                  | Tablica 36. Cr   | Chrom    | Chromium   | Tablica 57  | Fe               | Żelazo     | Iron       |
|  | Barium                   | Tablica 37. Cu   | Miedź    | Copper     | Tablica 58  | K                | Potas      | Potassium  |
|  | Beryllium                | Tablica 38. Fe   |          | Iron       | Tablica 59  | Li               | Lit        | Lithium    |
| 41576  | Carbon<br>Calcium        | Tablica 39. Hg   | Rteć     | Mercury    | Tablica 60  | Mg               | Magnez     | Magnesium  |
| [자연기 5.1 [하는 10 기계   | Cadmium                  | Tablica 40. Mg   |          | 4033       | Tablica 61  | 200              | -          | Manganese  |
|  | Cobalt                   | Tablica 41. Mn   |          |            | Tablica 62  |                  | Sód        |            |
|  | Chromium                 | Tablica 42. Ni   |          | Nickel     |             |                  |            | Sodium     |
|  | Copper                   |                  | Fosfor   | Phosphorus | Tablica 63  |                  | Nikiel     | Nickel     |
|  | Iron                     |                  | Ołów     | Lead       | Tablica 64  |                  | Fosfor     | Phosphorus |
| Party delicity and the party of | Mercury<br>Magnesium     |                  | Siarka   | Sulphur    | Tablica 65  | Pb               | Ołów       | Lead       |
|  | Manganese                |                  | Stront   | Strontium  | Tablica 66  | SiO <sub>2</sub> | Krzemionka | Silica     |
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| Tablica 22. Pb Ołów  | Lead                     | Tablica 49. Zn   |          | Zinc       | Tablica 69  |                  | Cynk       | Zinc       |
|  | Sulphur                  | Tablica 49. Zili | Супк     | Zilic      | raonea 09   | 2.11             | Cylik      | Zille      |
|  | Strontium                |                  |          |            |             |                  |            |            |
| [12] [12] [12] [12] [12] [12] [12] [12]  | Titanium                 |                  |          |            |             |                  |            |            |
| Terret La Calabilitation Company Company Company Company Company   | Vanadium<br>Zinc         |                  |          |            |             |                  |            |            |
| Tablica 27. Zli Cylik  | ZIIIC                    |                  |          |            |             |                  |            |            |

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### TABLICA A

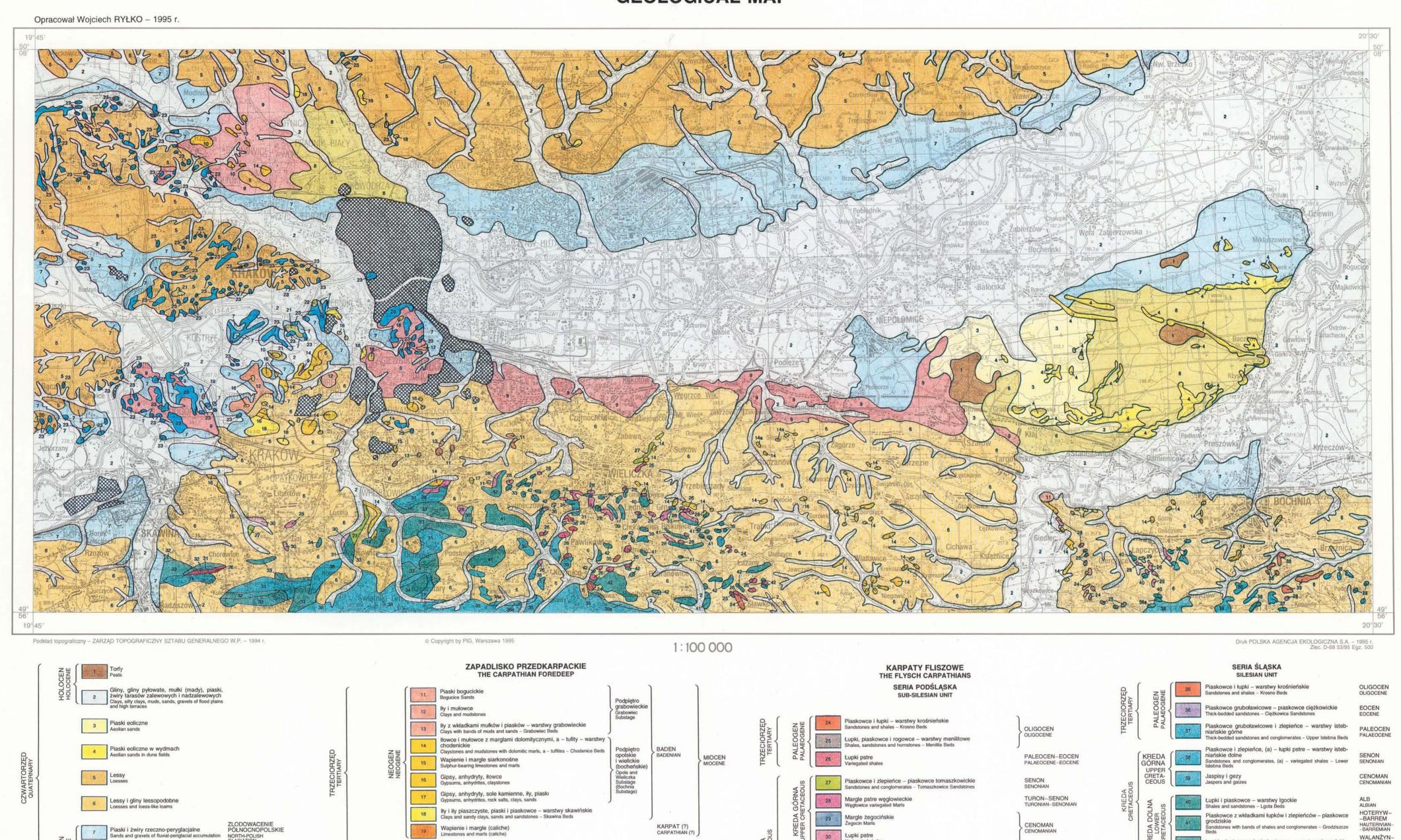
WALANŻYN-

-HOTERYW VALANGINIAN--HAUTERIVIAN

Opracowano na podstawie Szczegółowej mapy geologicznej Polski 1:50 000, arkusze: Kraków – J. Rutkowski, 1992, 1993; Niepołomice – R. Gradziński, 1955; Brzesko Nowe – J. Płonczyński, 1993; Myślenice – Z. Paul, W. Rączkowski, W. Rylko, A. Wójcik, 1995; Wieliczka – J. Burtan, 1954; Bochnia – K. Skoczylas-Ciszewska, J. Burtan, 1954.

J. Burtari, 1834. Compilation is based on the Detailed Geological Map of Poland on the scale 1:50,000, sheets: Kraków – J. Rutkowski, 1992, 1993; Niepołomice – R. Gradziński, 1955; Brzesko Nowe – J. Płonczyński, 1993; Myślenice – Z. Paul, W. Rączkowski, W. Rylko, A. Wójcik, 1995; Wieliczka – J. Burtan, 1954; Bochnia – K. Skoczylas-Ciszewska, J. Burtan, 1954.

#### MAPA GEOLOGICZNA **GEOLOGICAL MAP**



KREDA

SENON

TURON

TURONIAN

OKSFORD

Gezy i spongiolity z wkładkami margli i łupków – warstwy gezowe Gaizes and spongiolites with bands of marls and shales – Gaize Beds

hales (black) with bands of sandstones and siderites – Wierzów Shales

upki (czame) z wkładkami piaskowców, syderytów – łupki wierzow-

Piaskowce z wkładkami łupków i zlepieńców – piaskowce grodziskie Sandstones with bands of shales and conglomerates – Grodziszcze Sandstones

Łupki z wkładkami piaskowców cienkolawicowych i syderytów – war-

ALB-CENOMAN

BARREM-APTIAN

ALBIAN-CENOMANIAN

20 Rumosze krzemienne

Marls and gaizes (with cherts, in places)

Wapienie skaliste i wapienie ławicowe, miejscami z krzemieniami,

oraz wapienie płytowe Massive limestones and flaglike limestones, with cherts (in places), and platy

PALEOGEN [

KREDA GÓRNA

JURASSIC UPPER JURASSIC

CRETACEOUS

JURA GÓRNA

ZLODOWACENIE ŚRODKOWOPOLSKIE

ZLODOWACENIE POŁUDNIOWOPOLSKIE

PLIOCEN

MIDDLE-POLISH GLACIATION

SOUTH-POLISH GLACIATION

Utwory glacjalne

TRZECIO-RZĘD NEOGEN TERTIARY NEOGENE

#### **ZABUDOWA** LAND DEVELOPMENT

### **OPRÓBOWANIE** SAMPLING



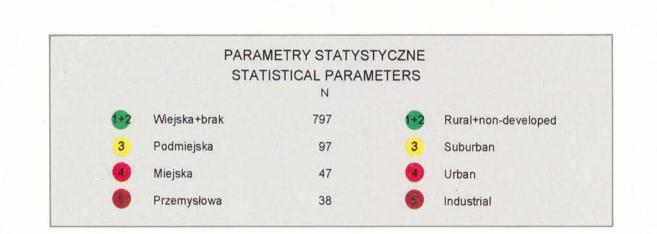


N 600\_

500

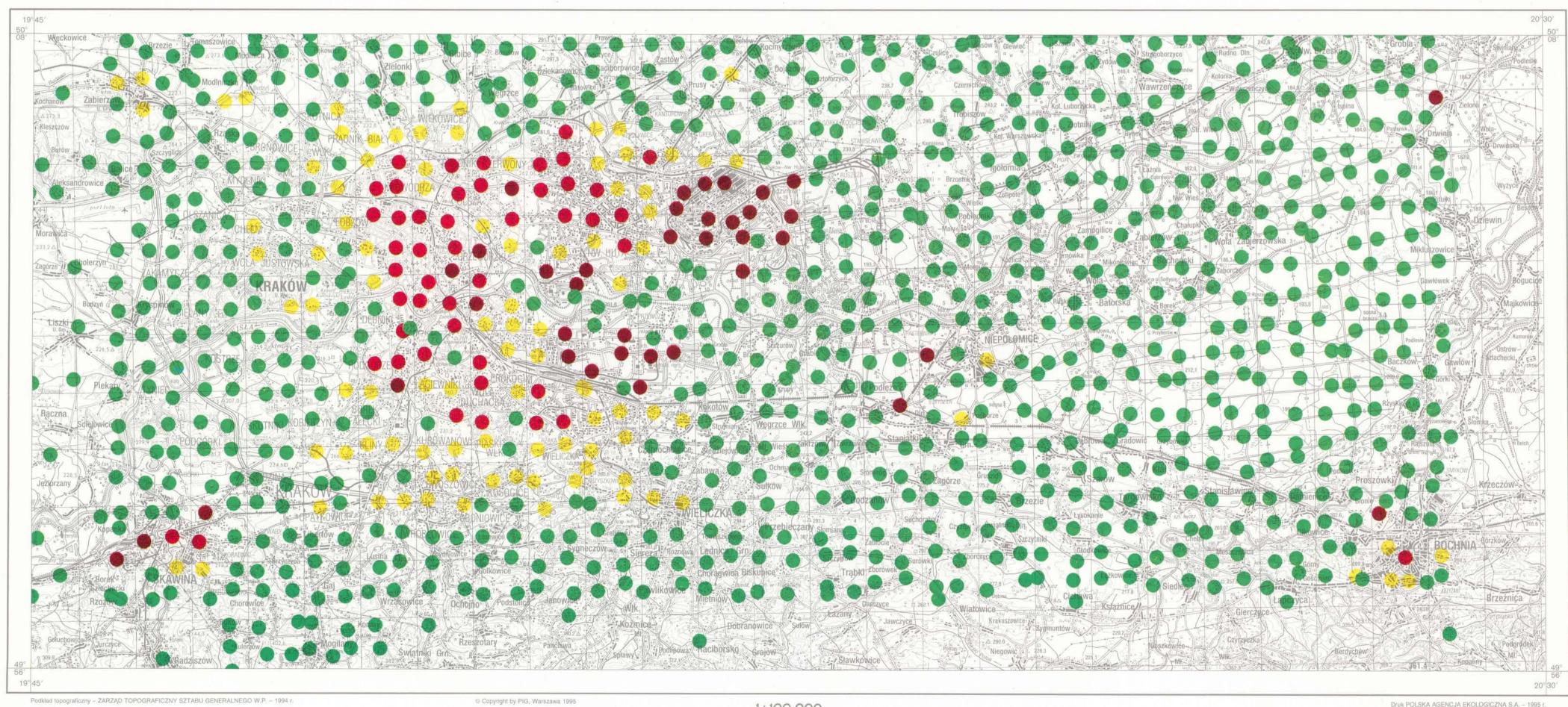
300

200



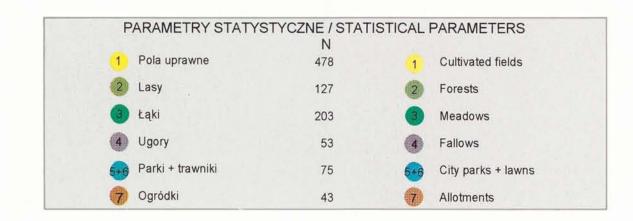
ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC

**GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS** 



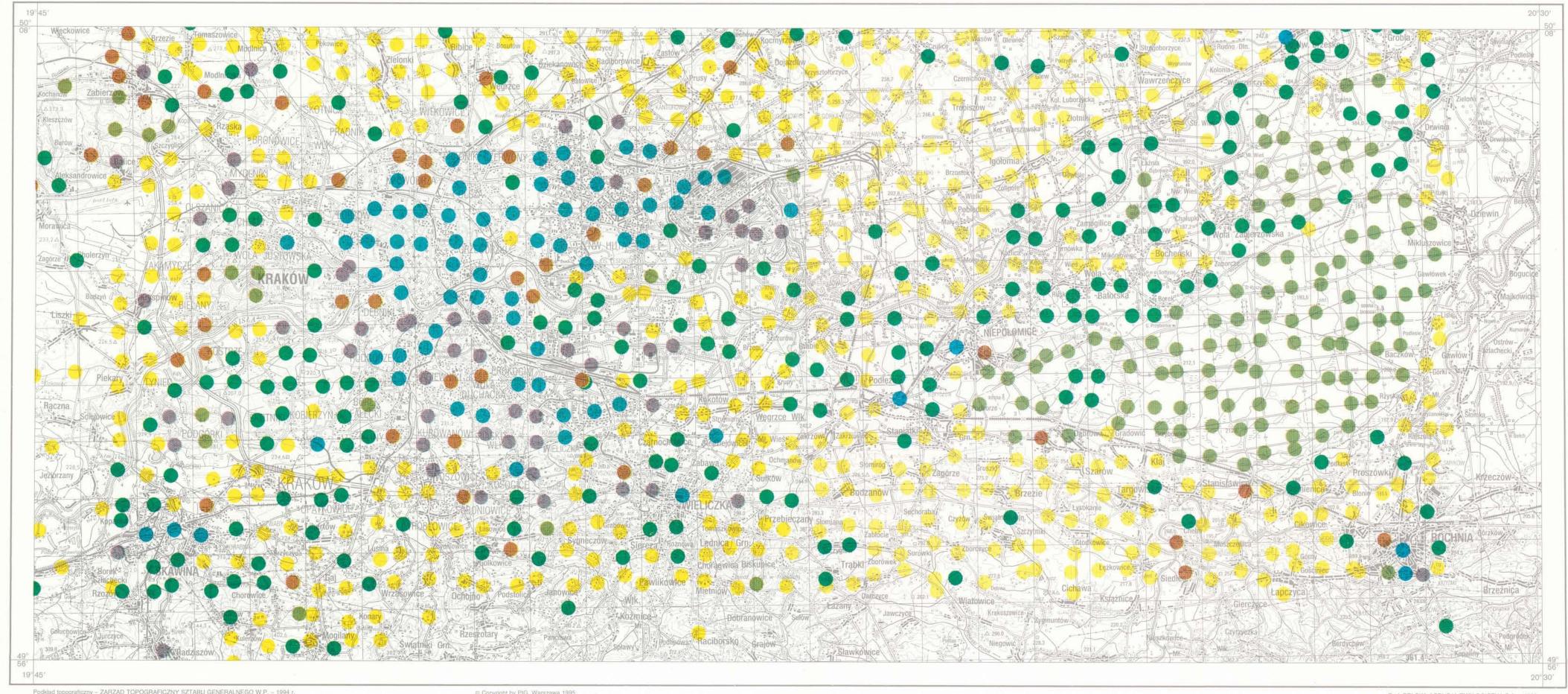
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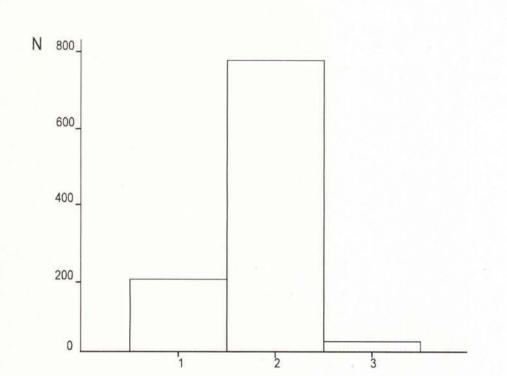
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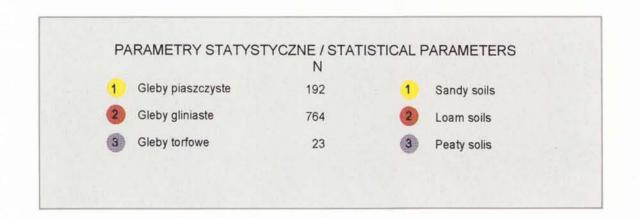


**UŻYTKOWANIE GLEB** SOILS EMPLOYMENT

**OPRÓBOWANIE SAMPLING** 

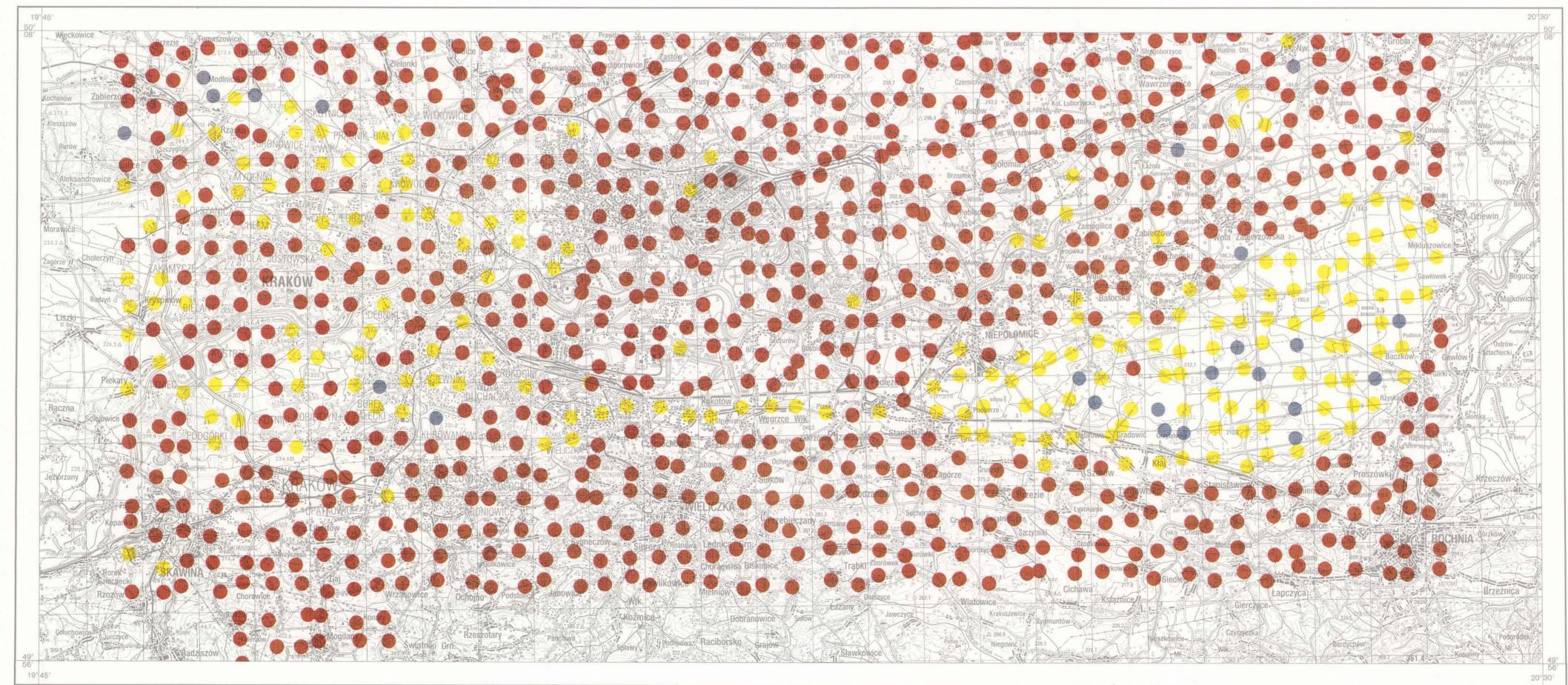






RODZAJE GLEB KINDS OF SOILS

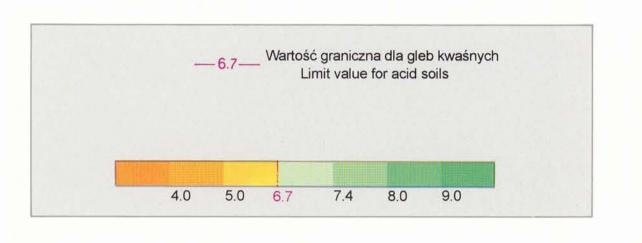
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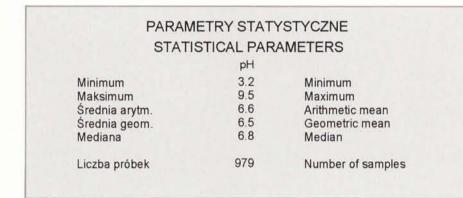


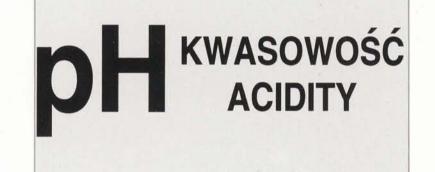
TABLICA PLATE

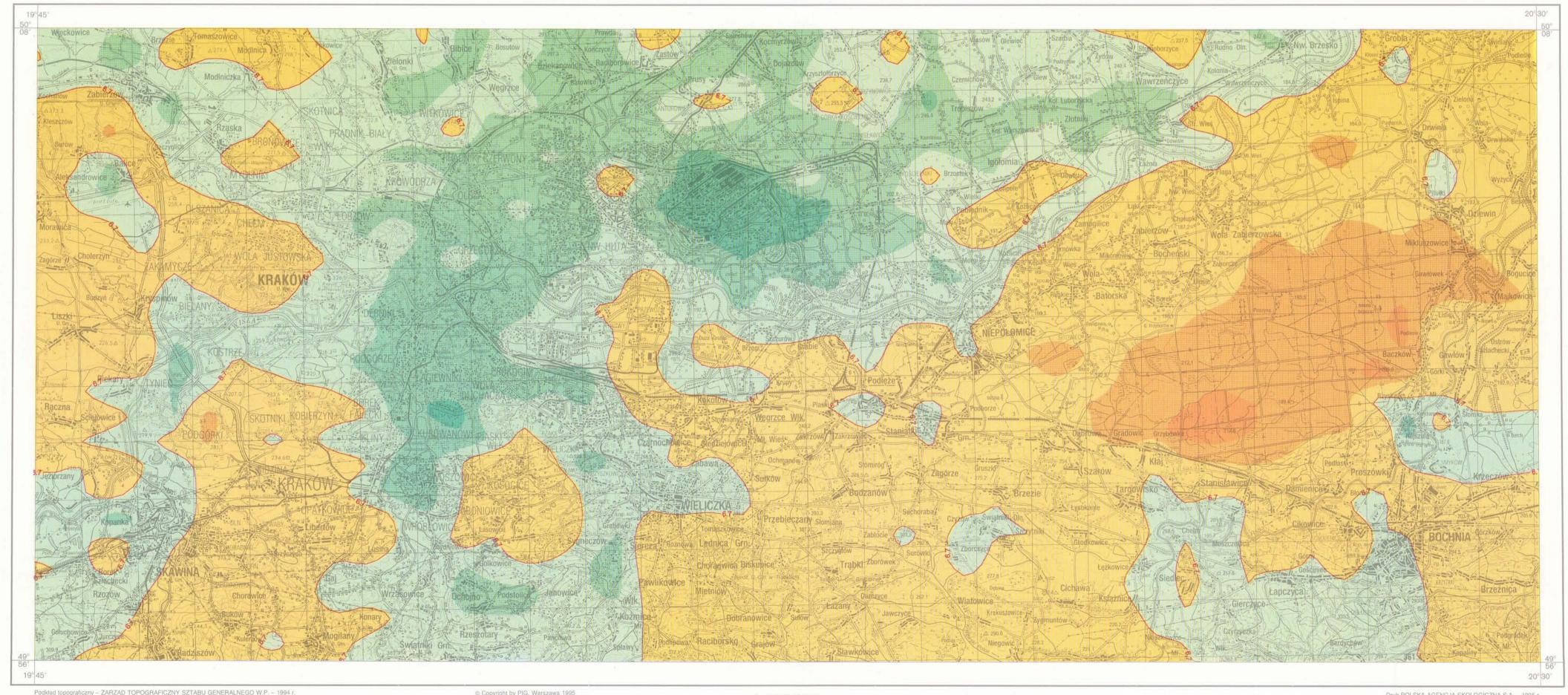


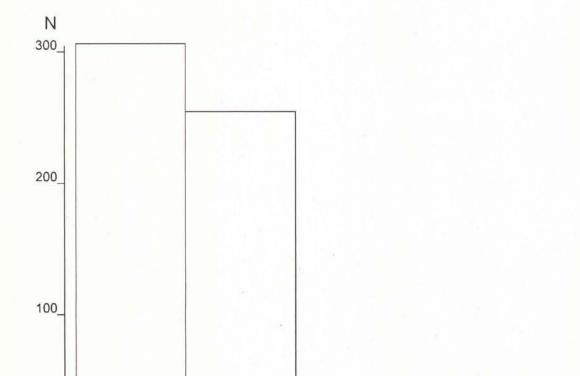




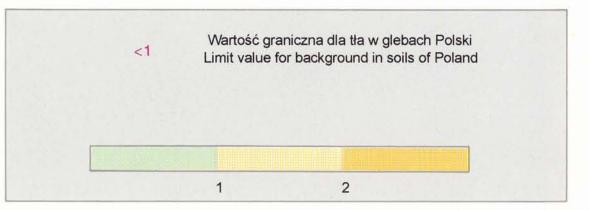


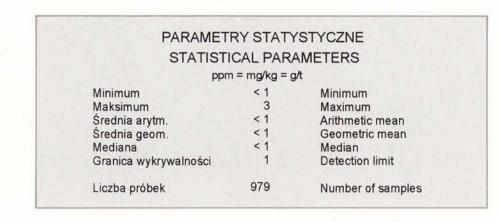




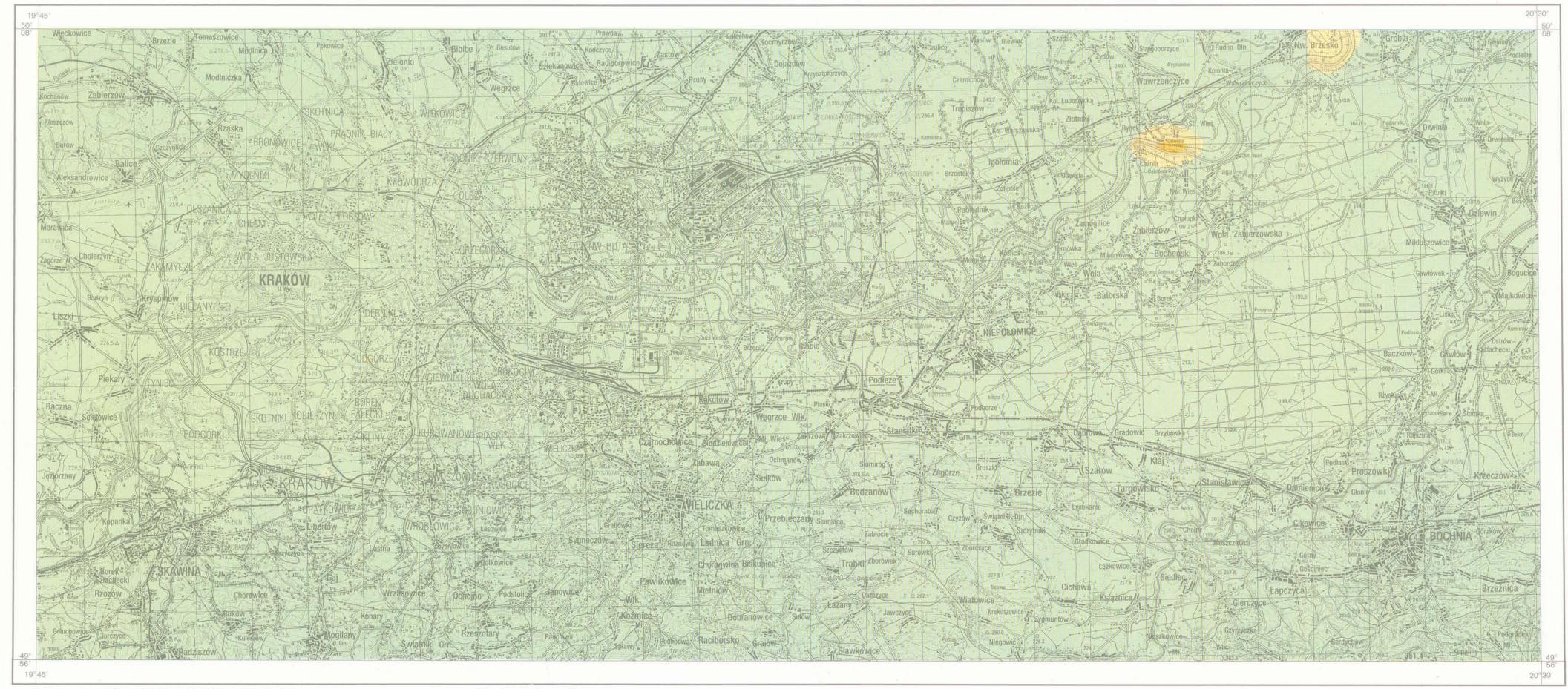


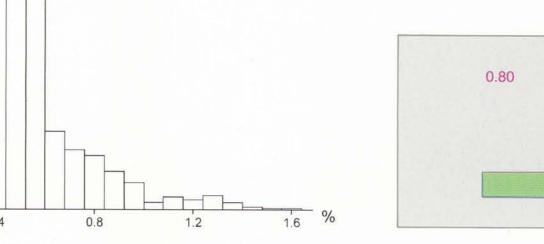
**GLEBY** SOILS

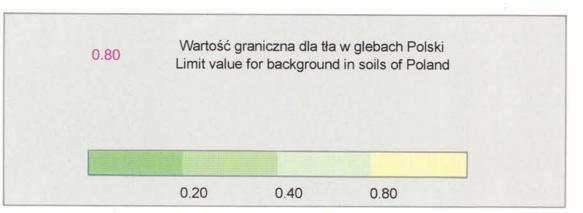


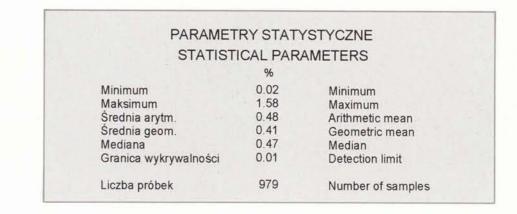


SREBRO SILVER

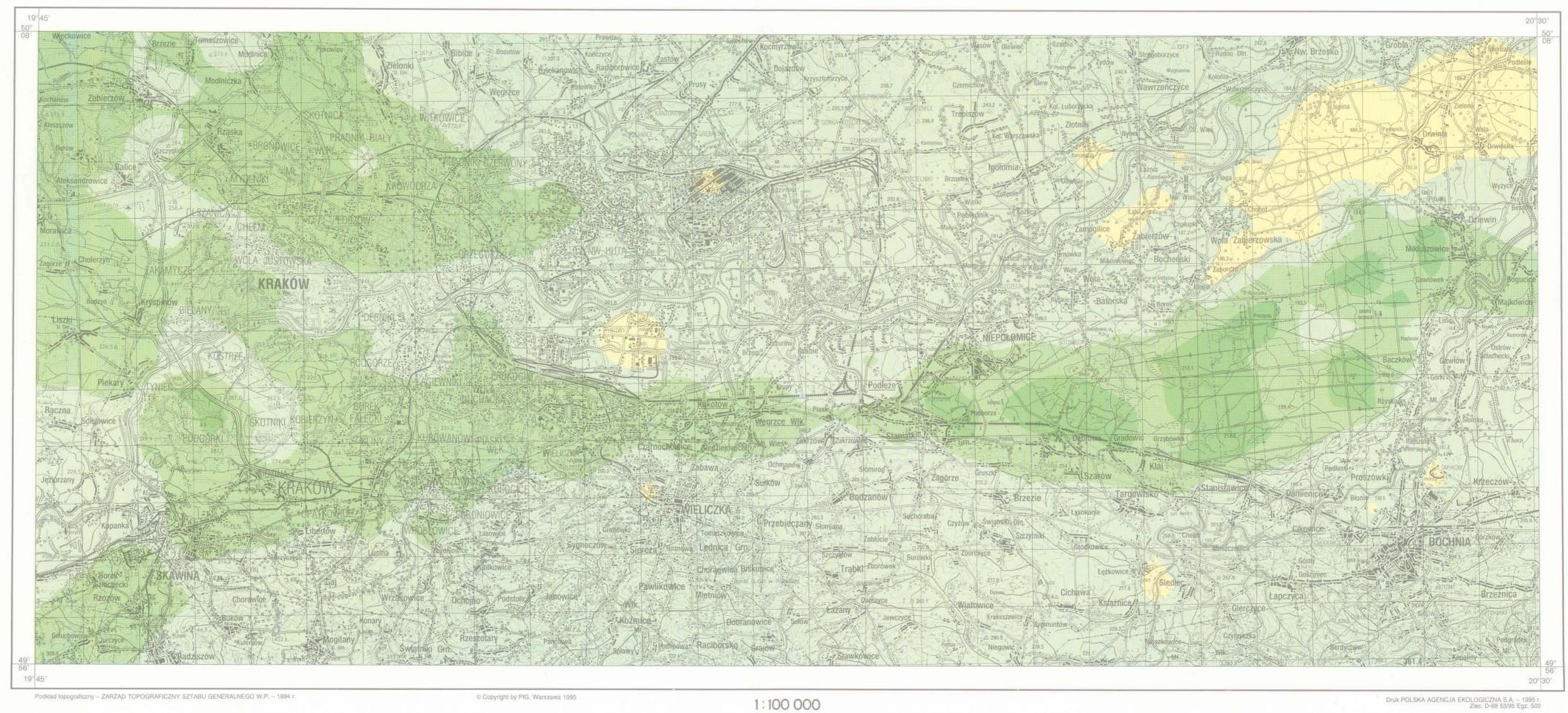




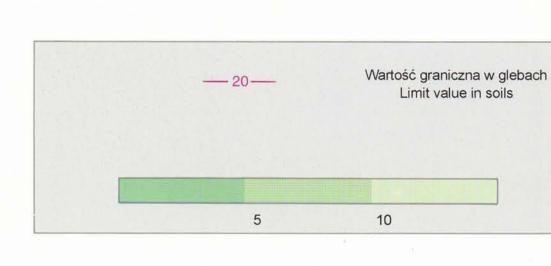


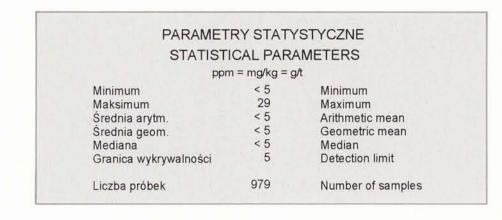


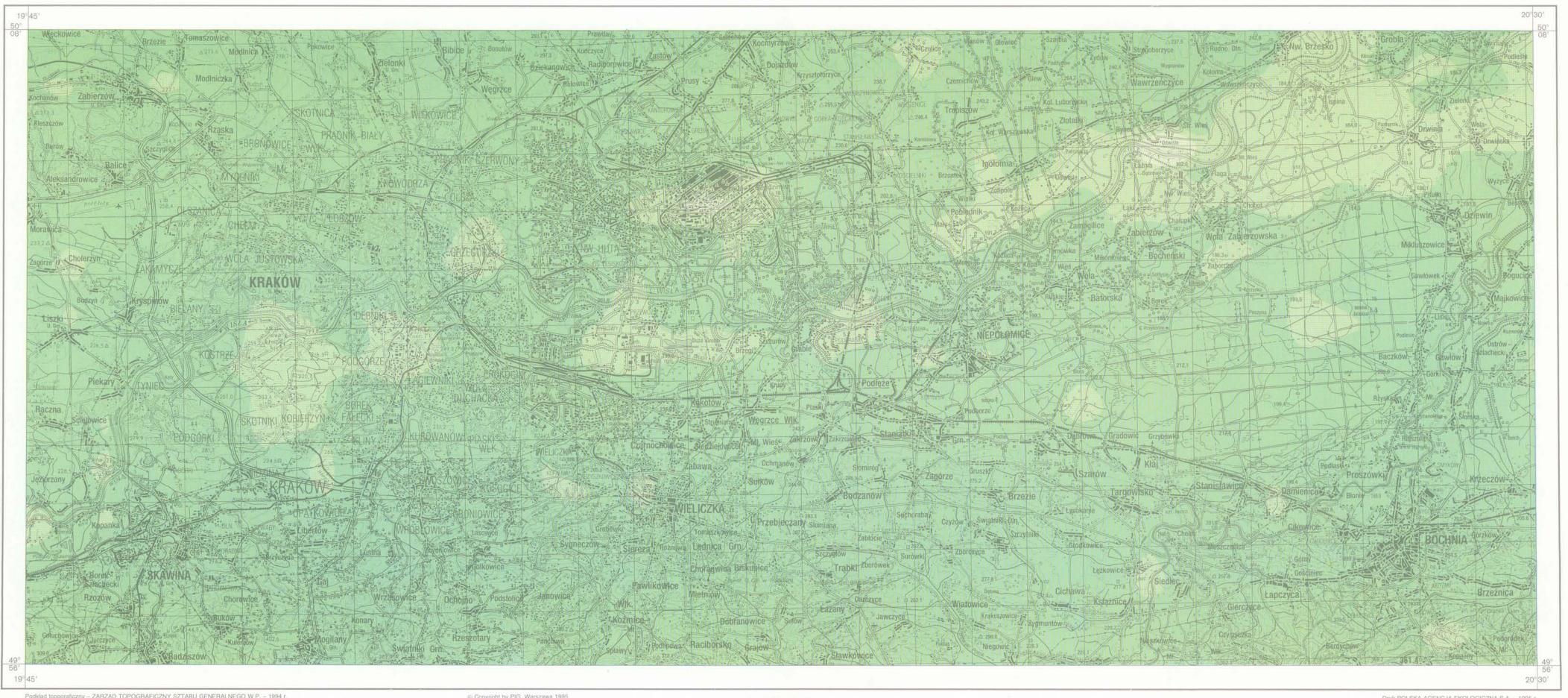


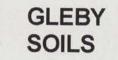




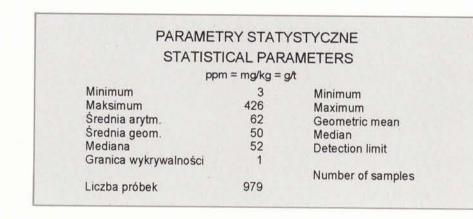




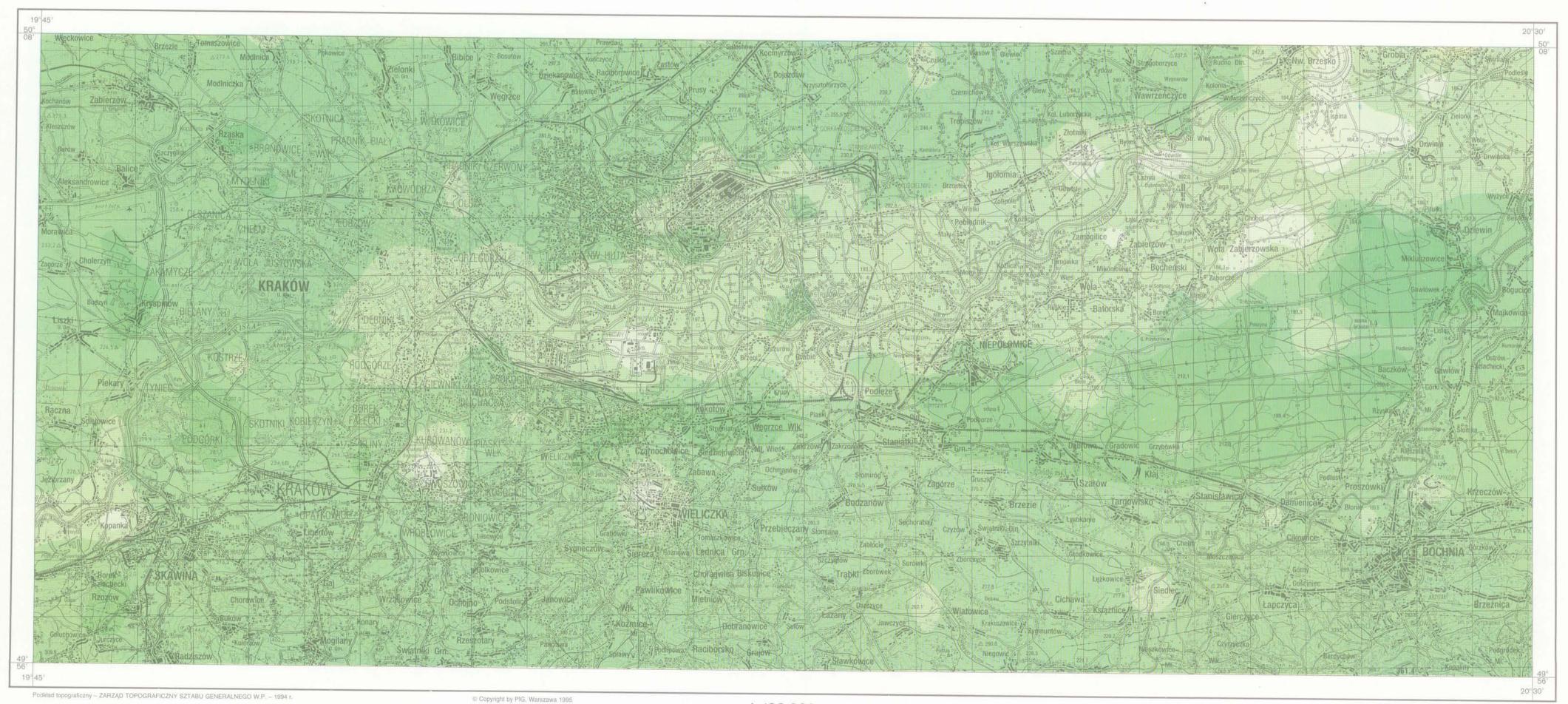








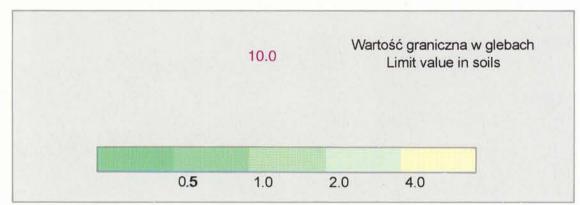




**GLEBY** SOILS

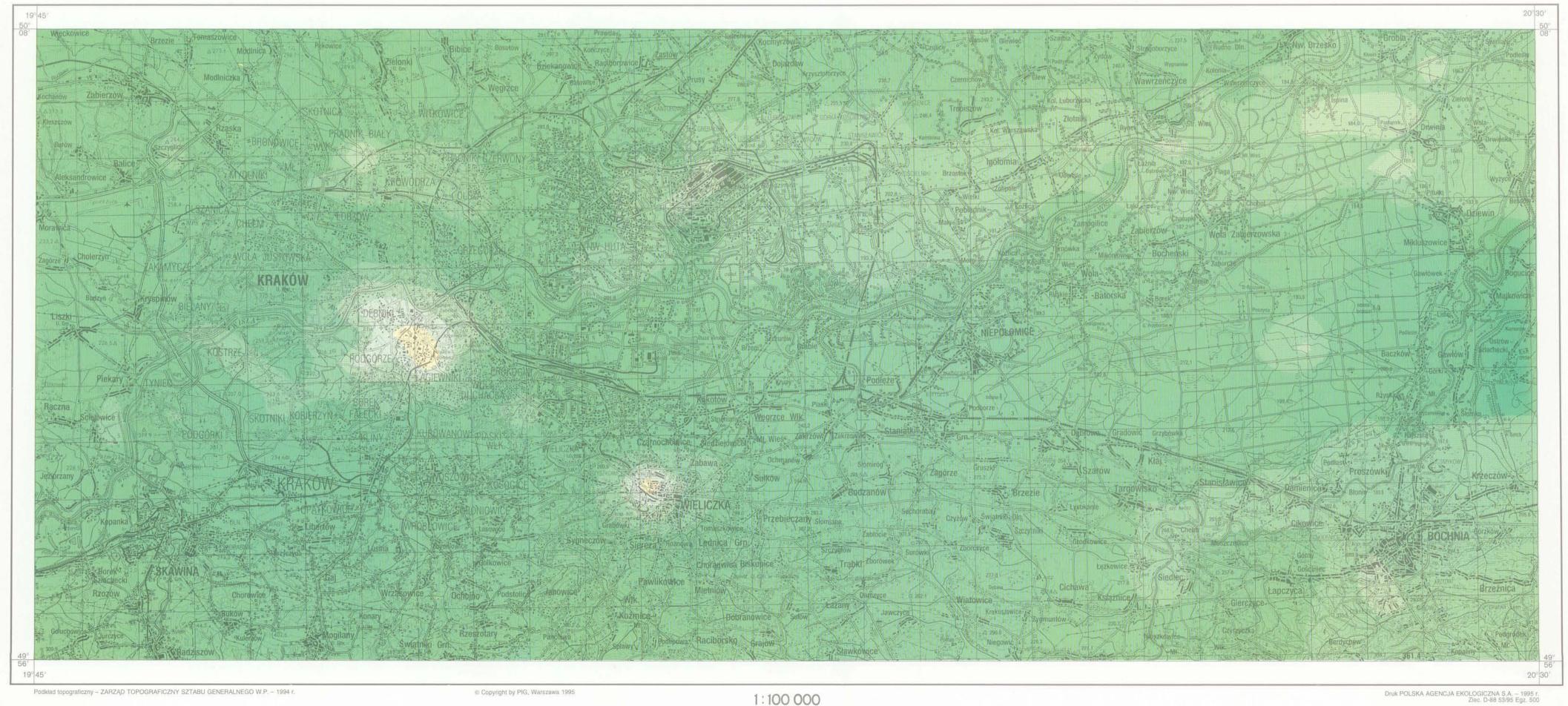


< 0.5 0.5



|                       |               | STYCZNE          |
|-----------------------|---------------|------------------|
| SIAIISI               | ICAL PAR      | AMETERS          |
| ppi                   | m = mg/kg = g | y/t              |
| Minimum               | < 0.5         | Minimum          |
| Maksimum              | 17            | Maximum          |
| Średnia arytm.        | < 0.5         | Arithmetic mean  |
| Średnia geom.         | < 0.5         | Geometric mean   |
| Mediana               | < 0.5         | Median           |
| Granica wykrywalności | 0.5           | Detection limit  |
| Liczba próbek         | 979           | Number of sample |

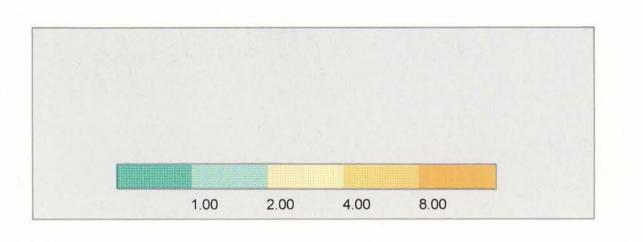


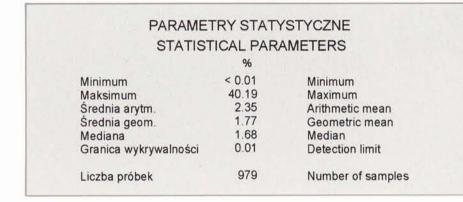


1 10

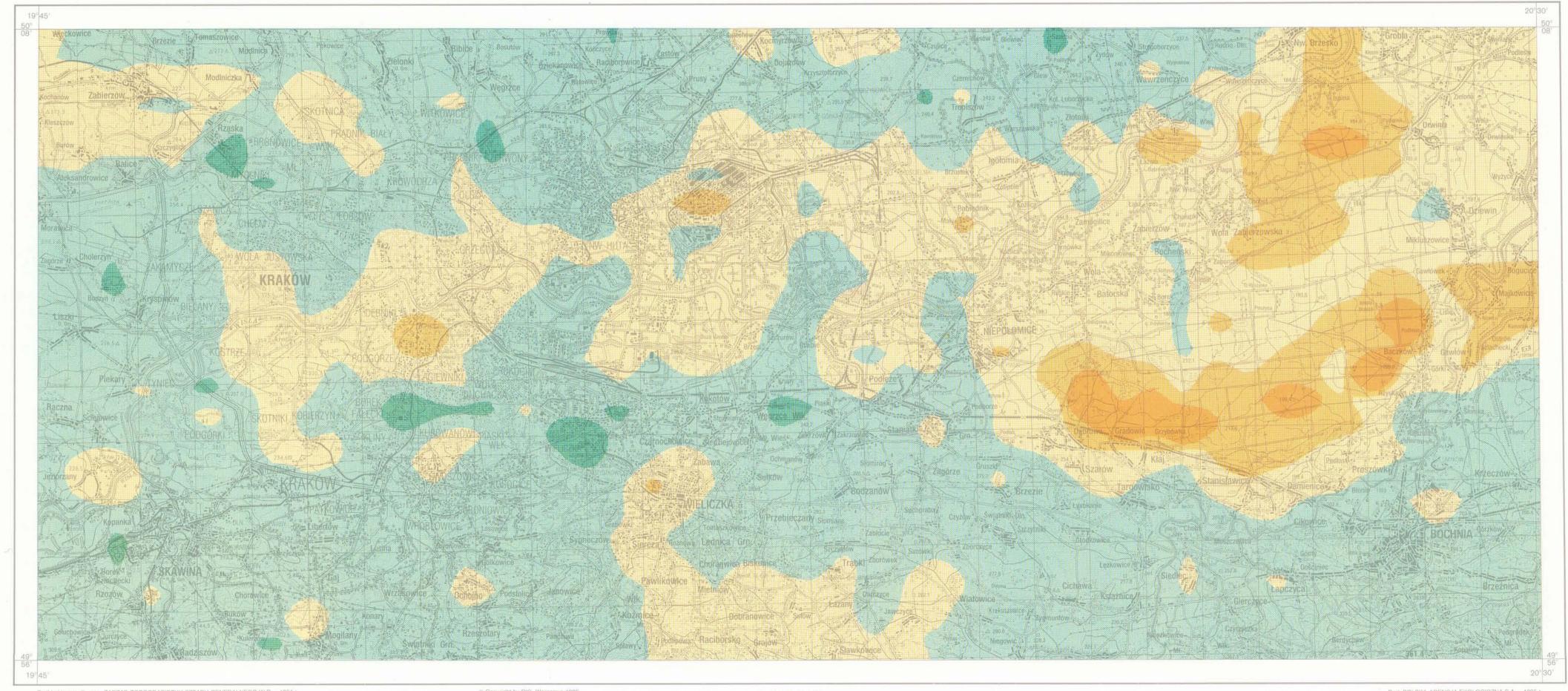
# MISTYTUT GEOF

### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS







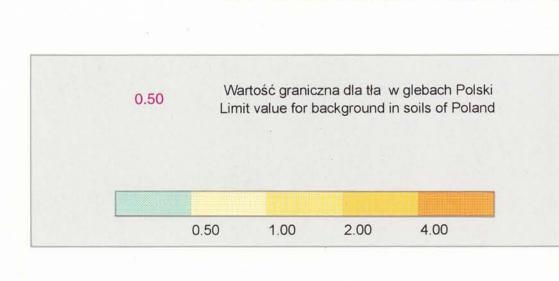


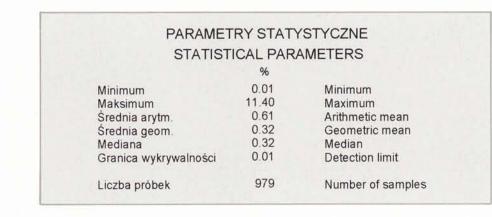
TABLICA PLATE



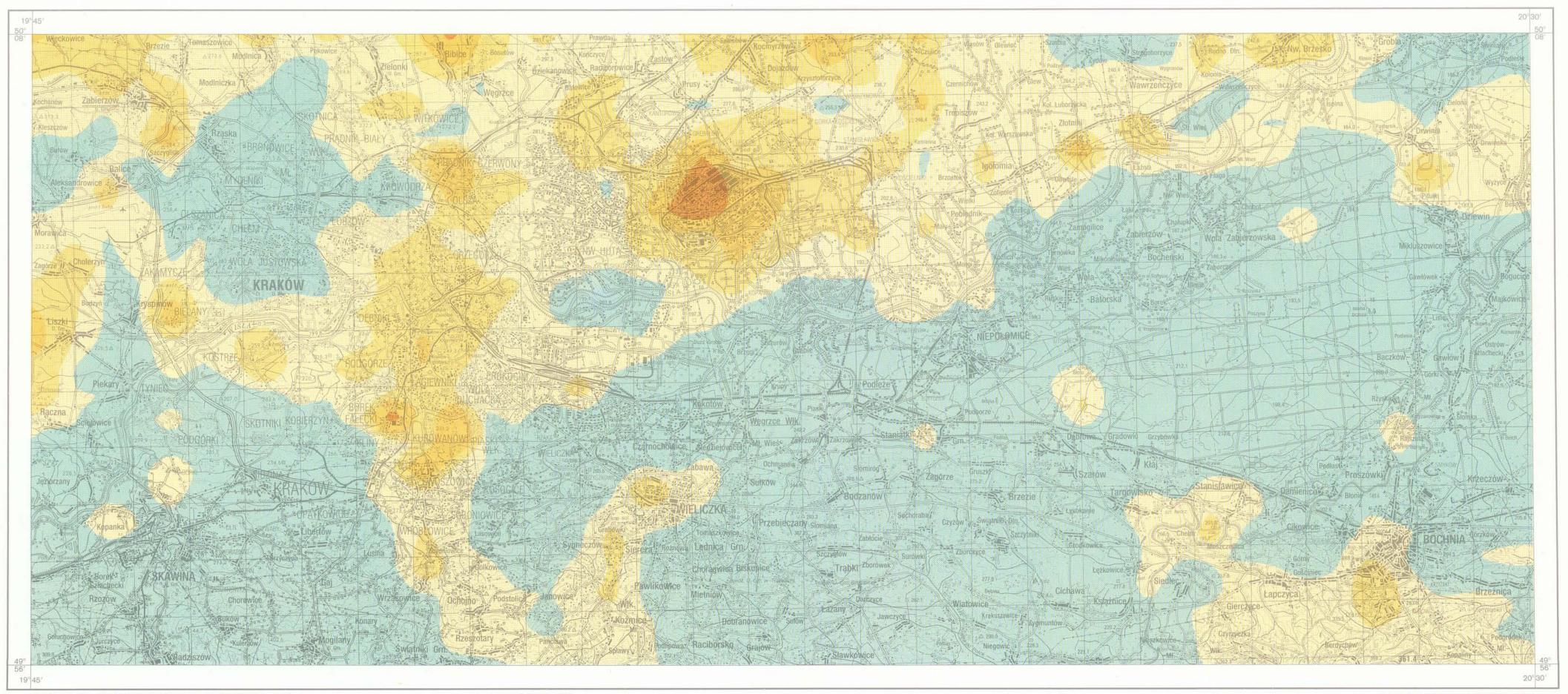
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

**GLEBY** SOILS





Ca WAPŃ CALCIUM

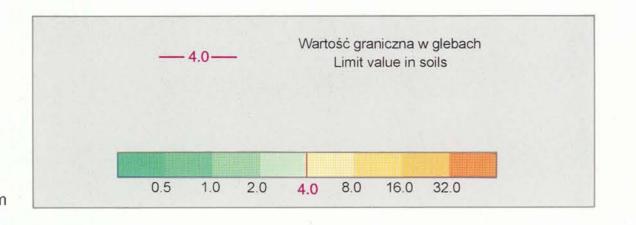


300\_

100\_

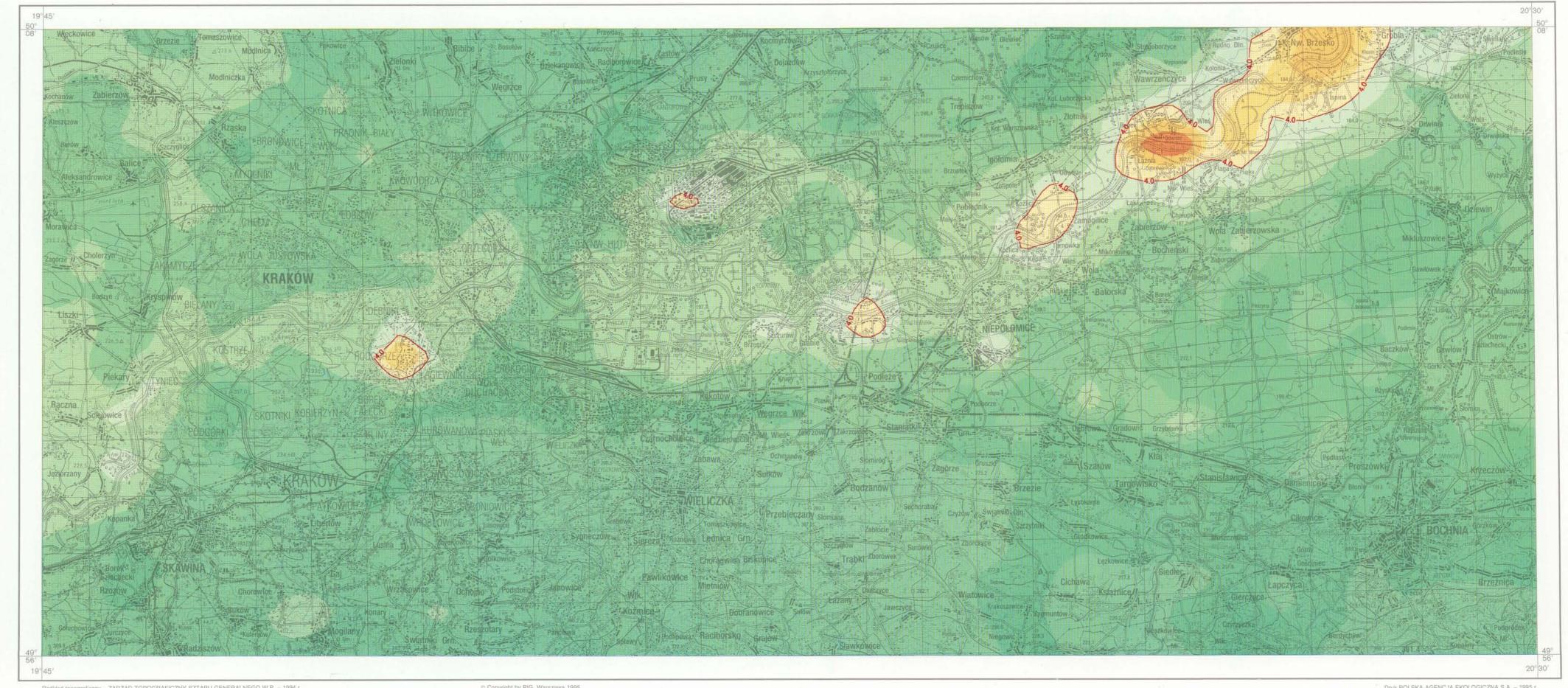


**GLEBY** SOILS



| Minimum        | ppm = mg/kg = (<br>< 0.5 | g/t<br>Minimum  |
|----------------|--------------------------|-----------------|
| Maksimum       | 68.4                     | Maximum         |
| Średnia arytm. | 1.2                      | Arithmetic mean |
| Średnia geom.  | 0.7                      | Geometric mean  |
| Mediana        | 0.7                      | Median          |
| Granica wykryw | alności 0.5              | Detection limit |





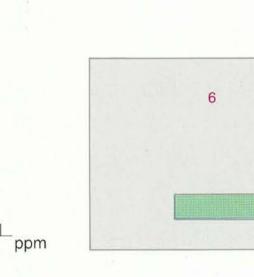
< 0.5 0.5

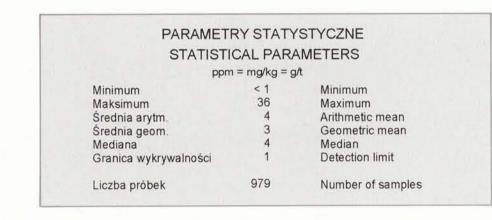
Wartość graniczna dla tła w glebach Polski Limit value for background in soils of Poland

TABLICA 13

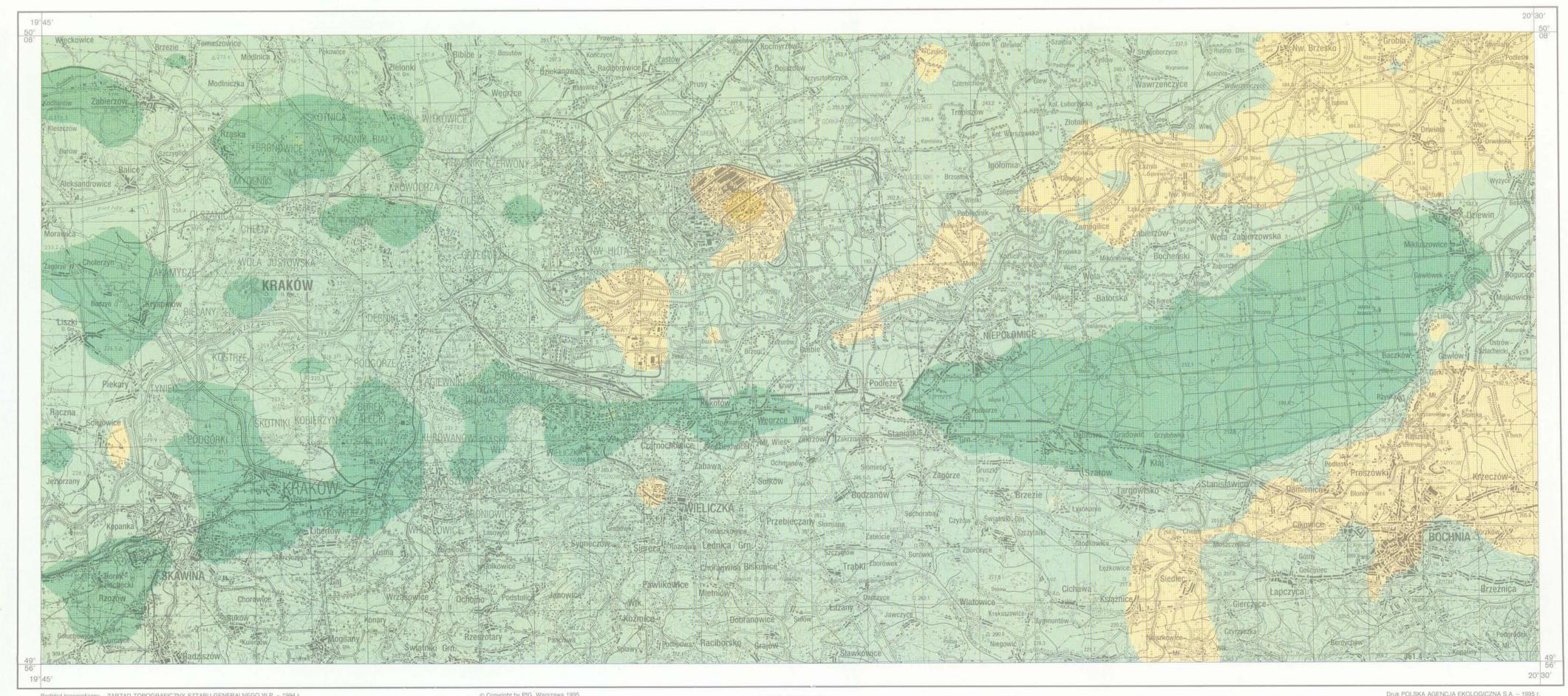


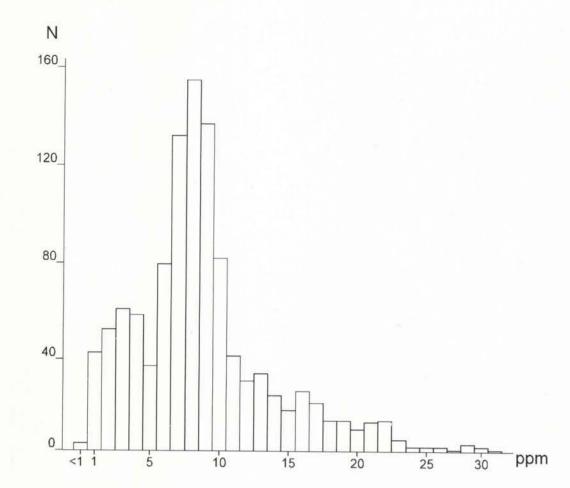
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

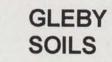


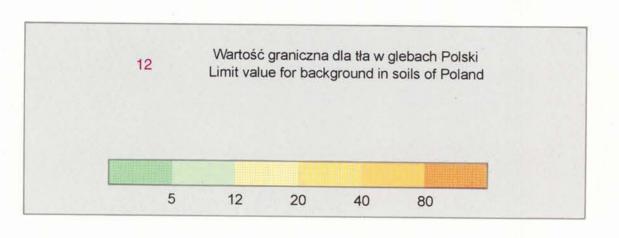


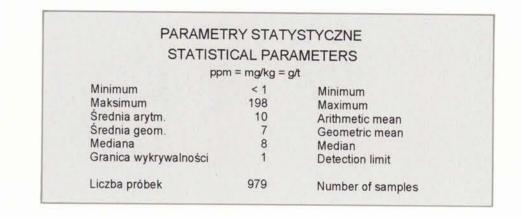


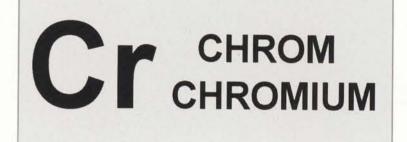


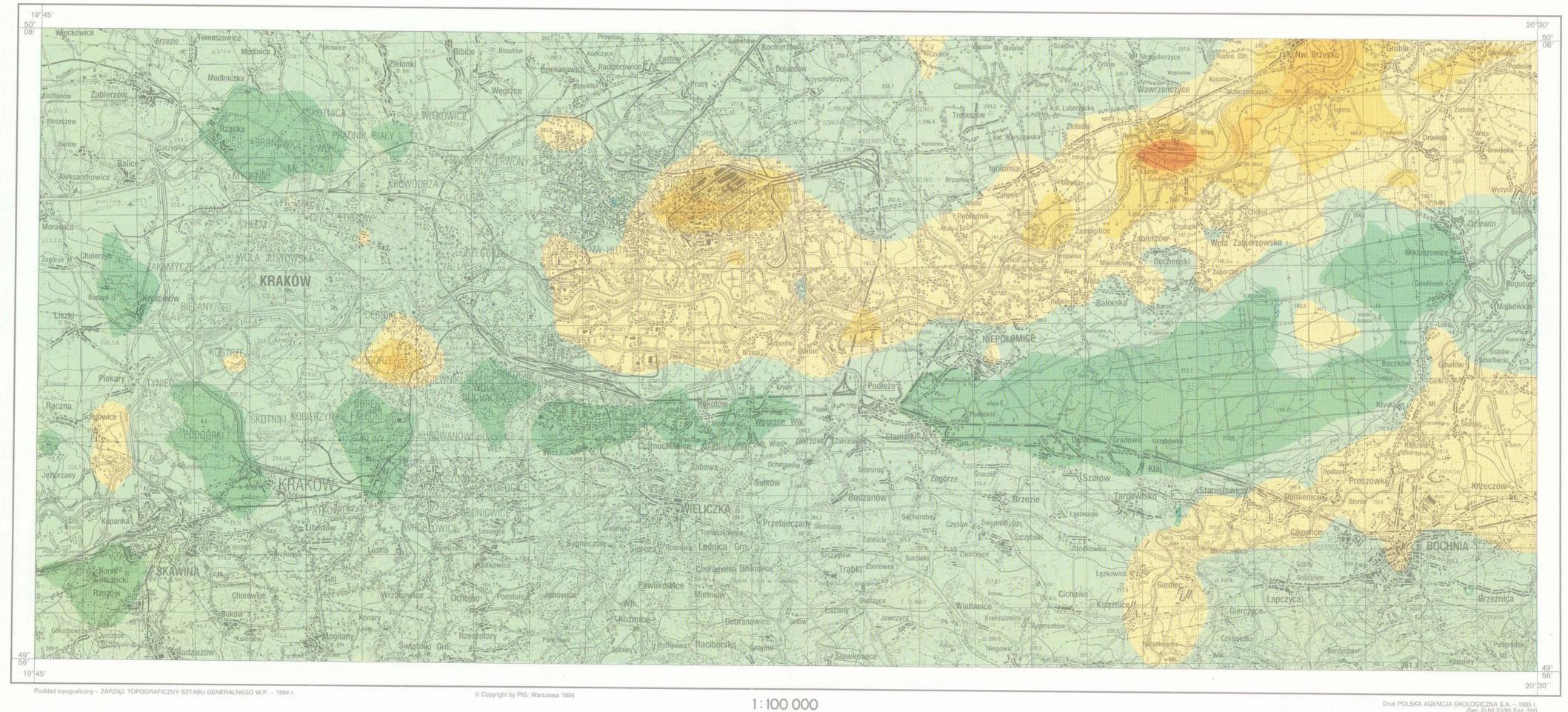








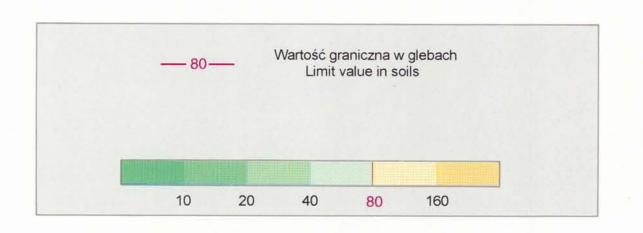


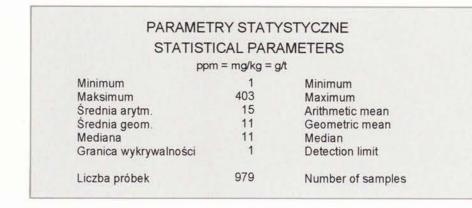


#### PAŃSTWOWY INSTYTUT GEOLOGICZNY

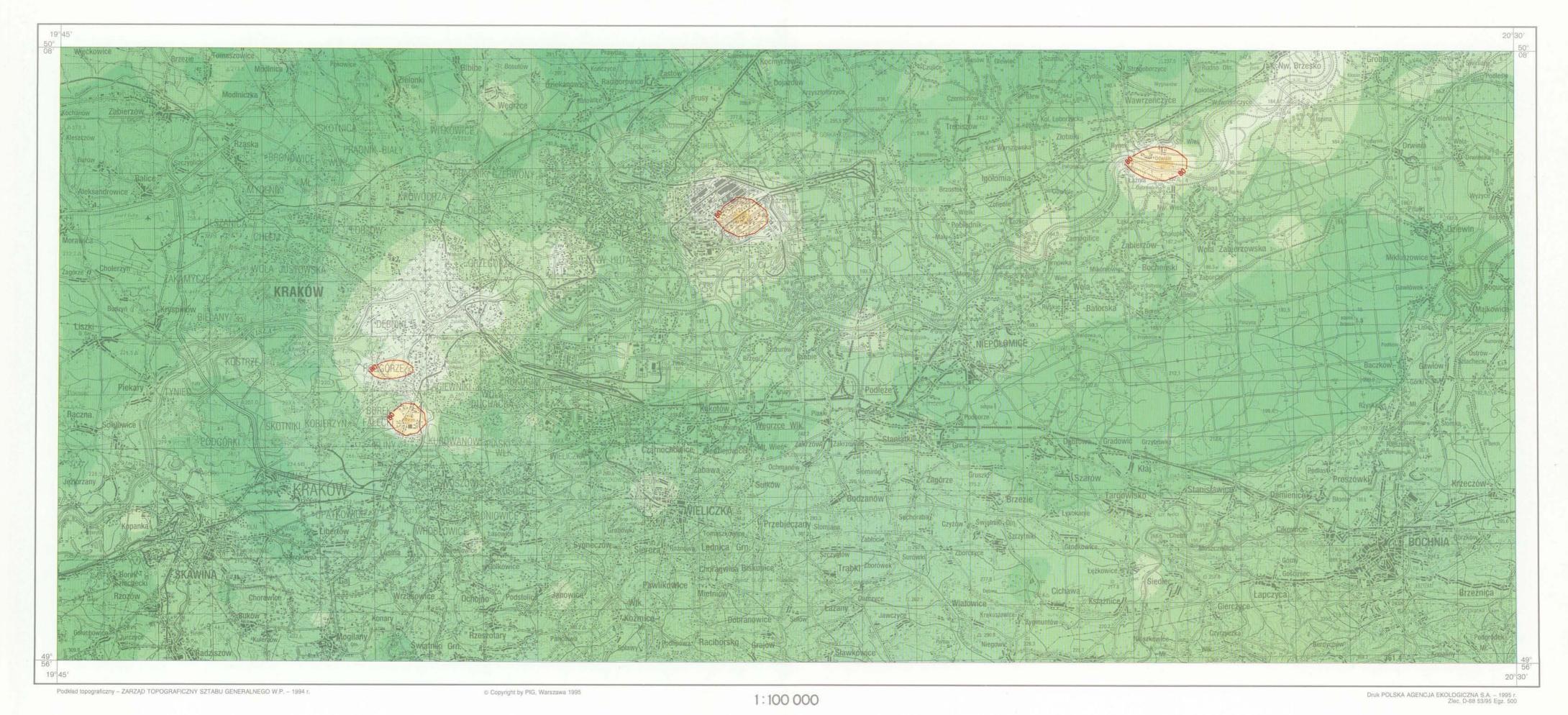
TABLICA 15

# ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS







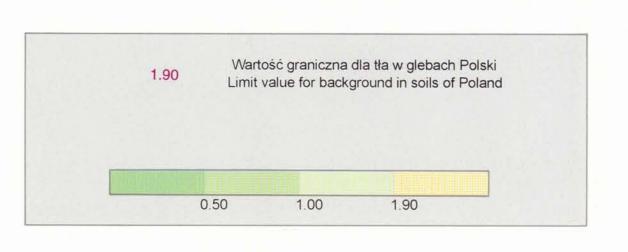


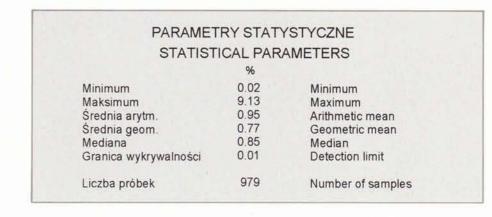
TABLICA 16



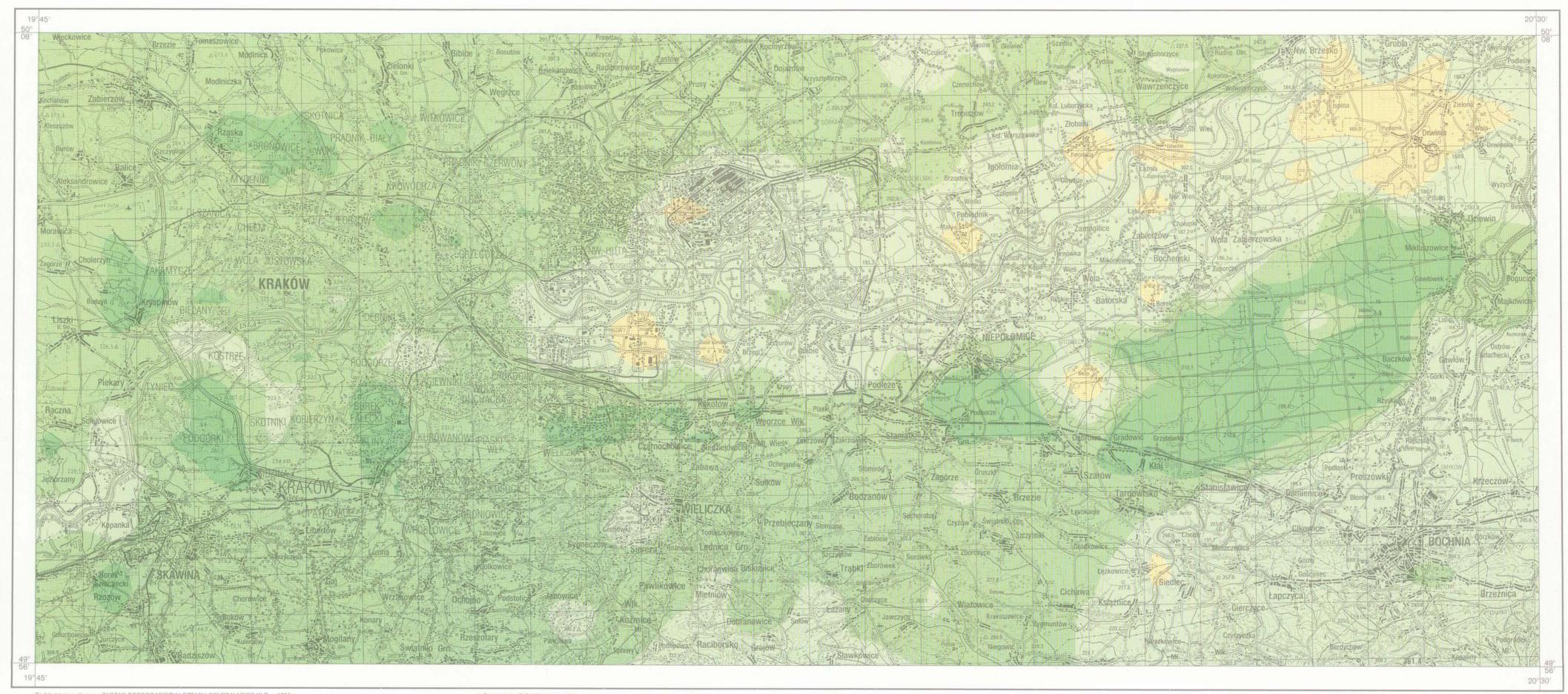
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

**GLEBY** SOILS





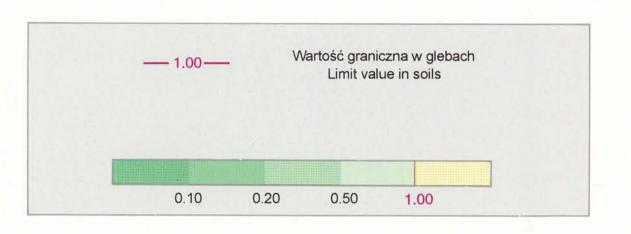
ŻELAZO

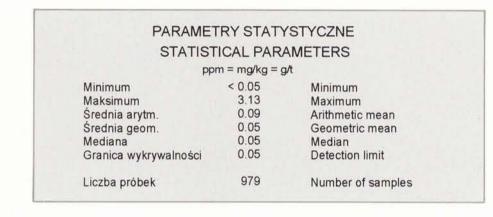


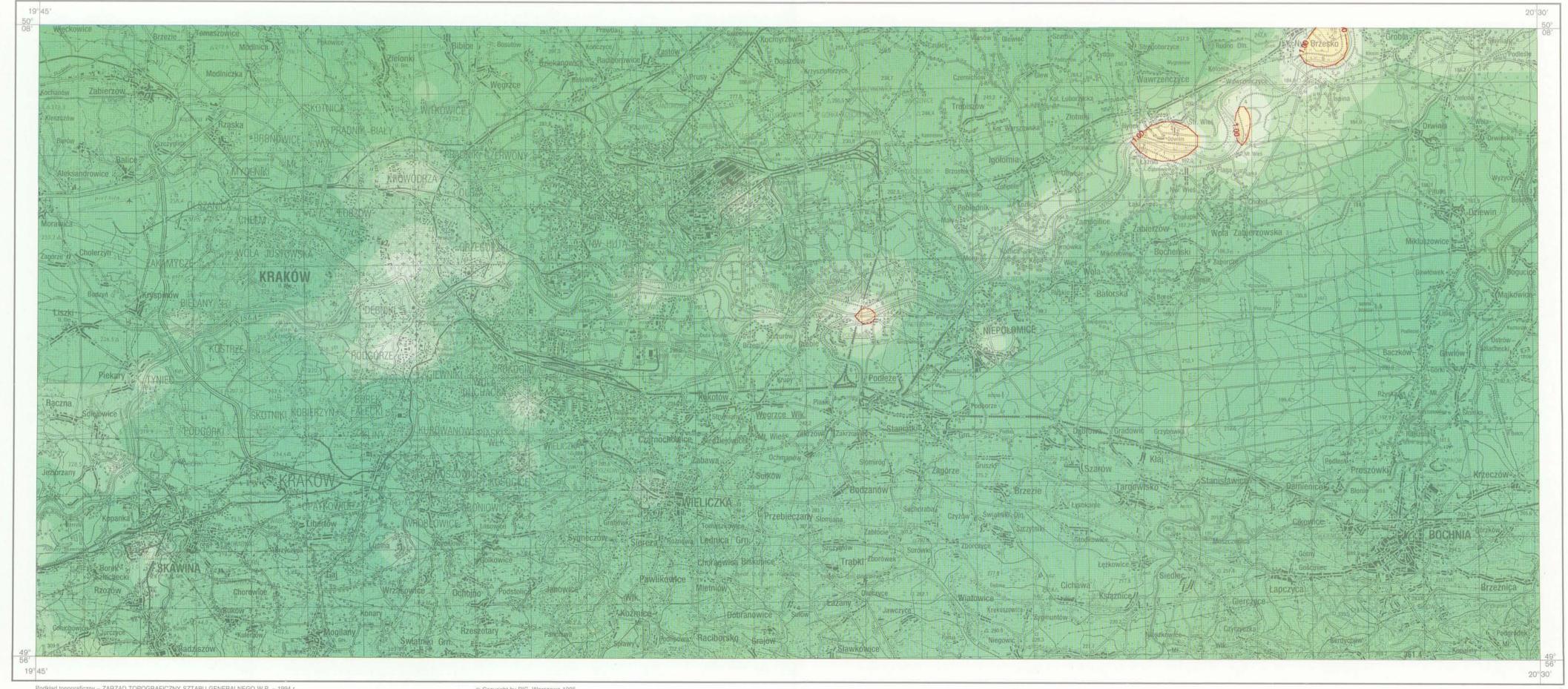
TABLICA 17



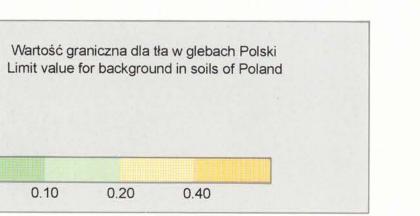
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

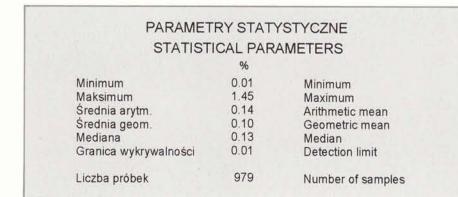




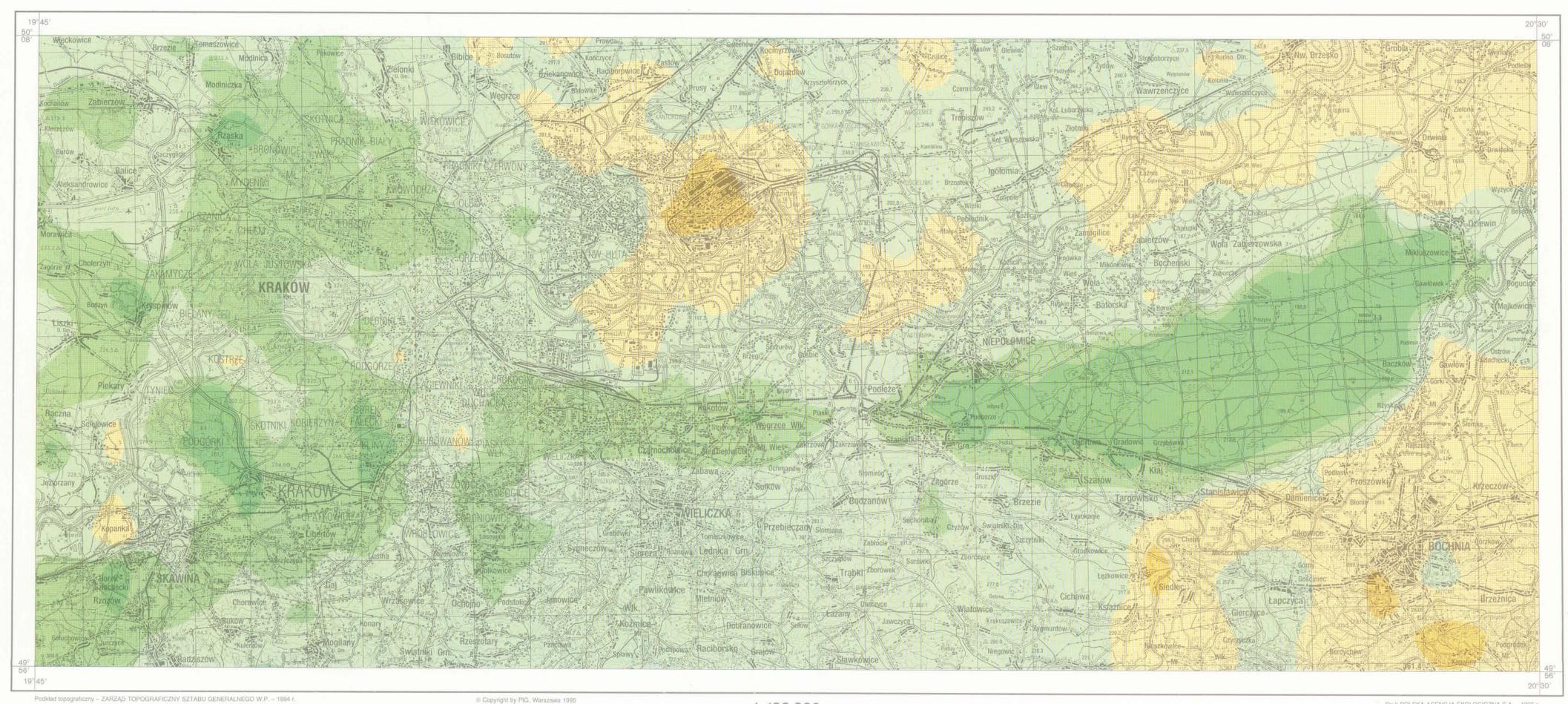




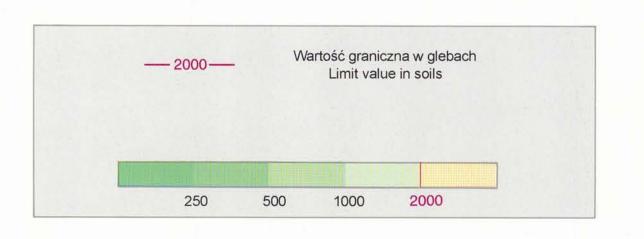


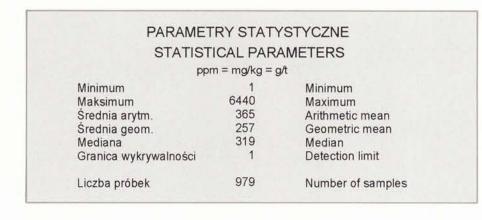




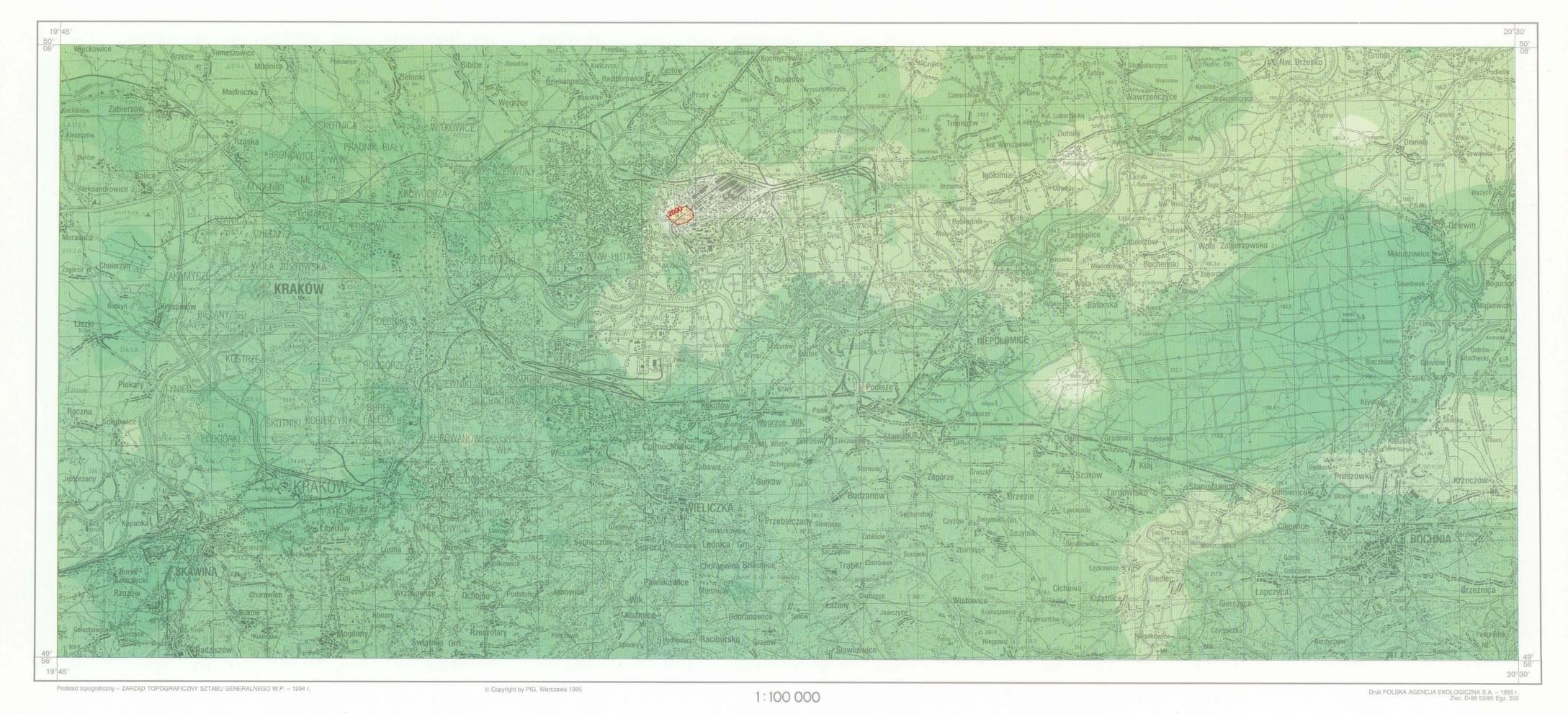








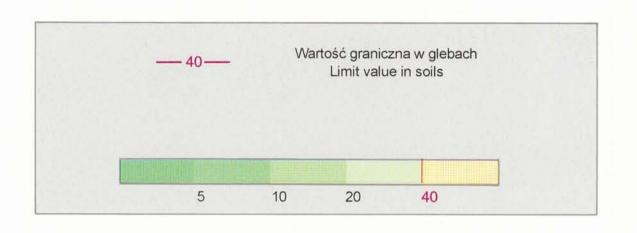


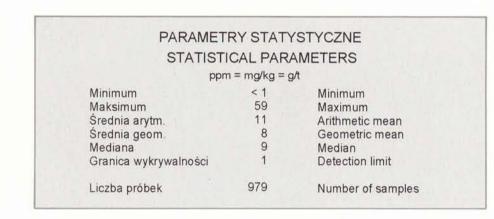


TABLICA 20

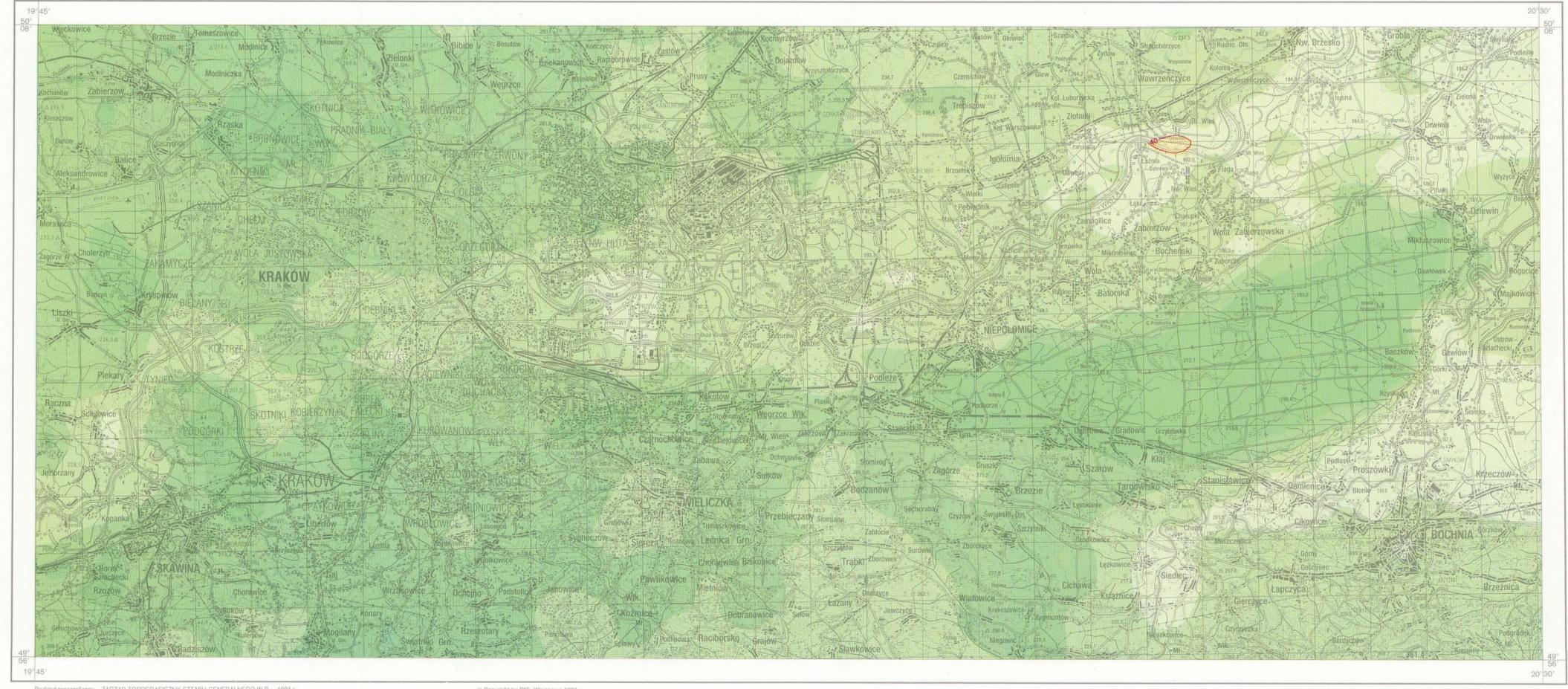




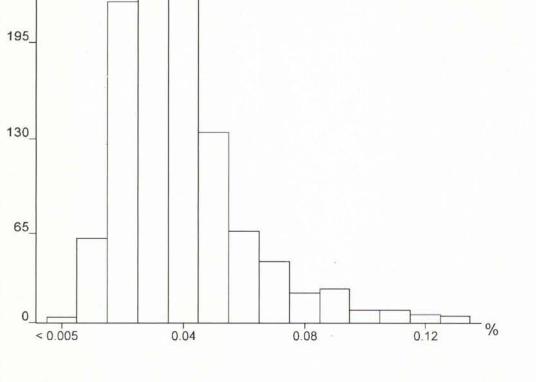


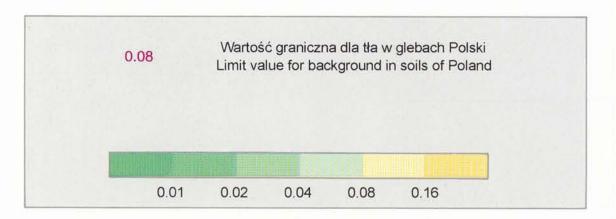


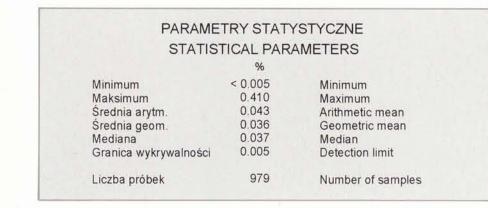


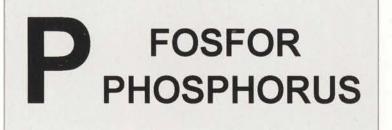


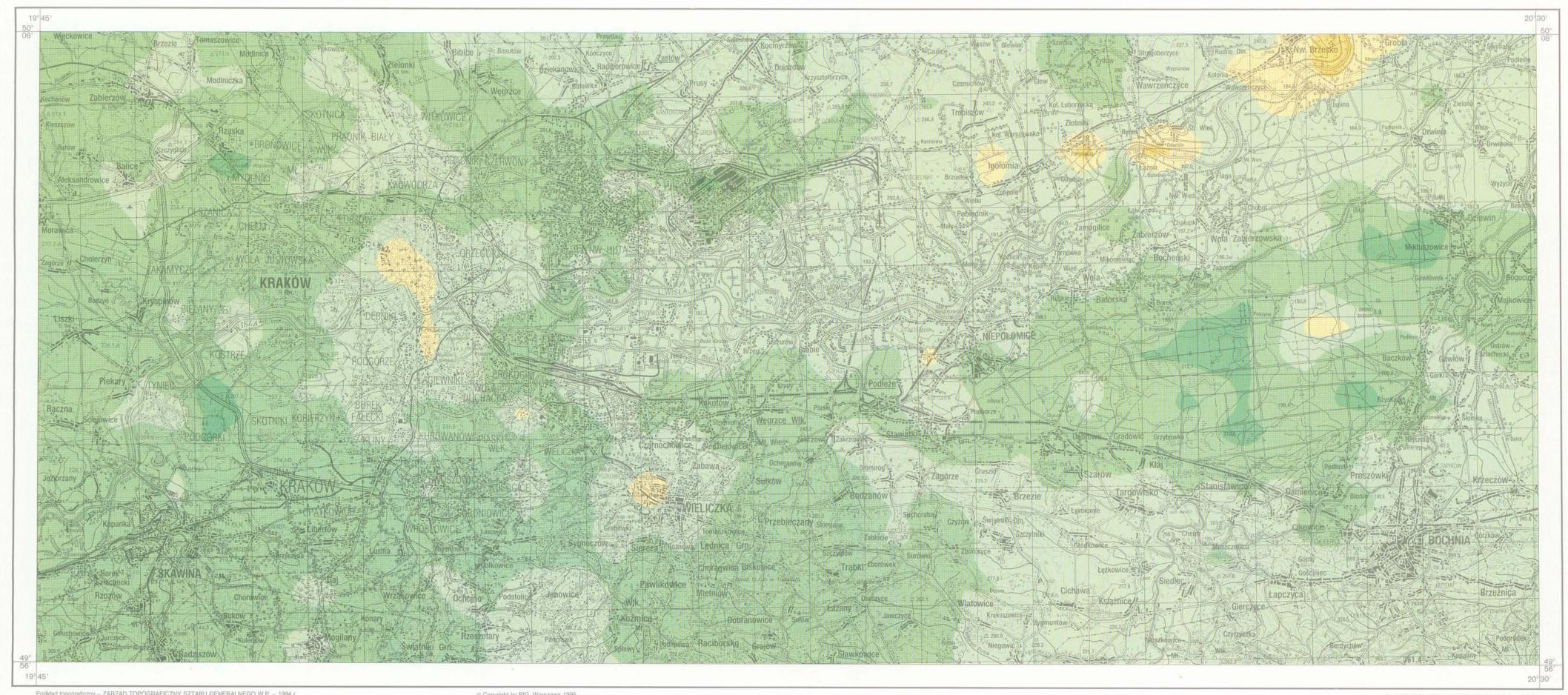






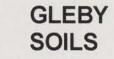


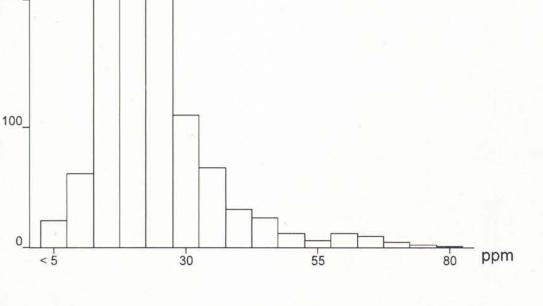


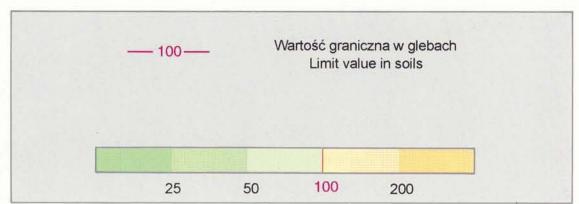


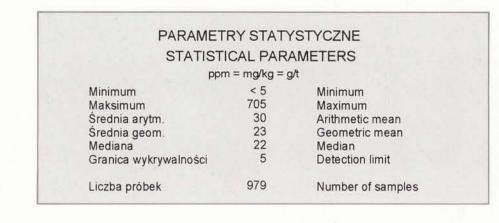
TABLICA 22



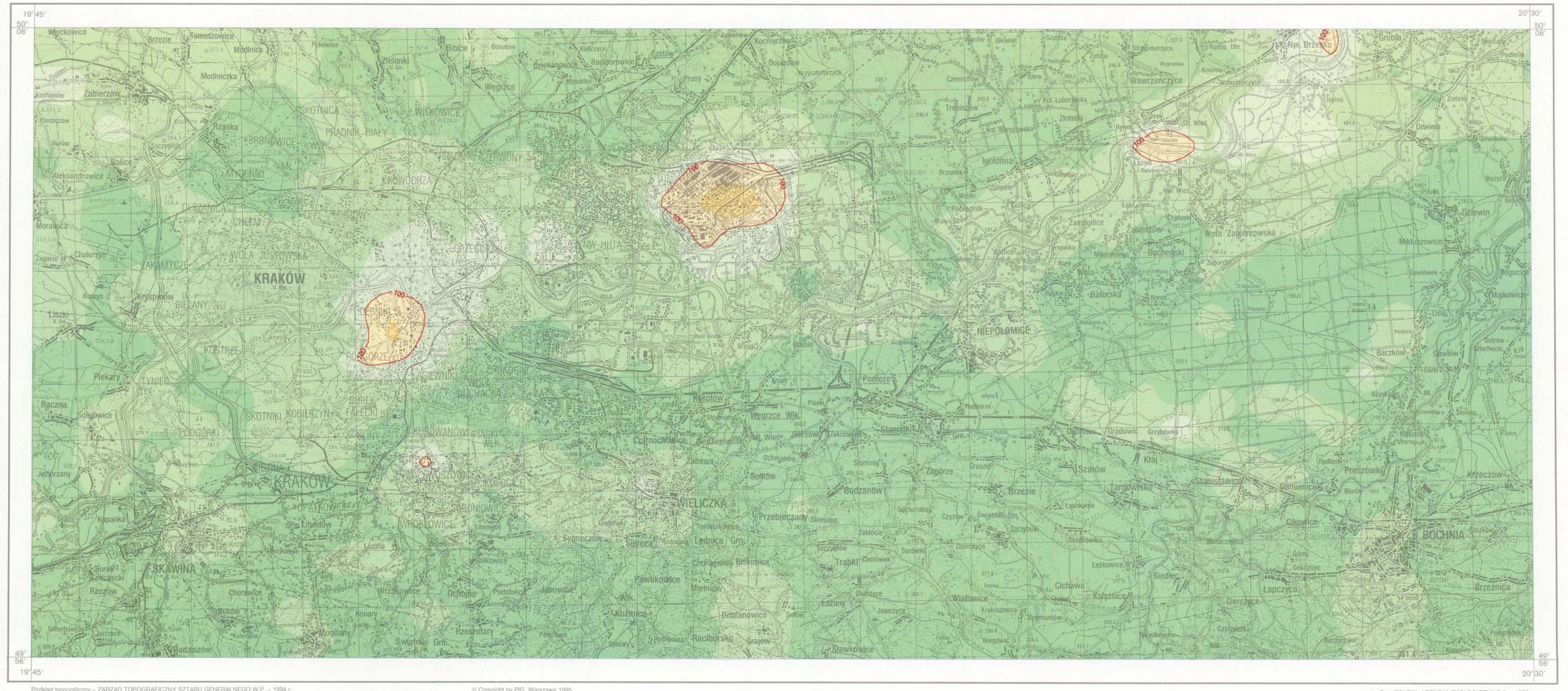




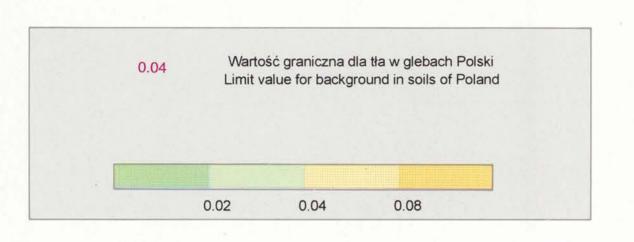


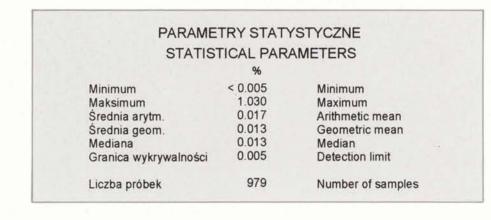




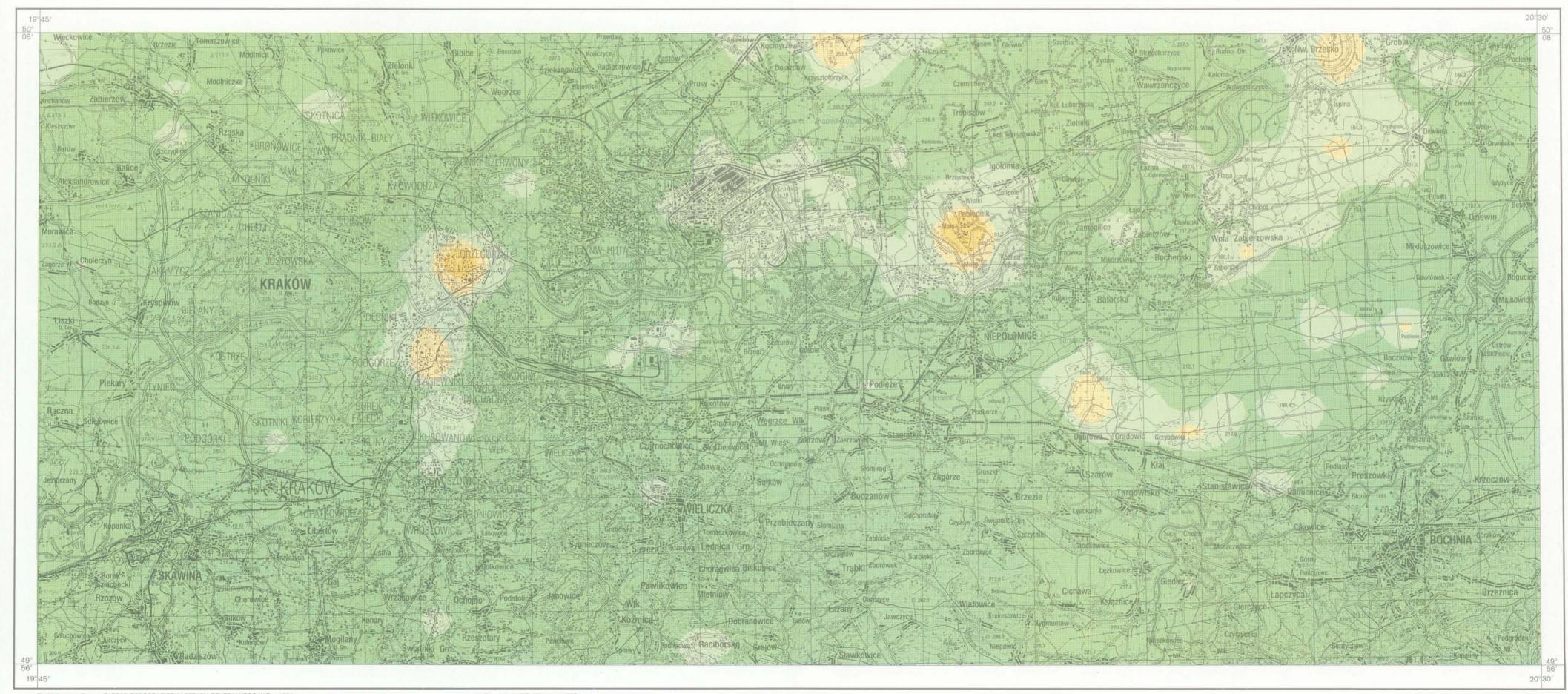










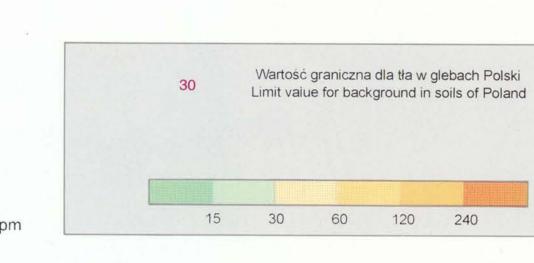


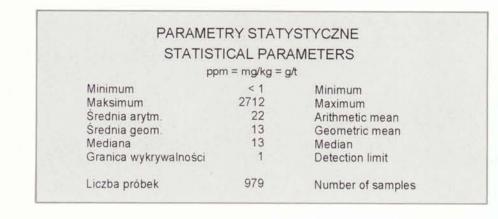
< 0.005

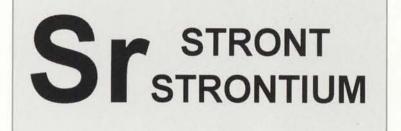
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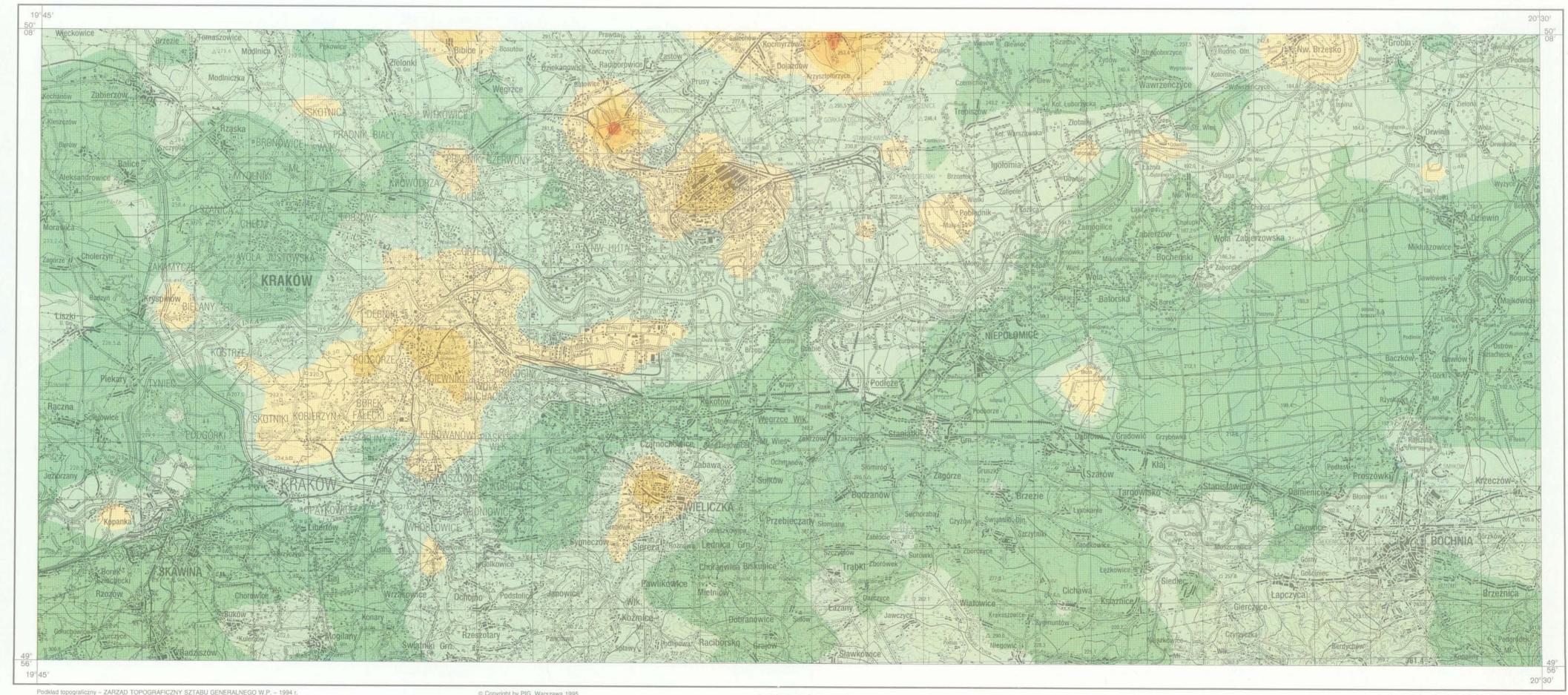


### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**



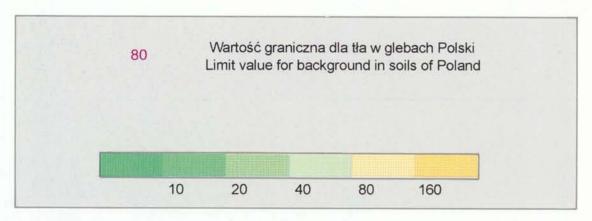






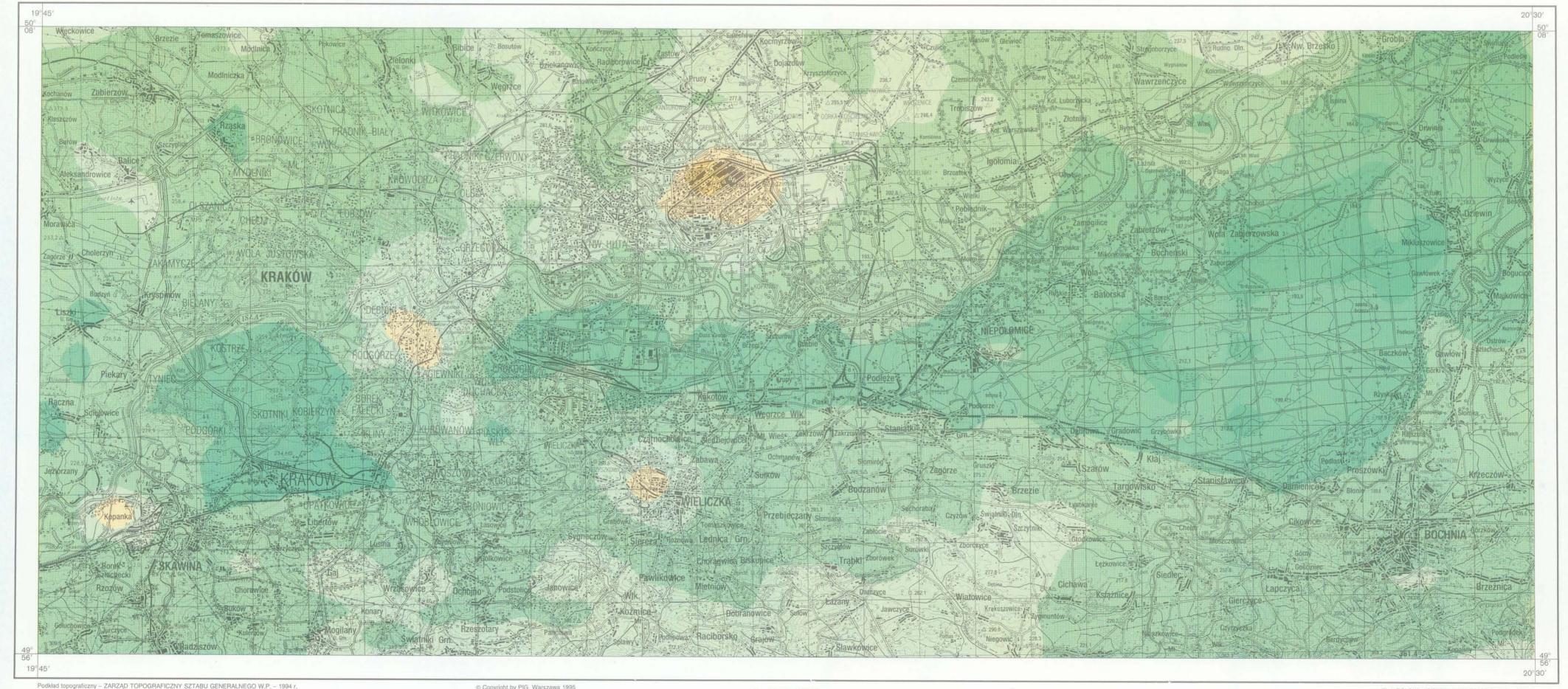


**GLEBY** SOILS



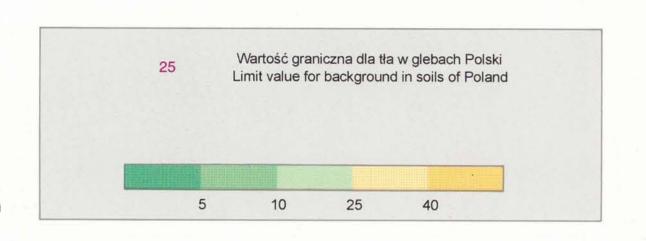
| STATIST               | ICAL PAR      | AMETERS           |
|-----------------------|---------------|-------------------|
| ppr                   | m = mg/kg = g | g/t               |
| Minimum               | 2             | Minimum           |
| Maksimum              | 382           | Maximum           |
| Średnia arytm.        | 30            | Arithmetic mean   |
| Średnia geom.         | 25            | Geometric mean    |
| Mediana               | 28            | Median            |
| Granica wykrywalności | 1             | Detection limit   |
| Liczba próbek         | 979           | Number of samples |

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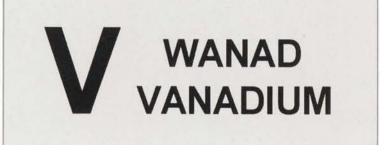


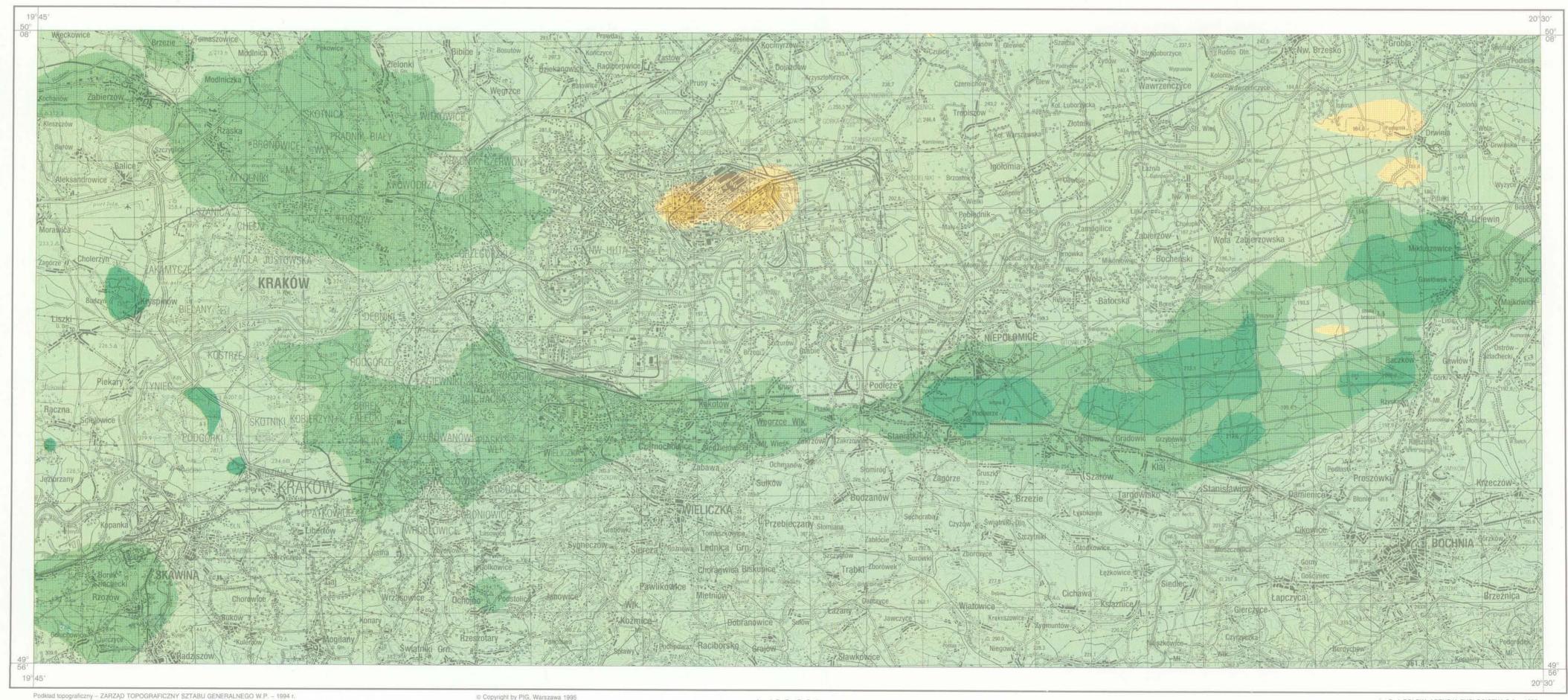


**GLEBY** SOILS



| PARAMET               | RY STAT       | YSTYCZNE          |
|-----------------------|---------------|-------------------|
| STATIST               | ICAL PAR      | AMETERS           |
| ppn                   | n = mg/kg = g | g/t               |
| Minimum               | < 1           | Minimum           |
| Maksimum              | 85            | Maximum           |
| Średnia arytm.        | 12            | Arithmetic mean   |
| Średnia geom.         | 10            | Geometric mean    |
| Mediana               | 12            | Median            |
| Granica wykrywalności | 1             | Detection limit   |
| Liczba próbek         | 979           | Number of samples |



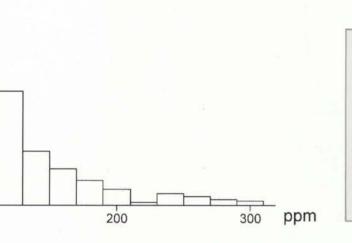


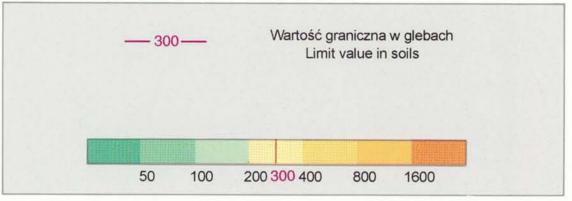
TABLICA 27

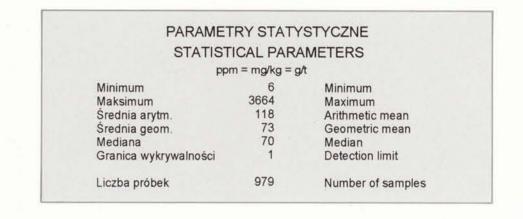
# T919

## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS

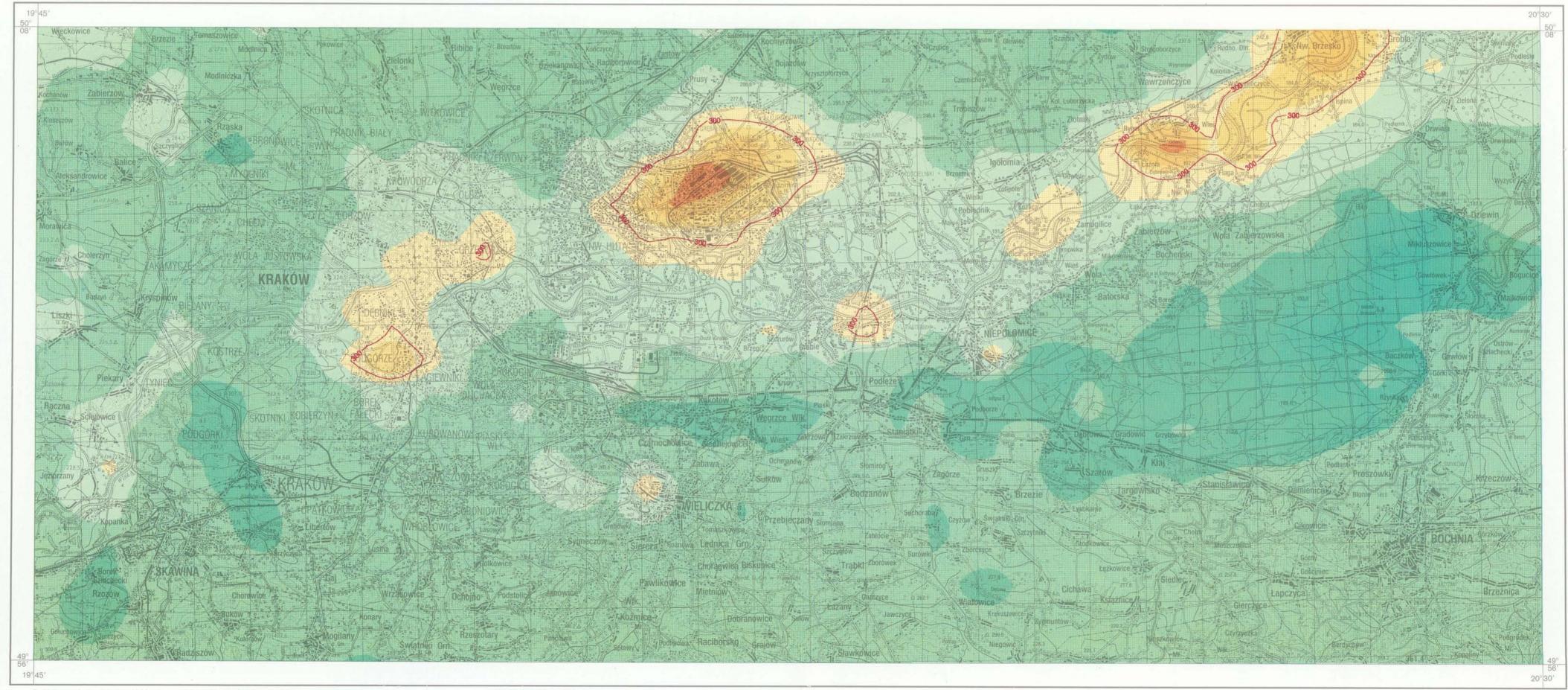
GLEBY SOILS







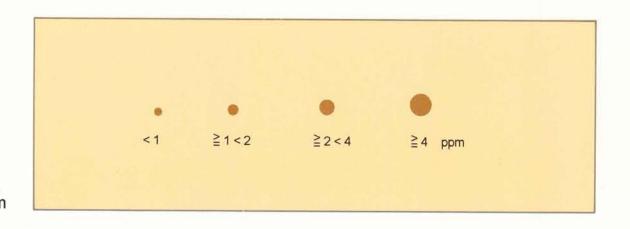
Zn cynk zinc



200\_

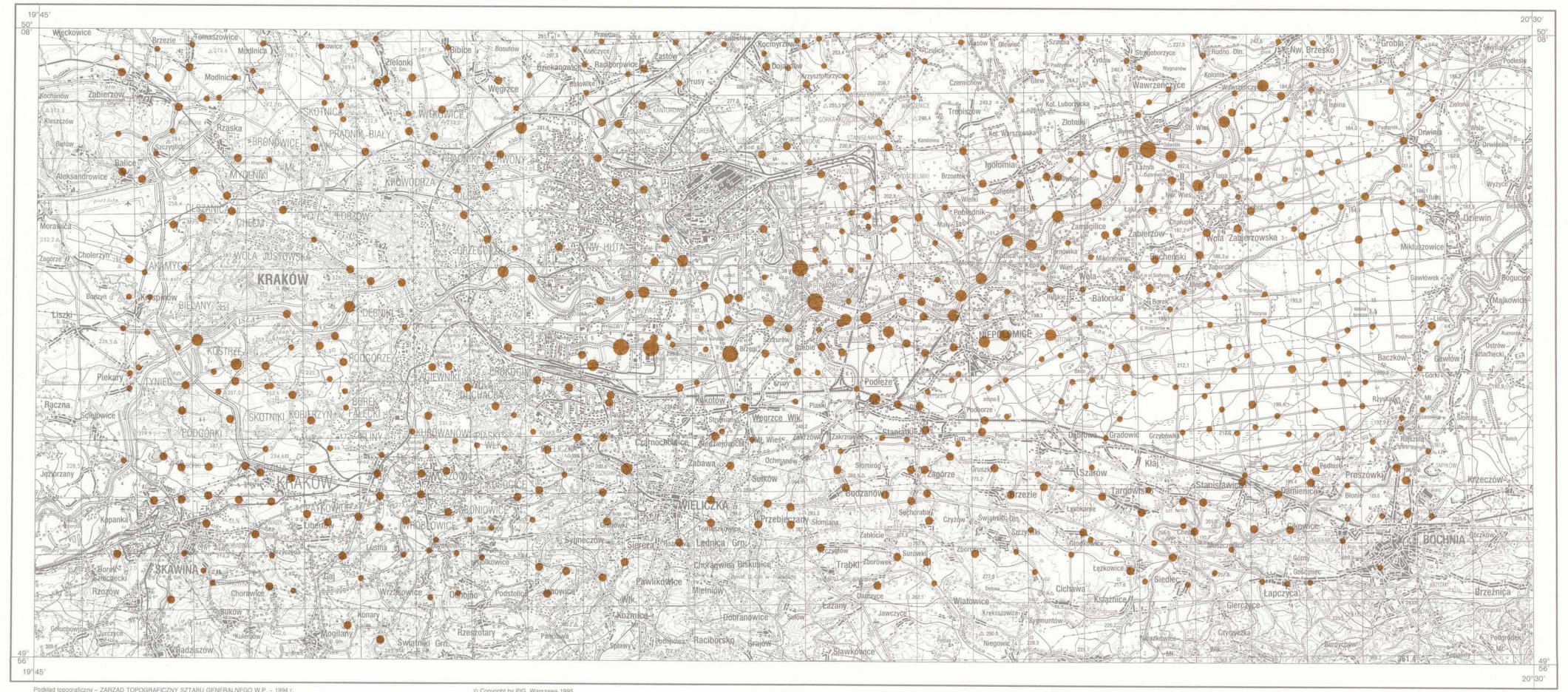


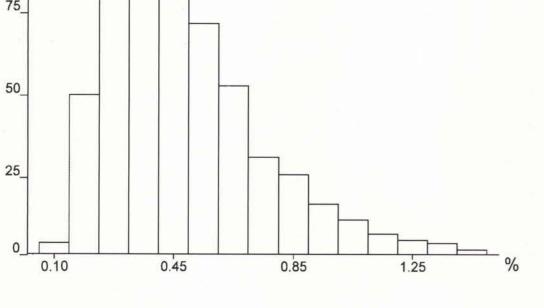
## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

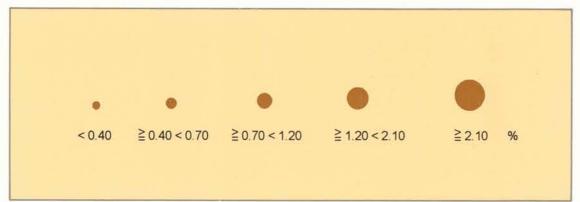


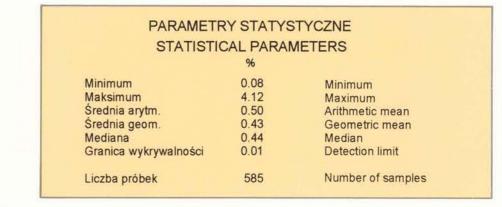
|                       | CAL PARAM     | METERS           |
|-----------------------|---------------|------------------|
| ppm                   | = mg/kg = g/t |                  |
| Minimum               | < 1           | Minimum          |
| Maksimum              | 13            | Maximum          |
| Średnia arytm.        | < 1           | Arithmetic mean  |
| Średnia geom.         | < 1           | Geometric mean   |
| Mediana               | < 1           | Median           |
| Granica wykrywalności | 1             | Detection limit  |
| Liczba próbek         | 585           | Number of sample |



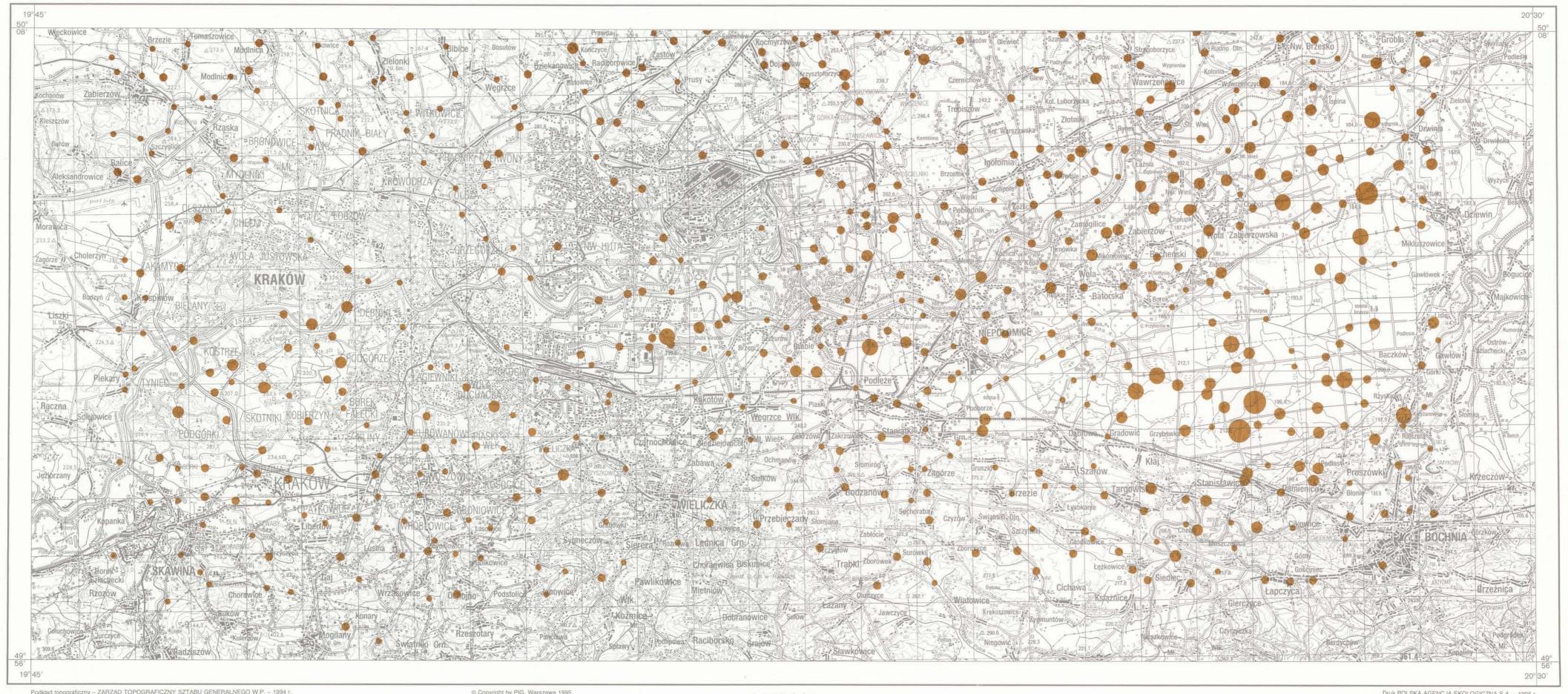








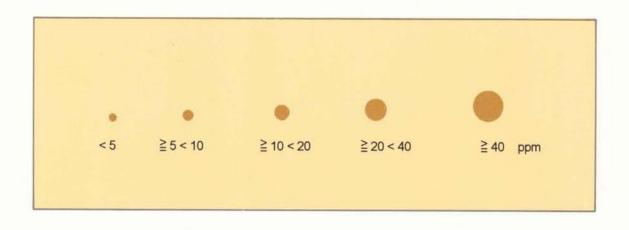


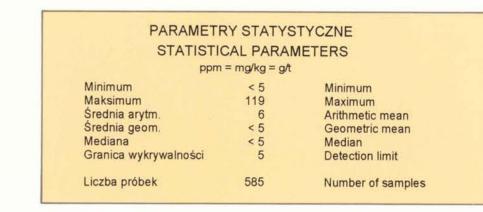


N 340\_ 255\_ 170\_ 85\_



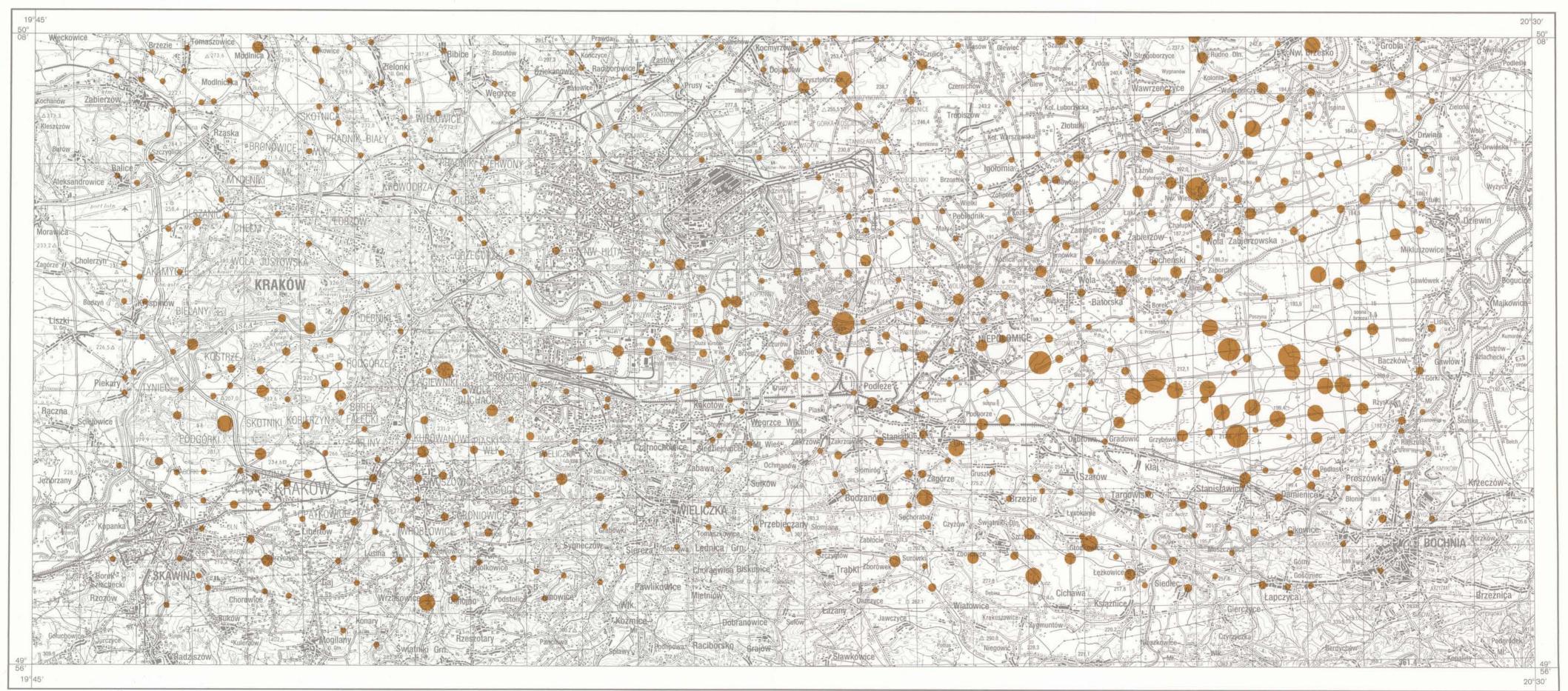
## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS



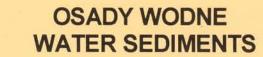


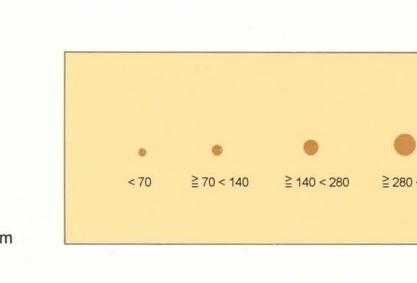
OSADY WODNE WATER SEDIMENTS

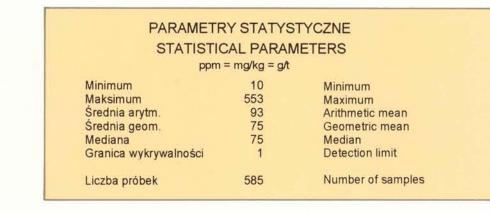
AS ARSENIC



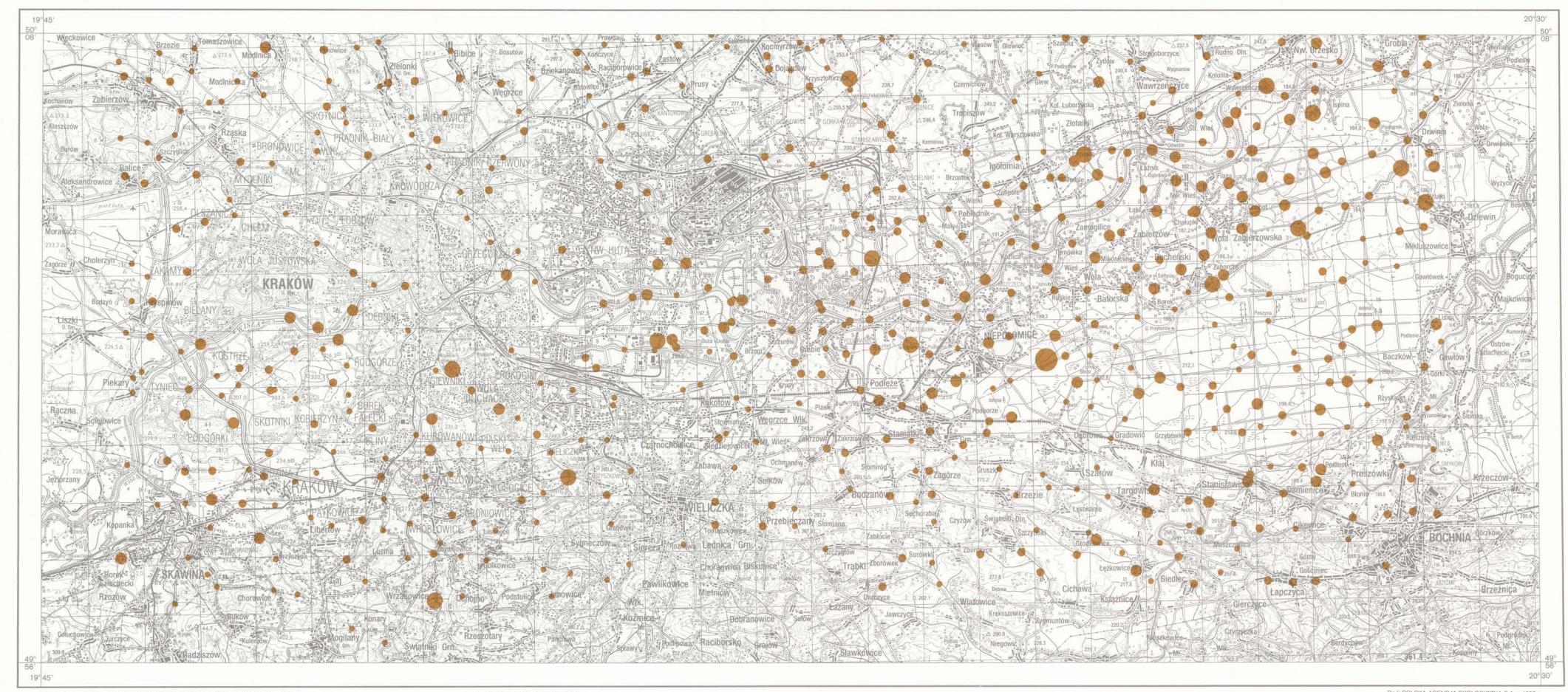










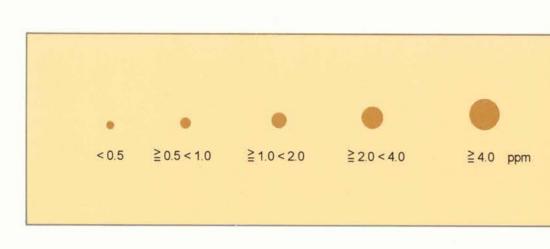


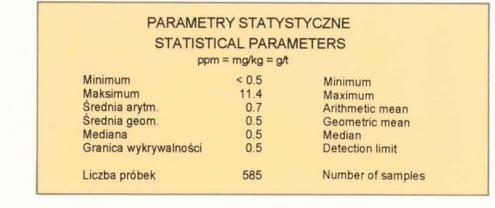
TABLICA 32



### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

**OSADY WODNE** WATER SEDIMENTS





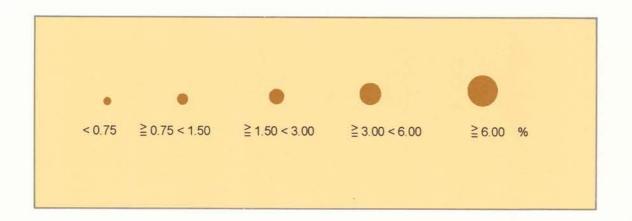
Be BERYLLIUM

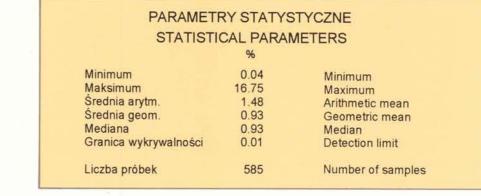




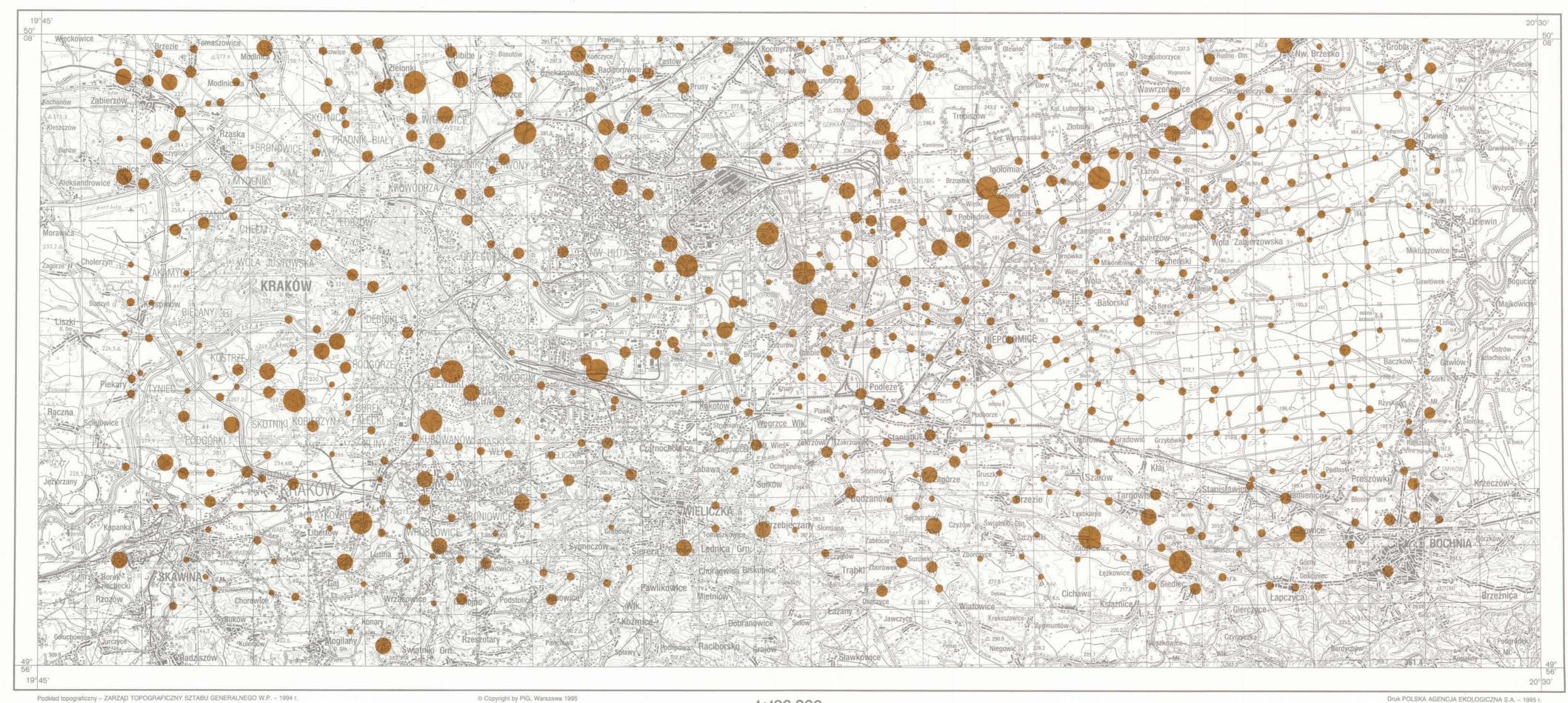
8.00

## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**



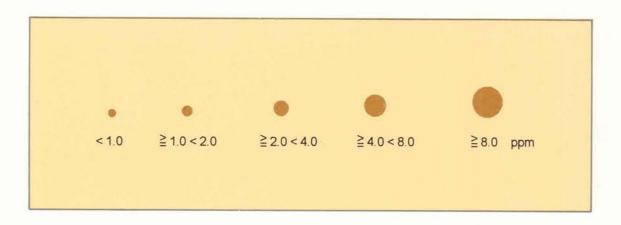


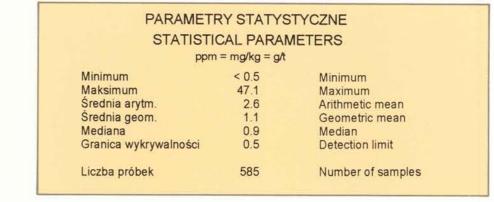




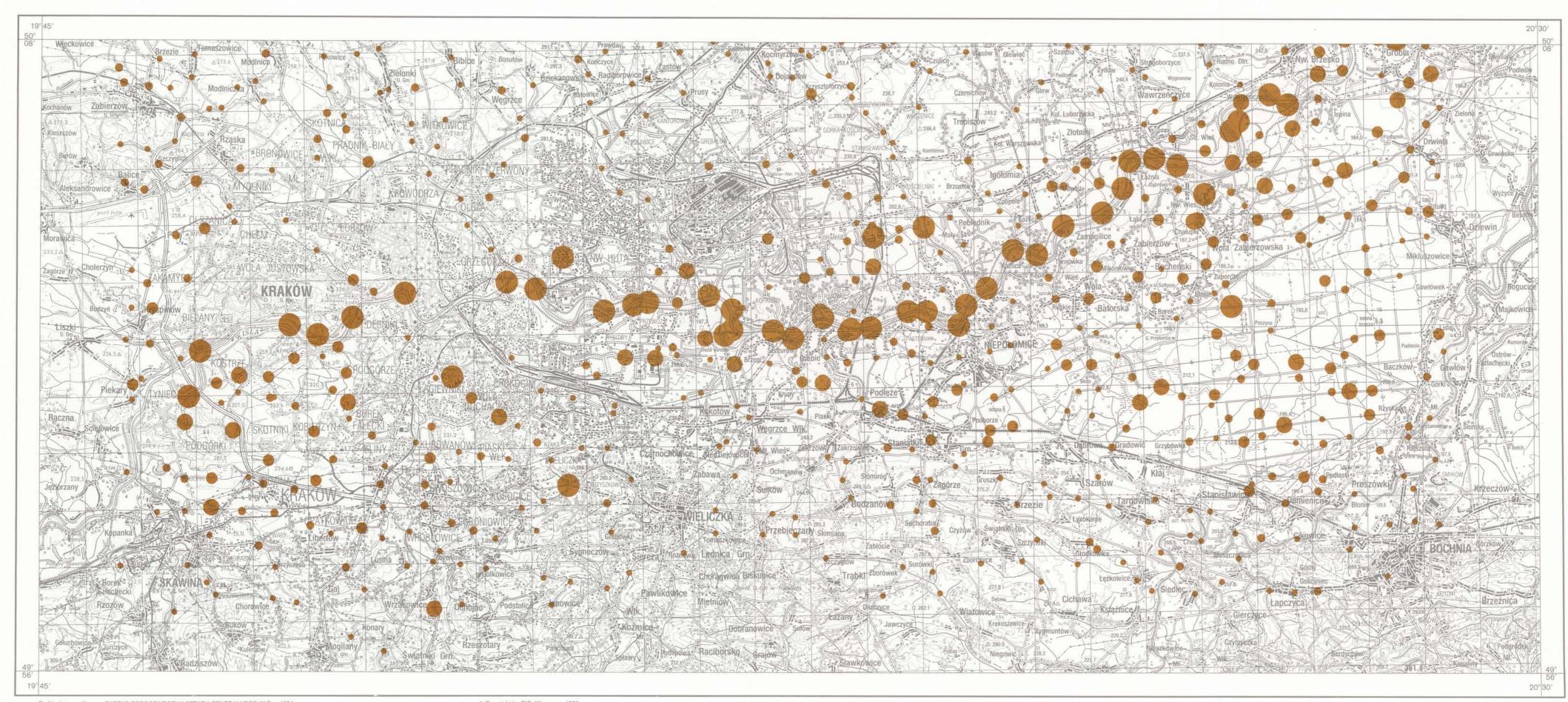
# T919

## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS



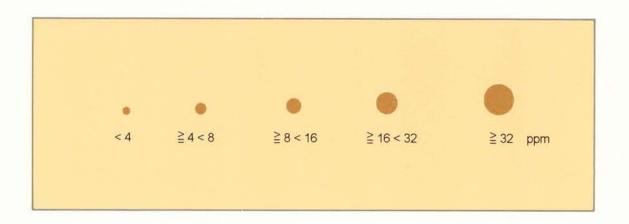


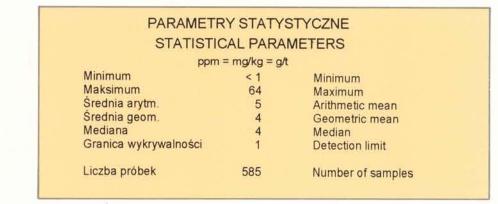




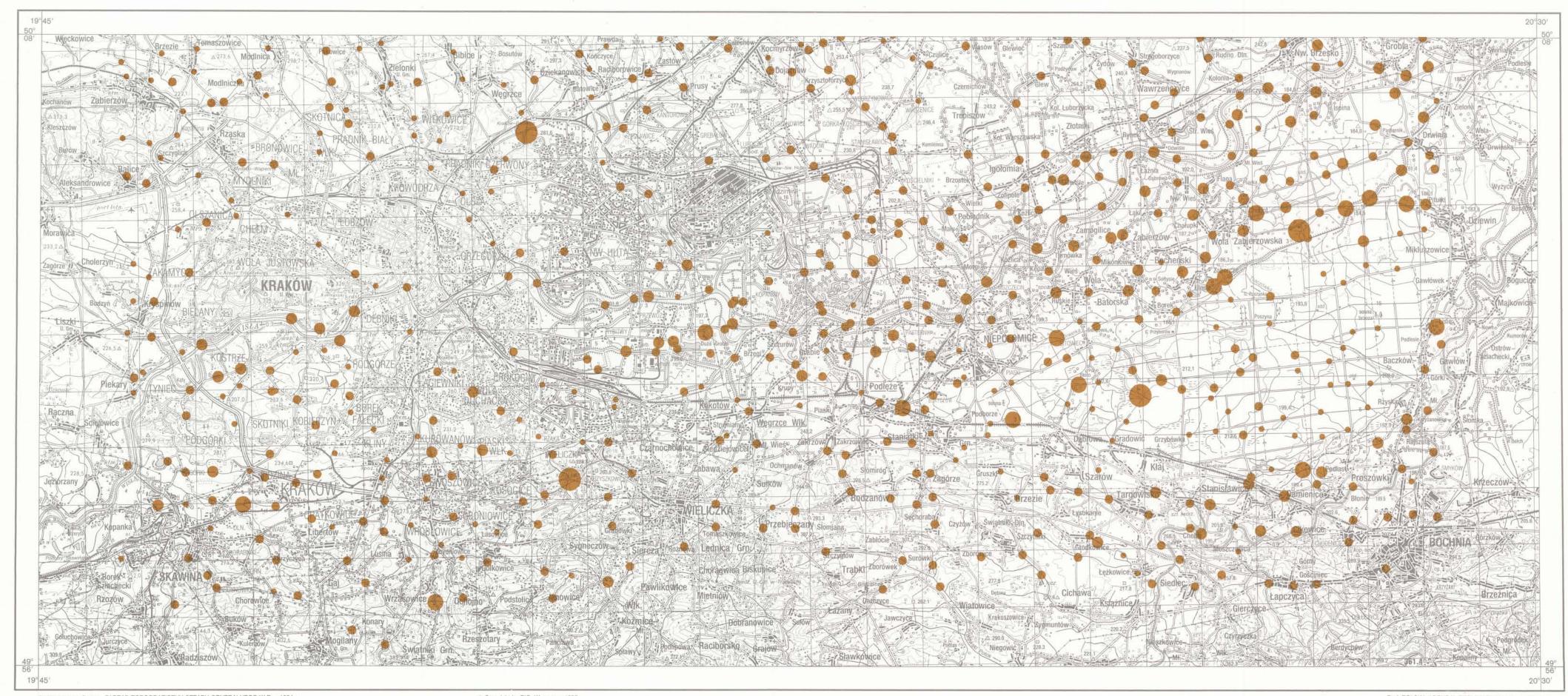


OSADY WODNE WATER SEDIMENTS

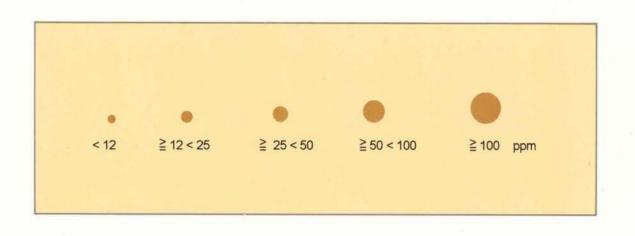


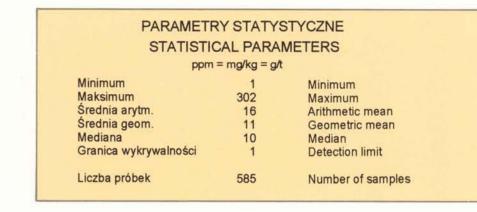


CO KOBALT COBALT



220





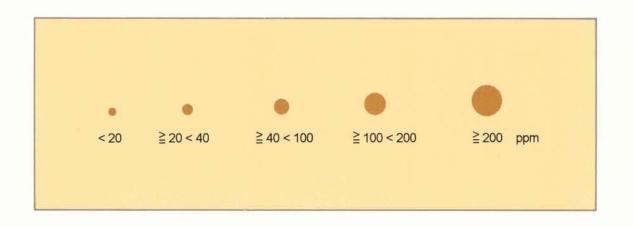


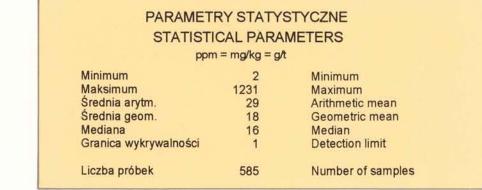


### TABLICA 37

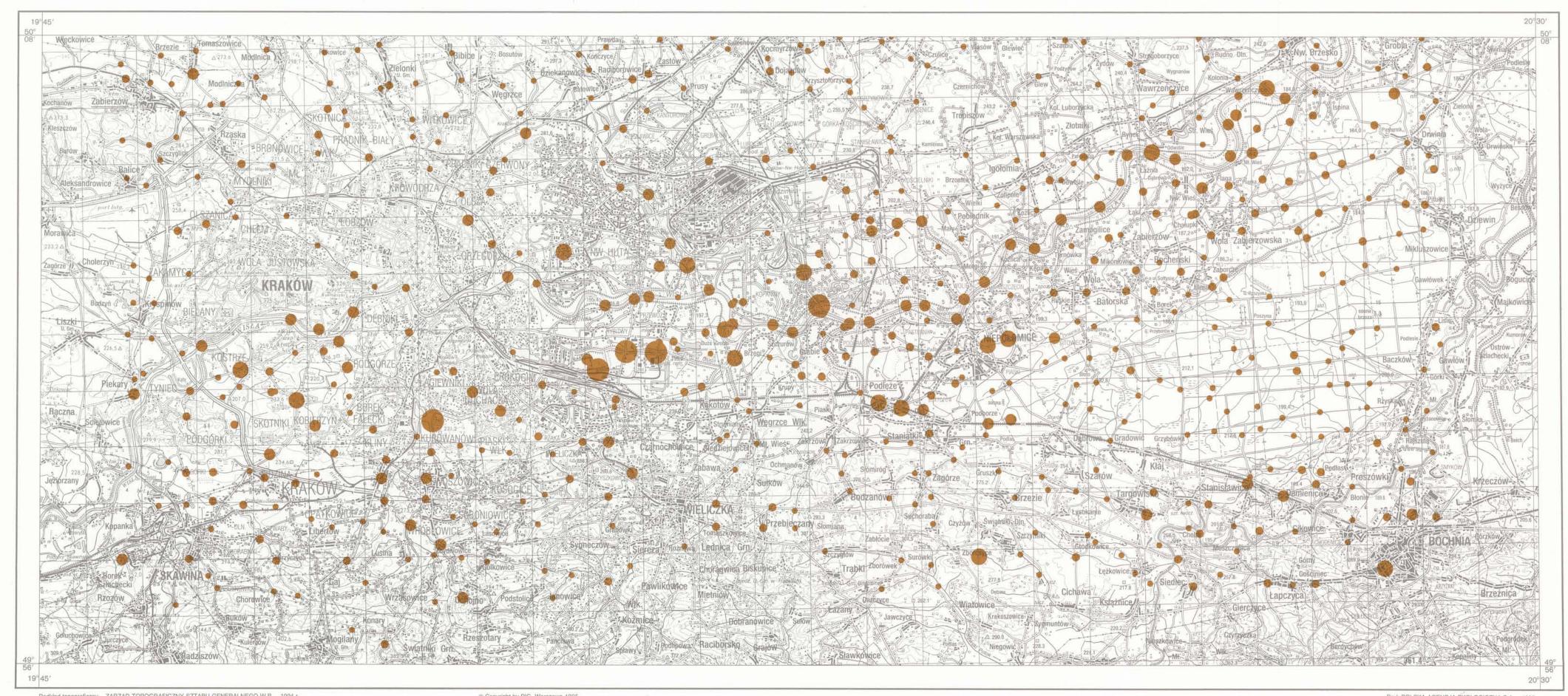


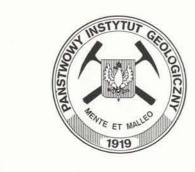
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**



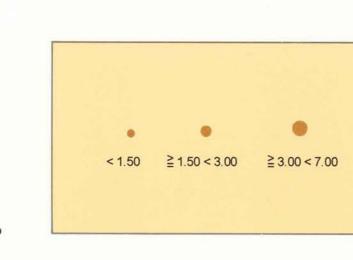


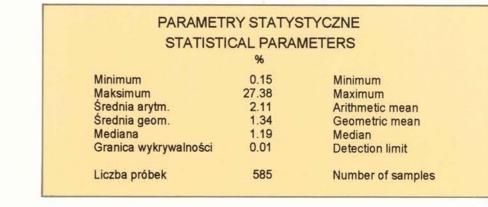






OSADY WODNE WATER SEDIMENTS

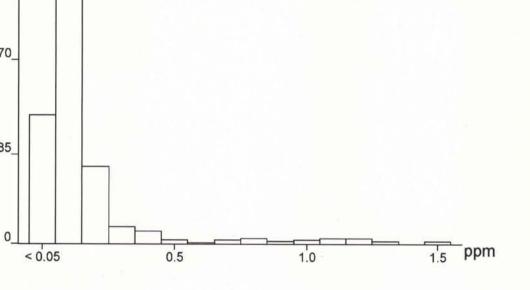


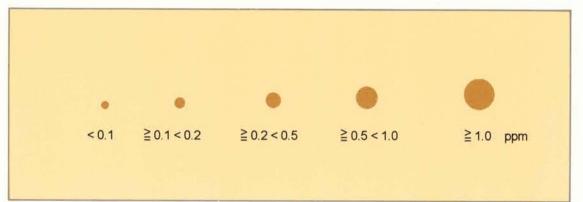


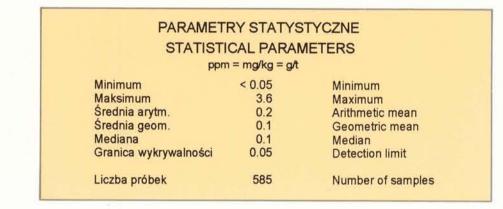
Fe ŻELAZO IRON



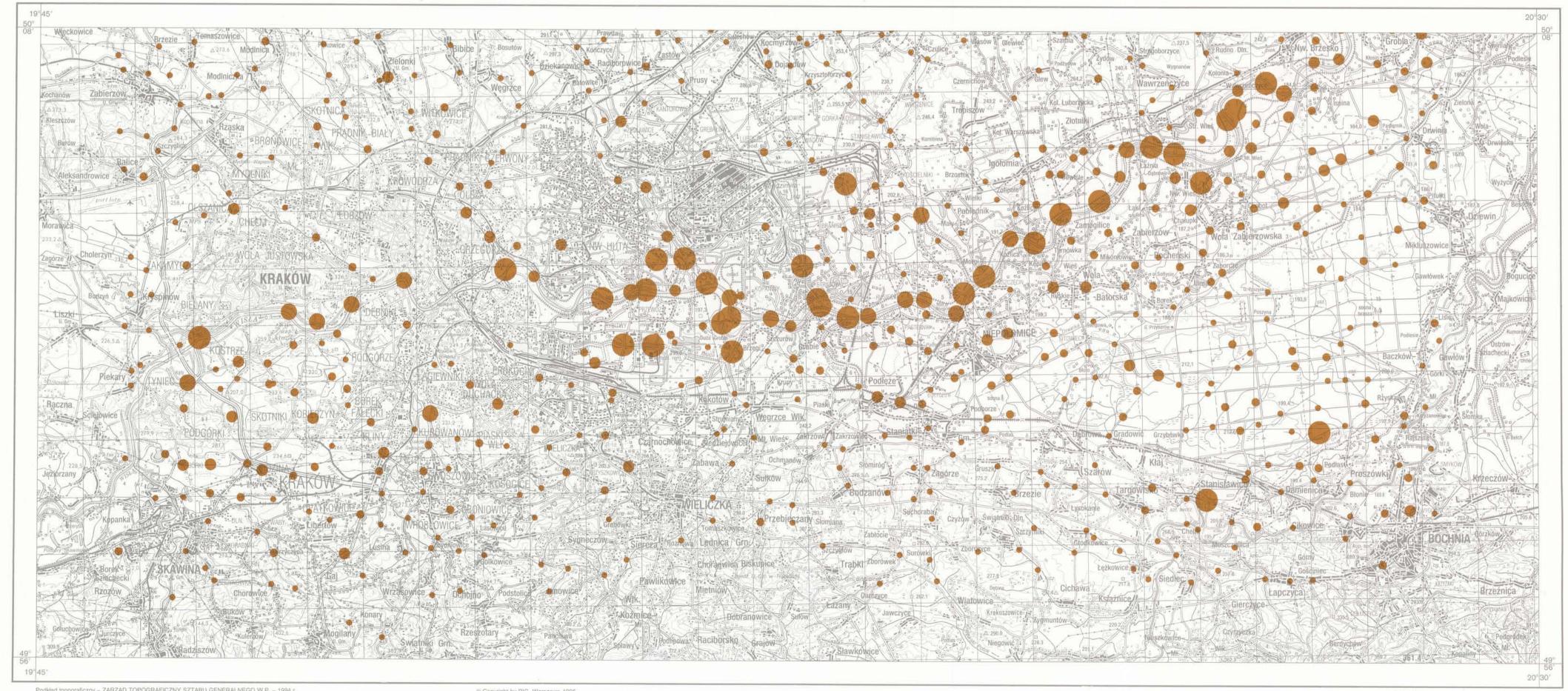
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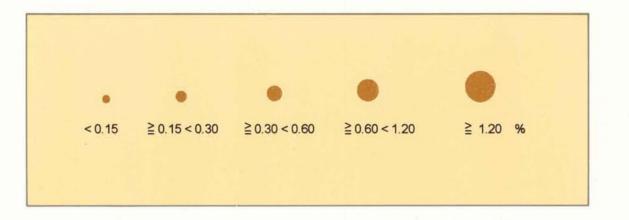






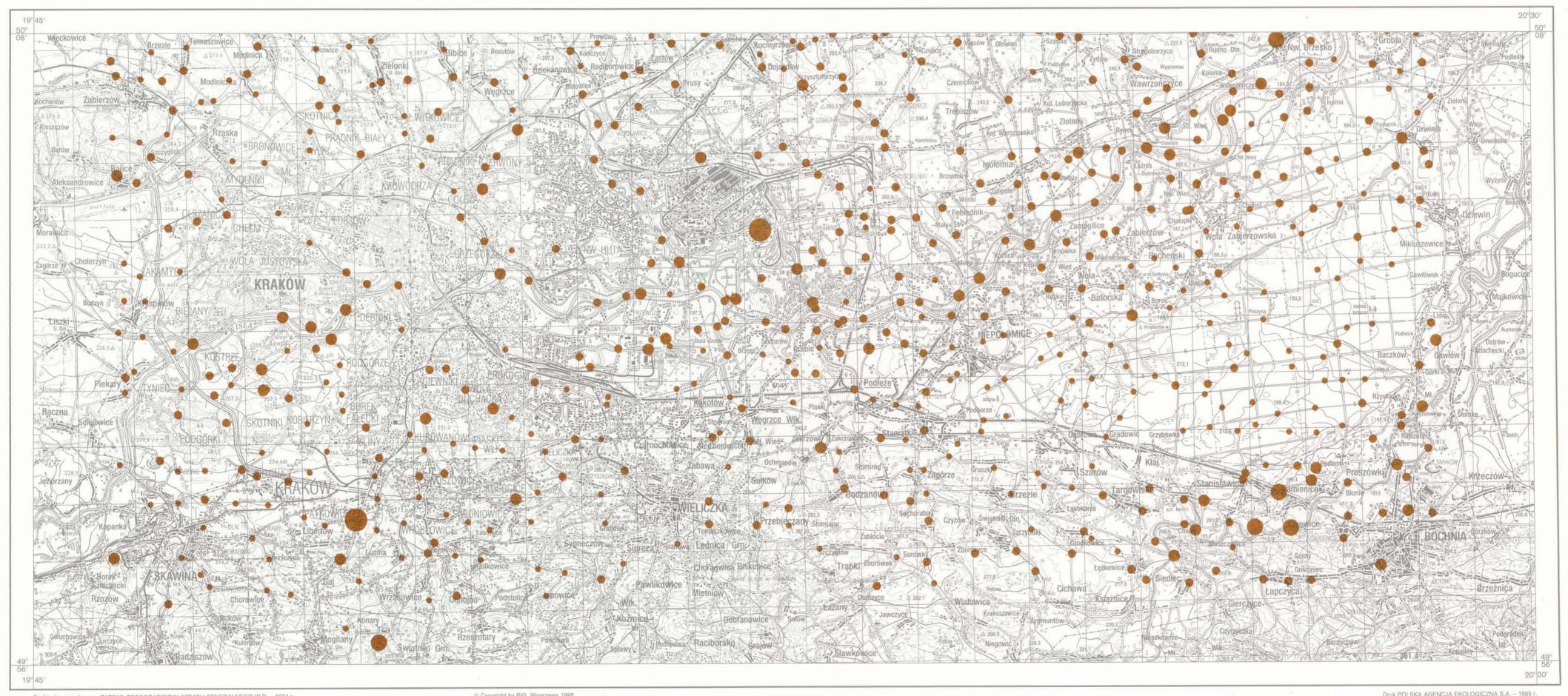




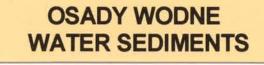


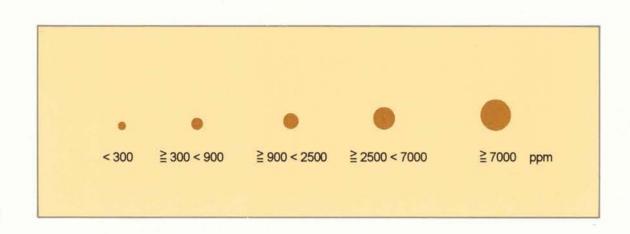
| STATISTIC             | CAL PARAM | METERS            |
|-----------------------|-----------|-------------------|
|                       | %         |                   |
| Minimum               | 0.02      | Minimum           |
| Maksimum              | 2.77      | Maximum           |
| Średnia arytm.        | 0.18      | Arithmetic mean   |
| Średnia geom.         | 0.15      | Geometric mean    |
| Mediana               | 0.16      | Median            |
| Granica wykrywalności | 0.01      | Detection limit   |
| Liczba próbek         | 585       | Number of samples |

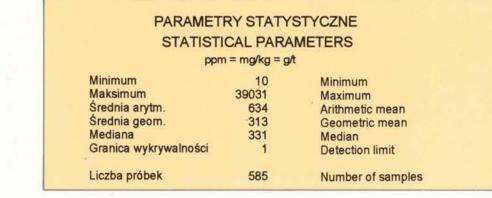








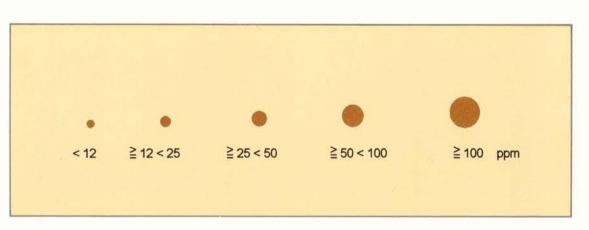


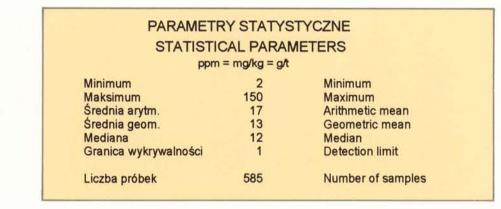


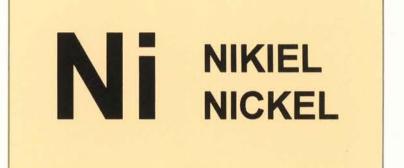


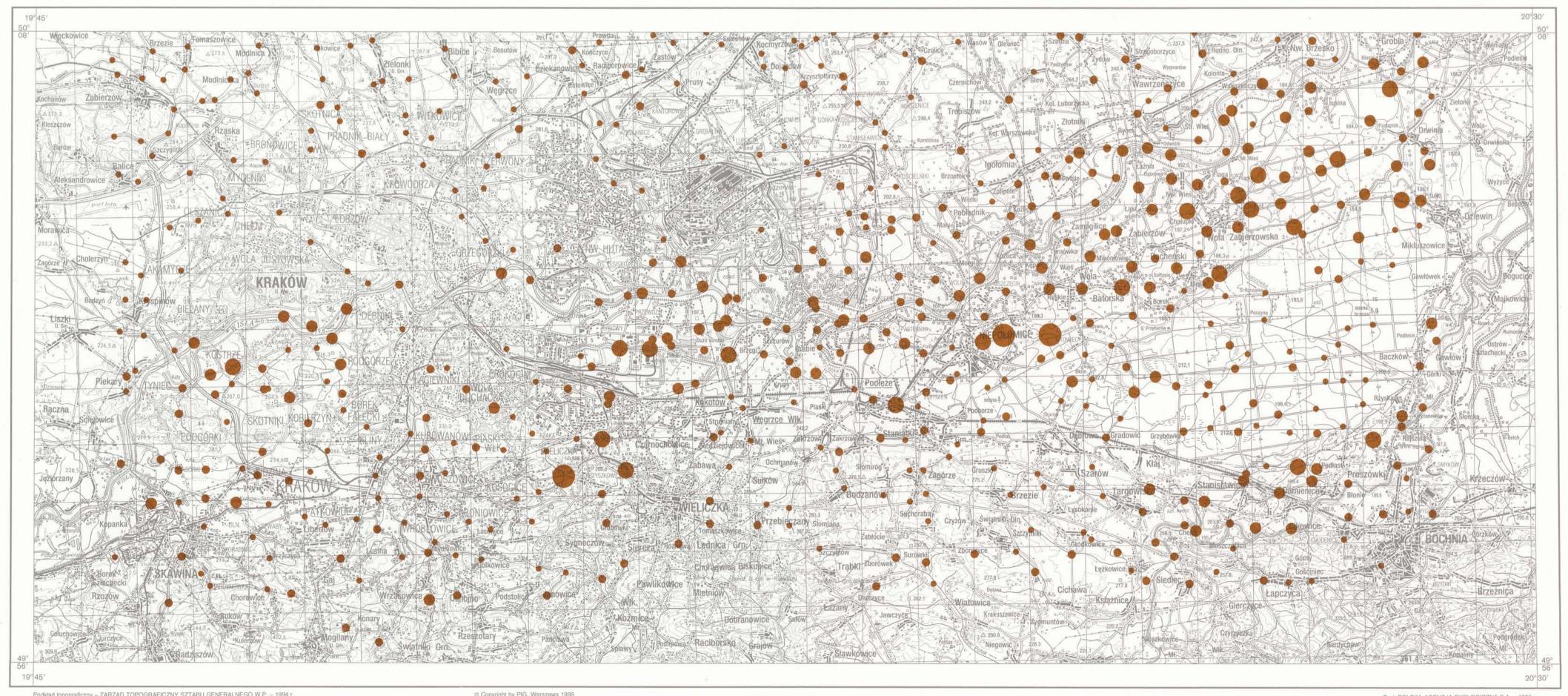








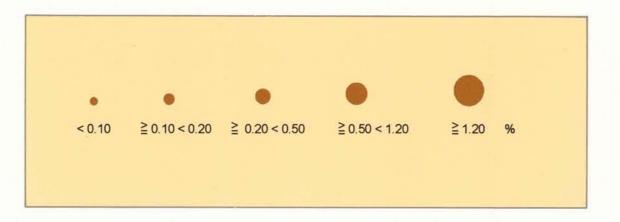


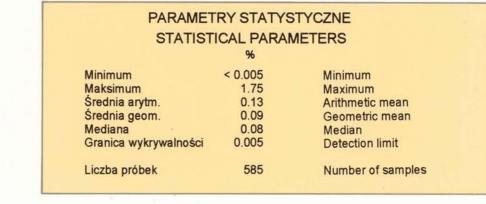


### TABLICA 43

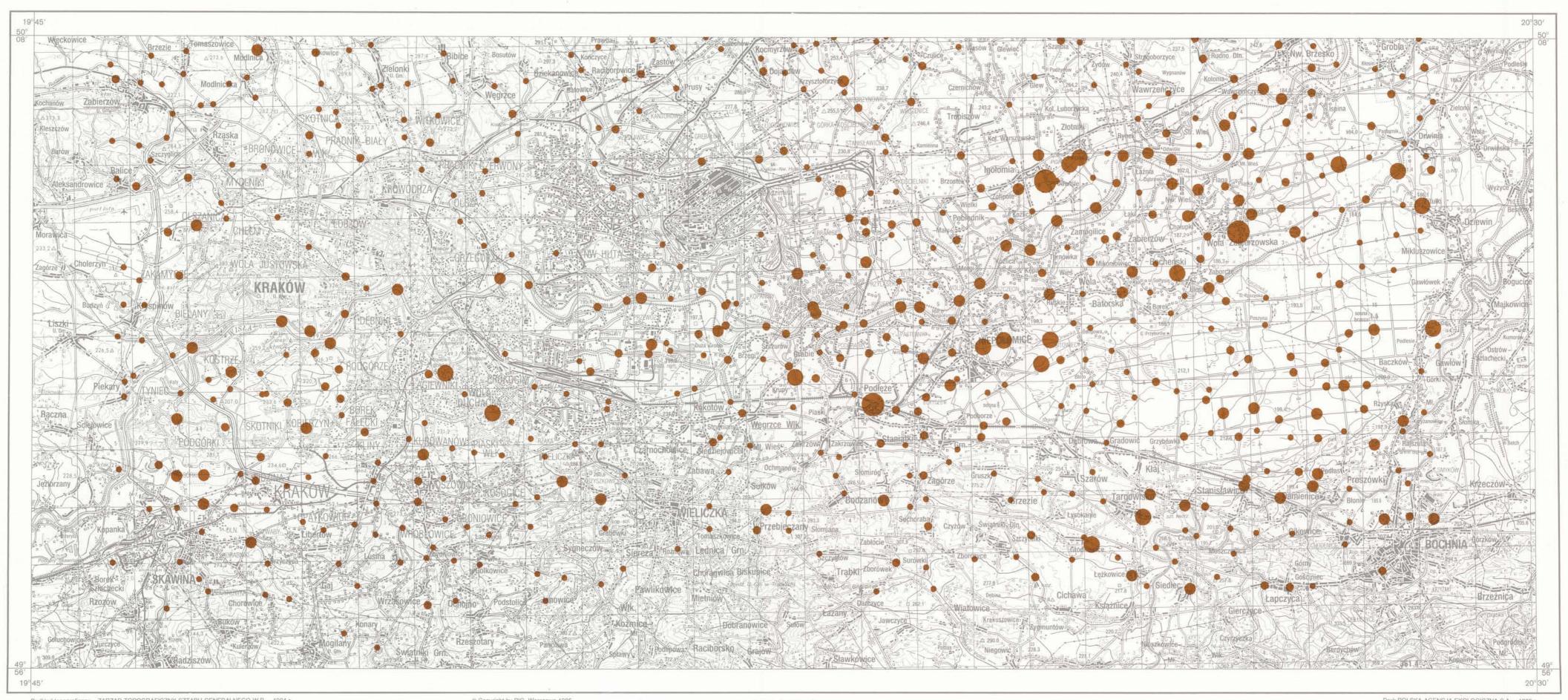


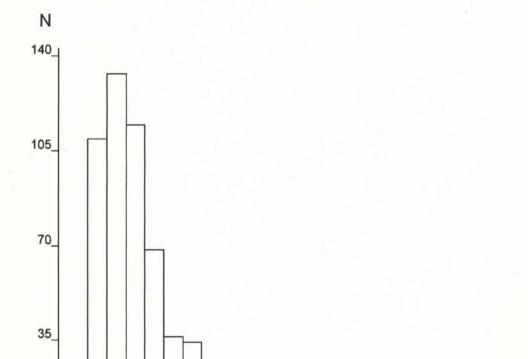
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**



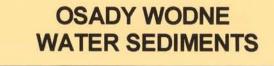


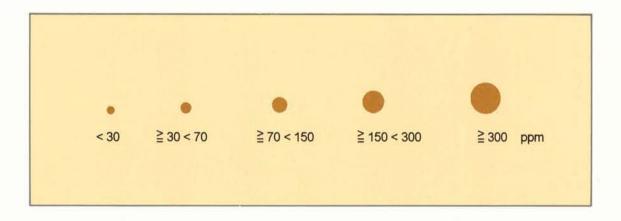


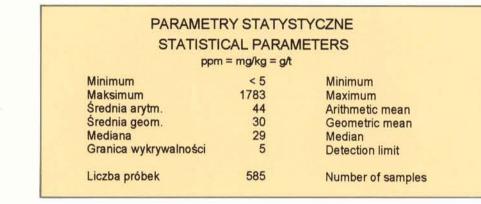




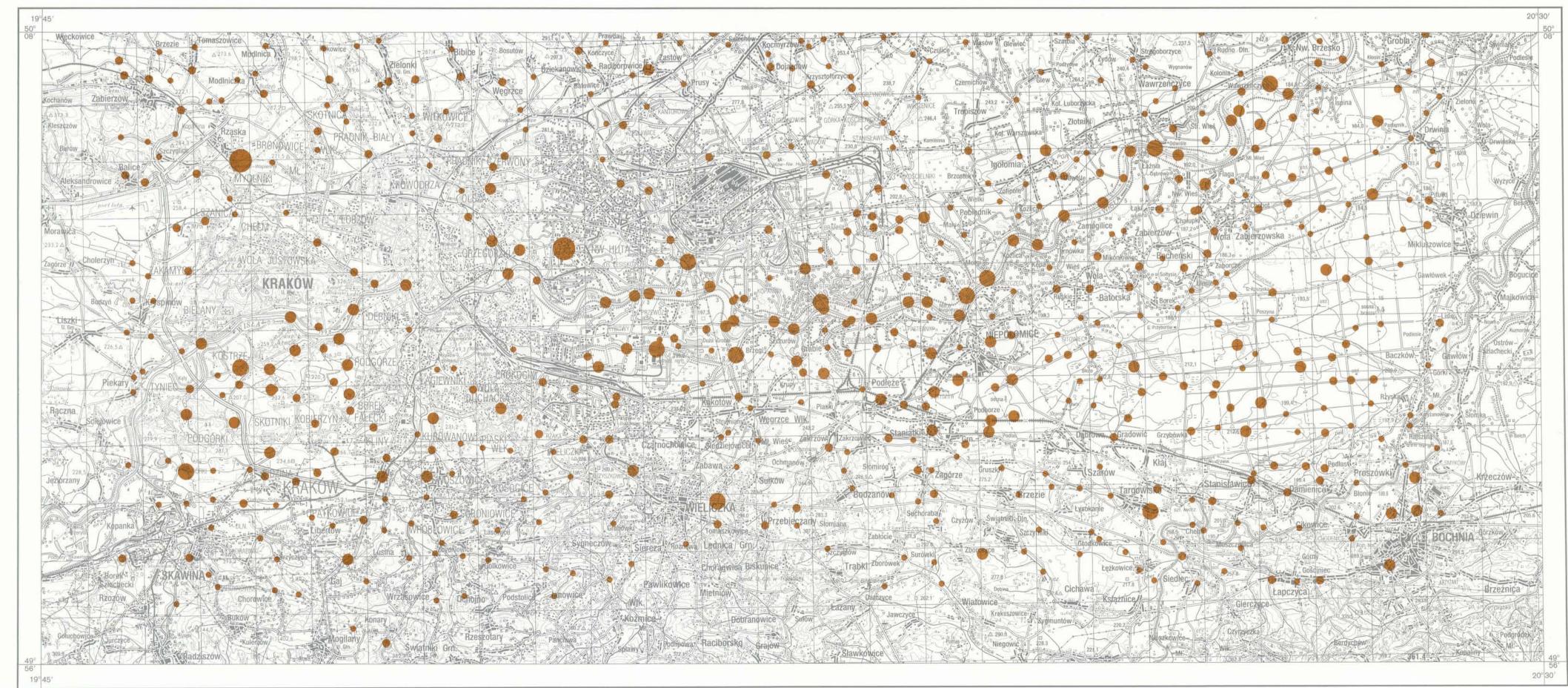




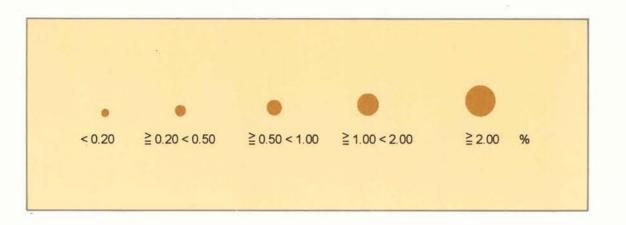


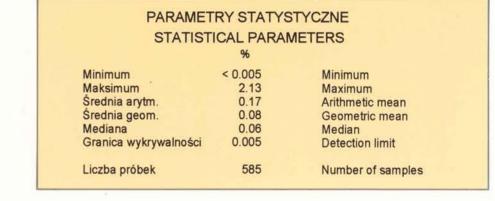




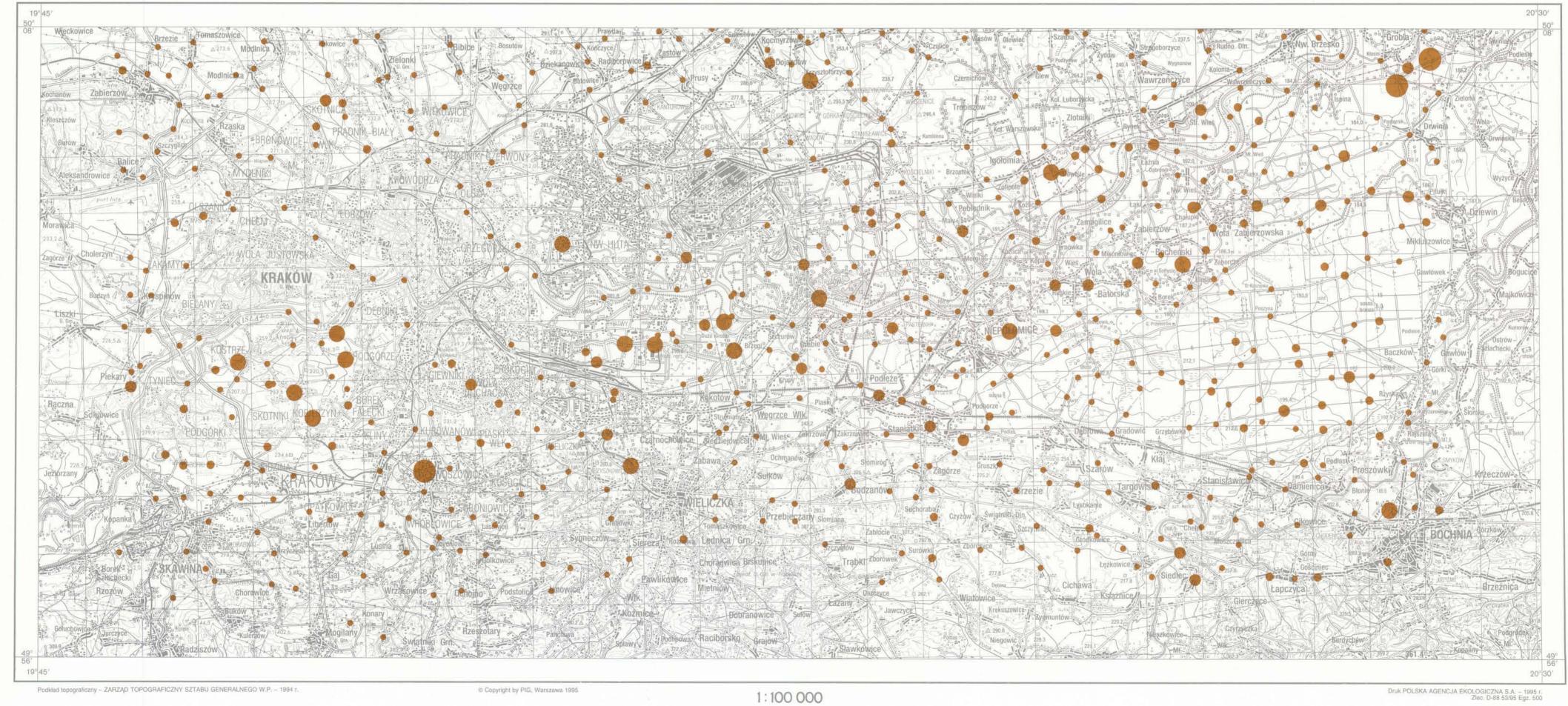


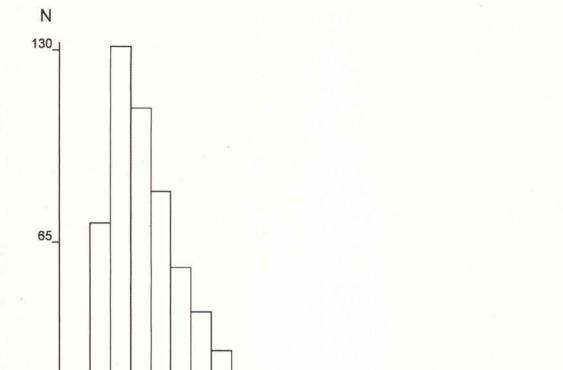






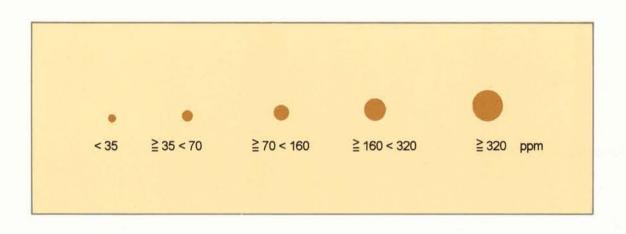


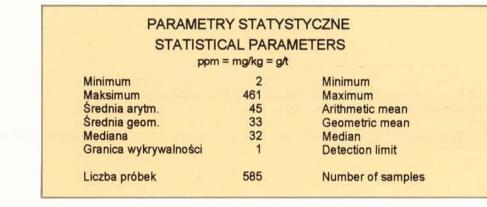




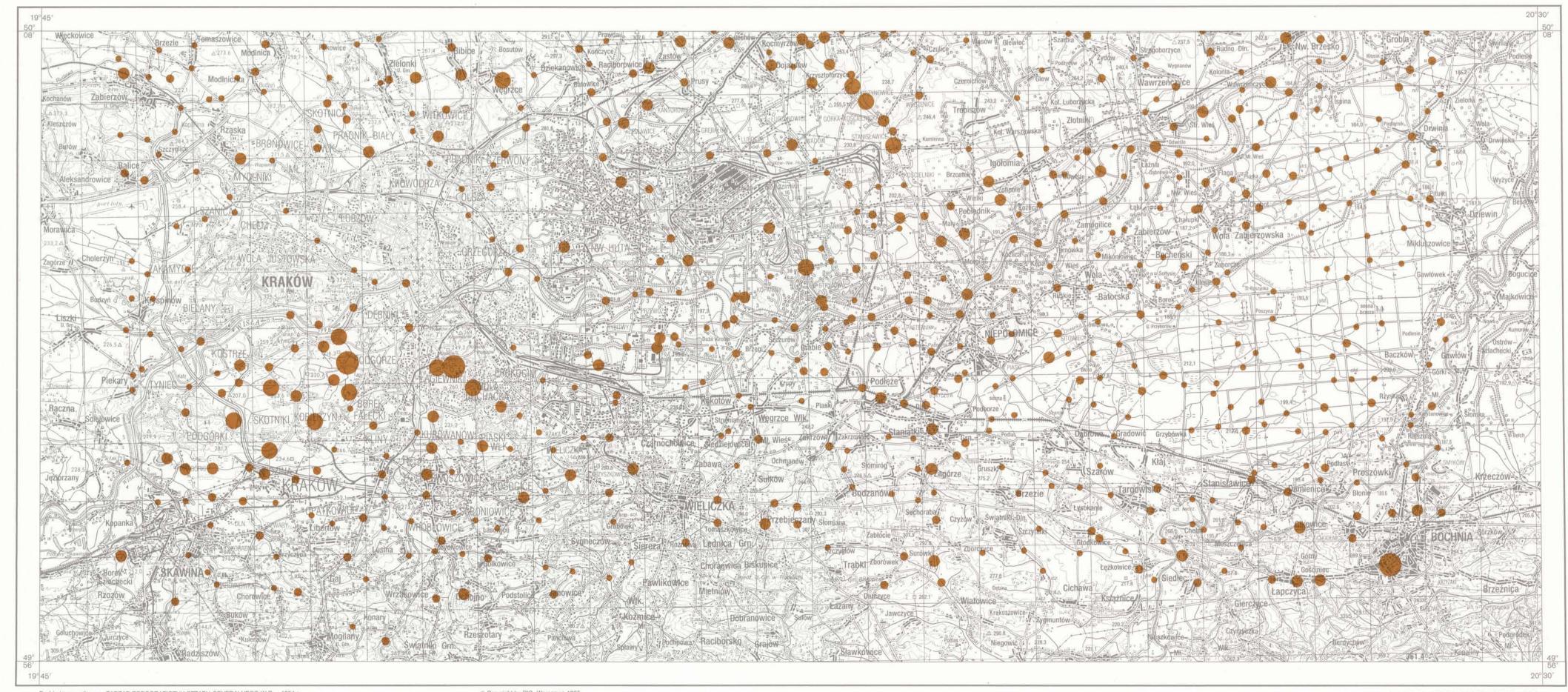


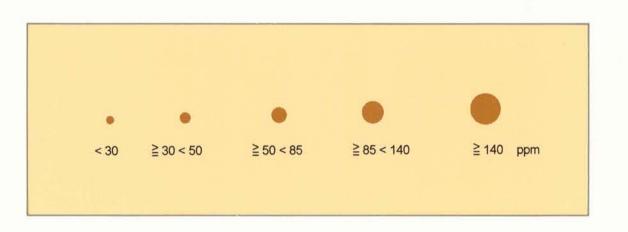


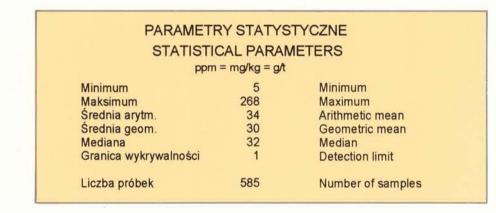




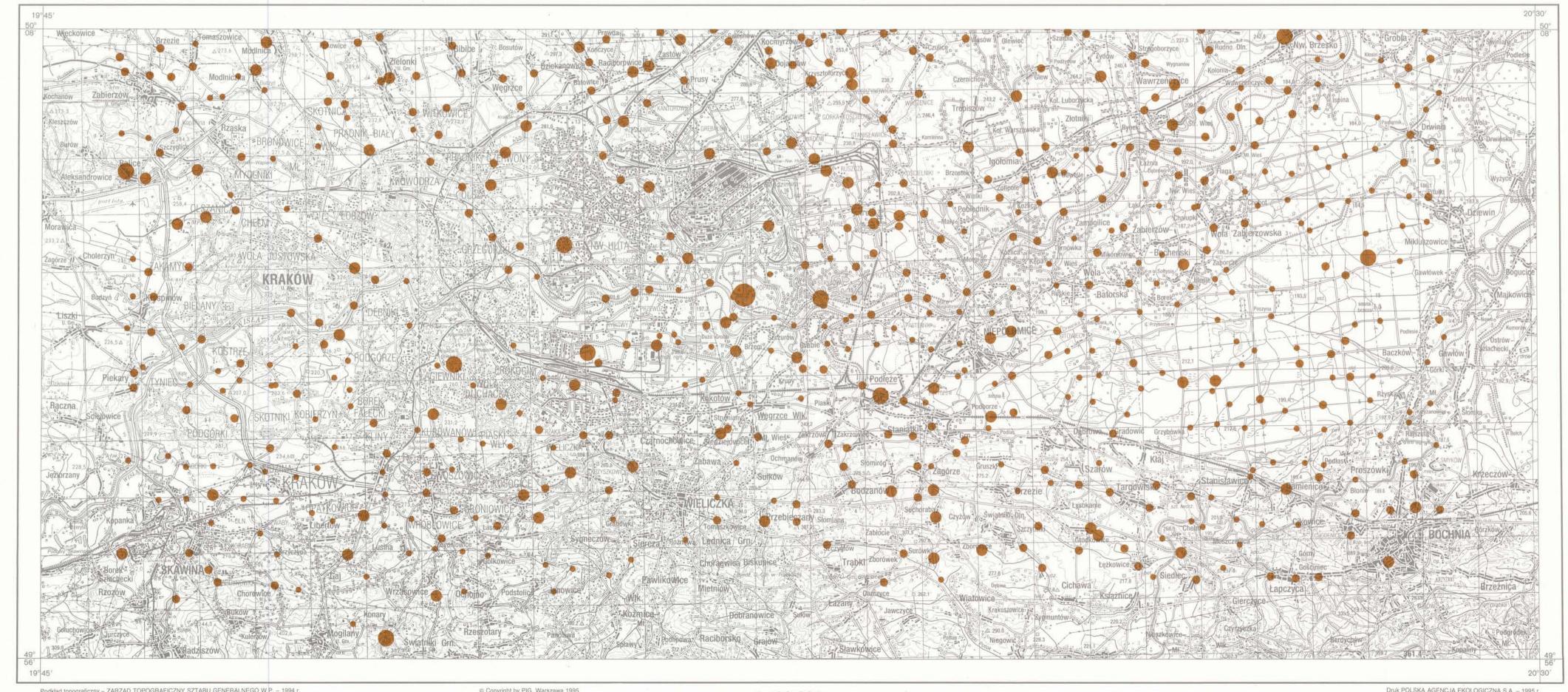






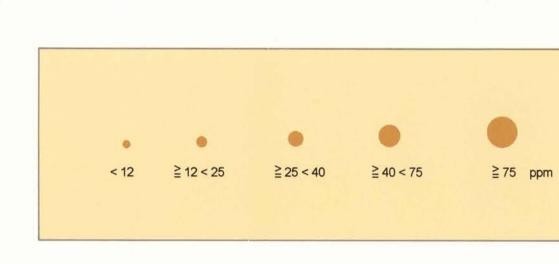


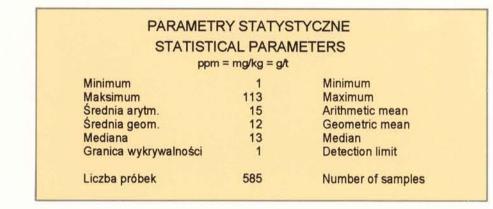




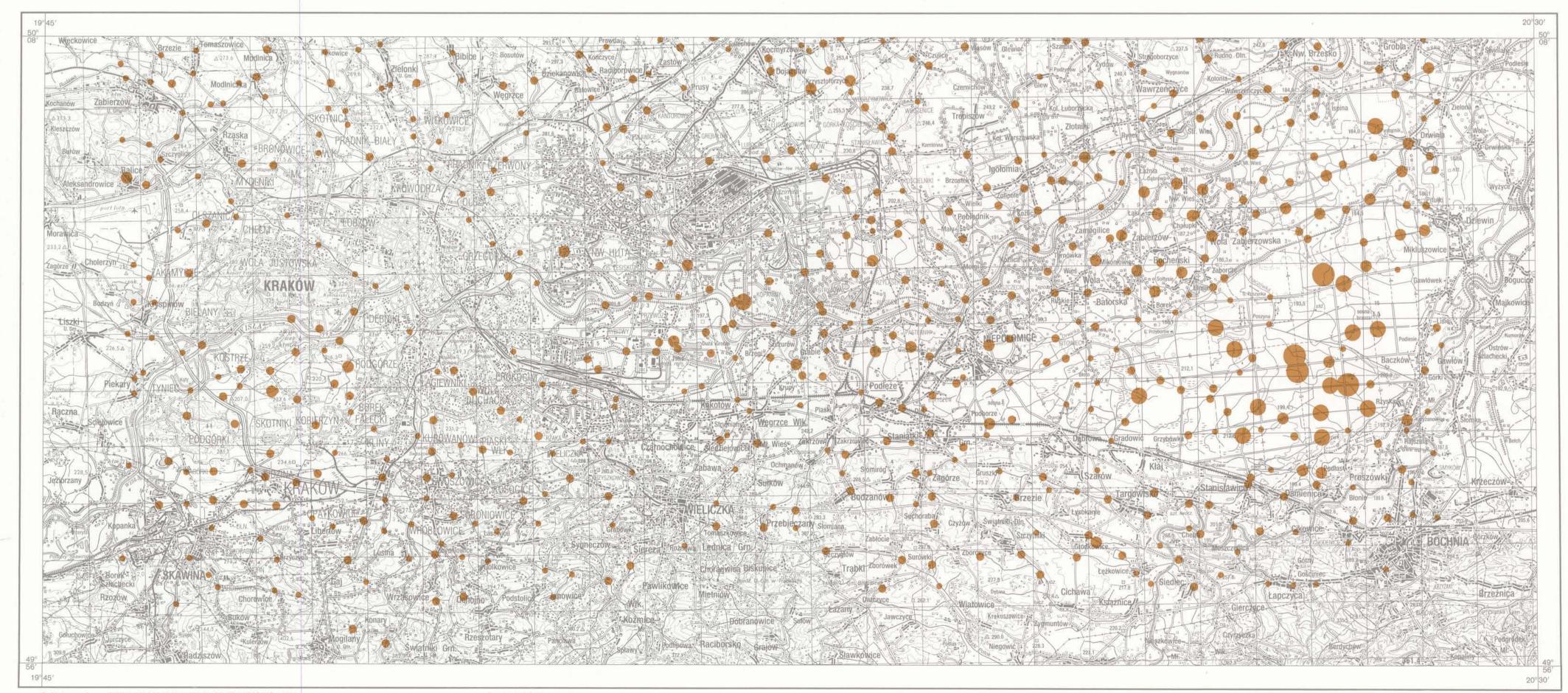
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## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS

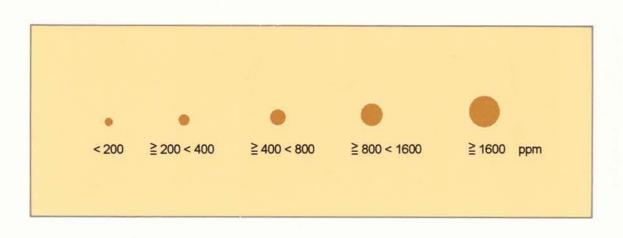


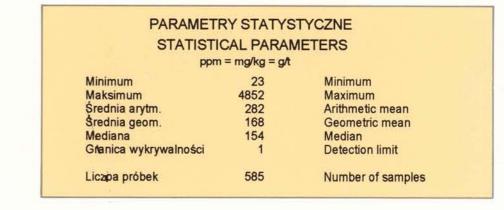




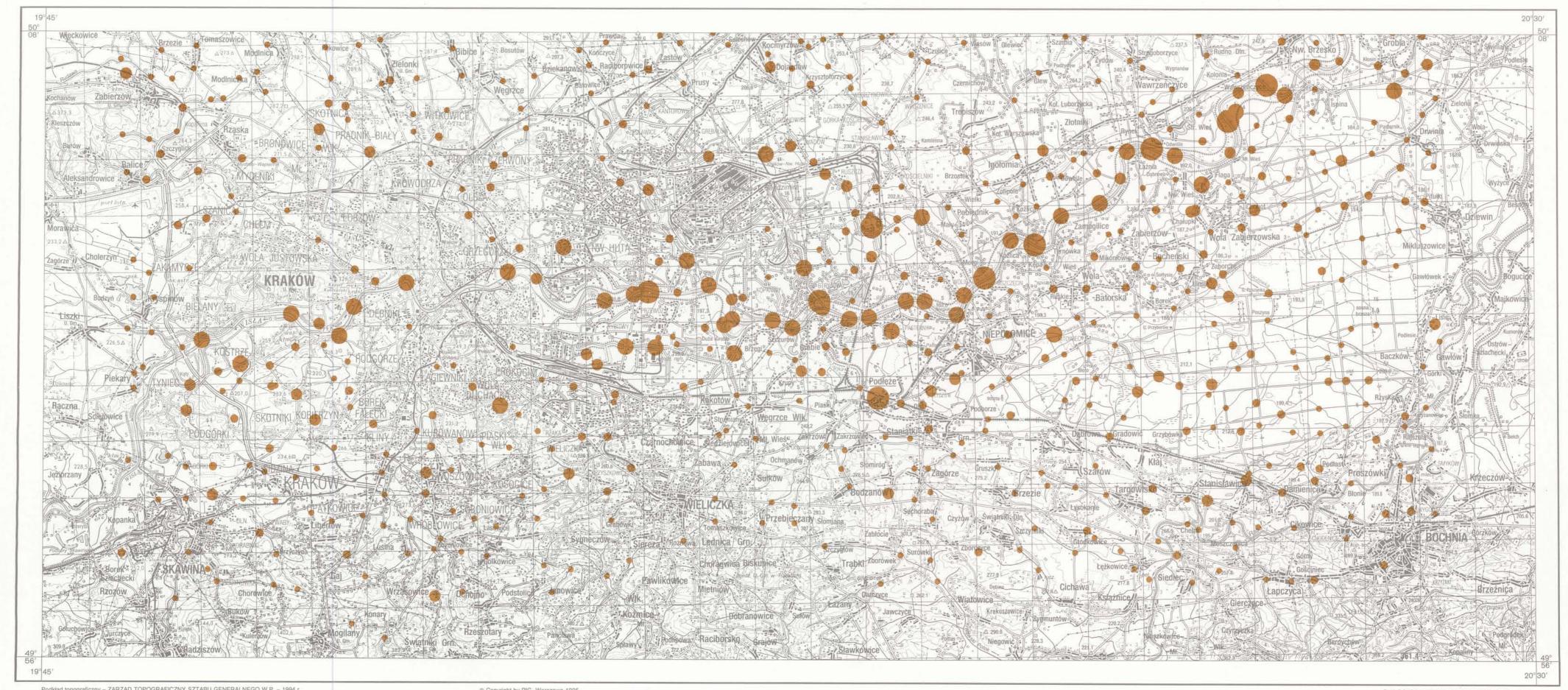






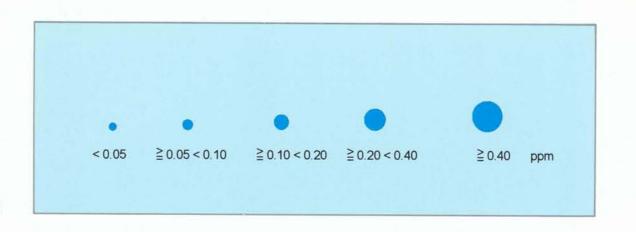


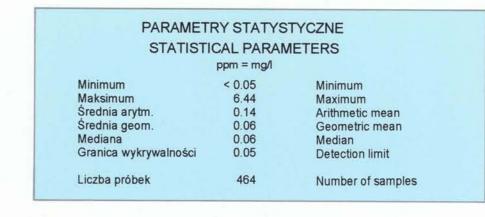




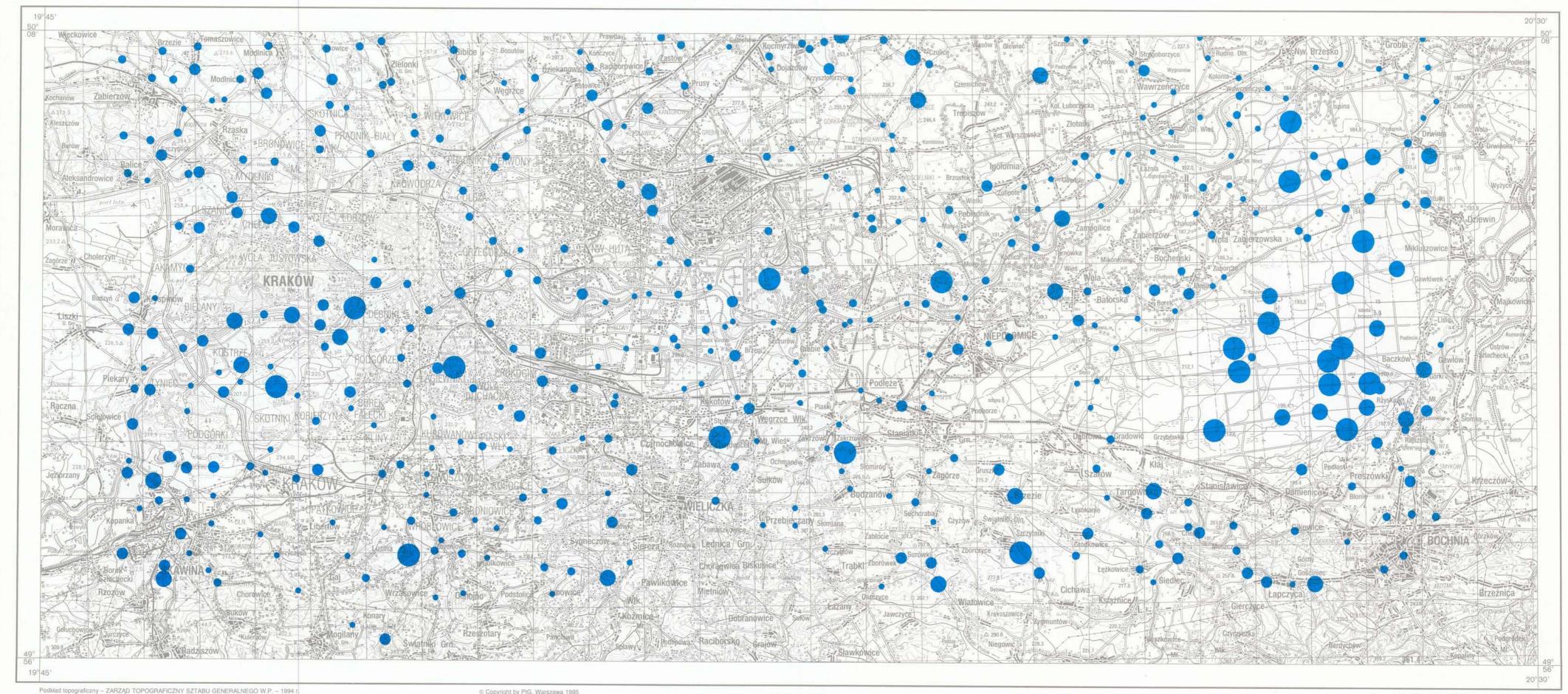


**WODY POWIERZCHNIOWE SURFACE WATERS** 



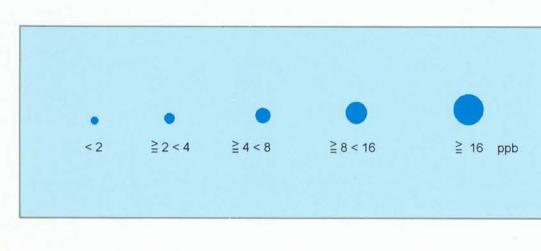


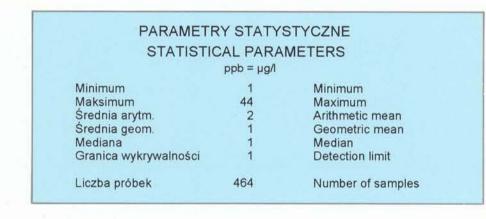


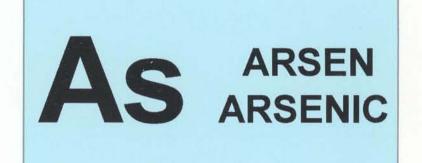


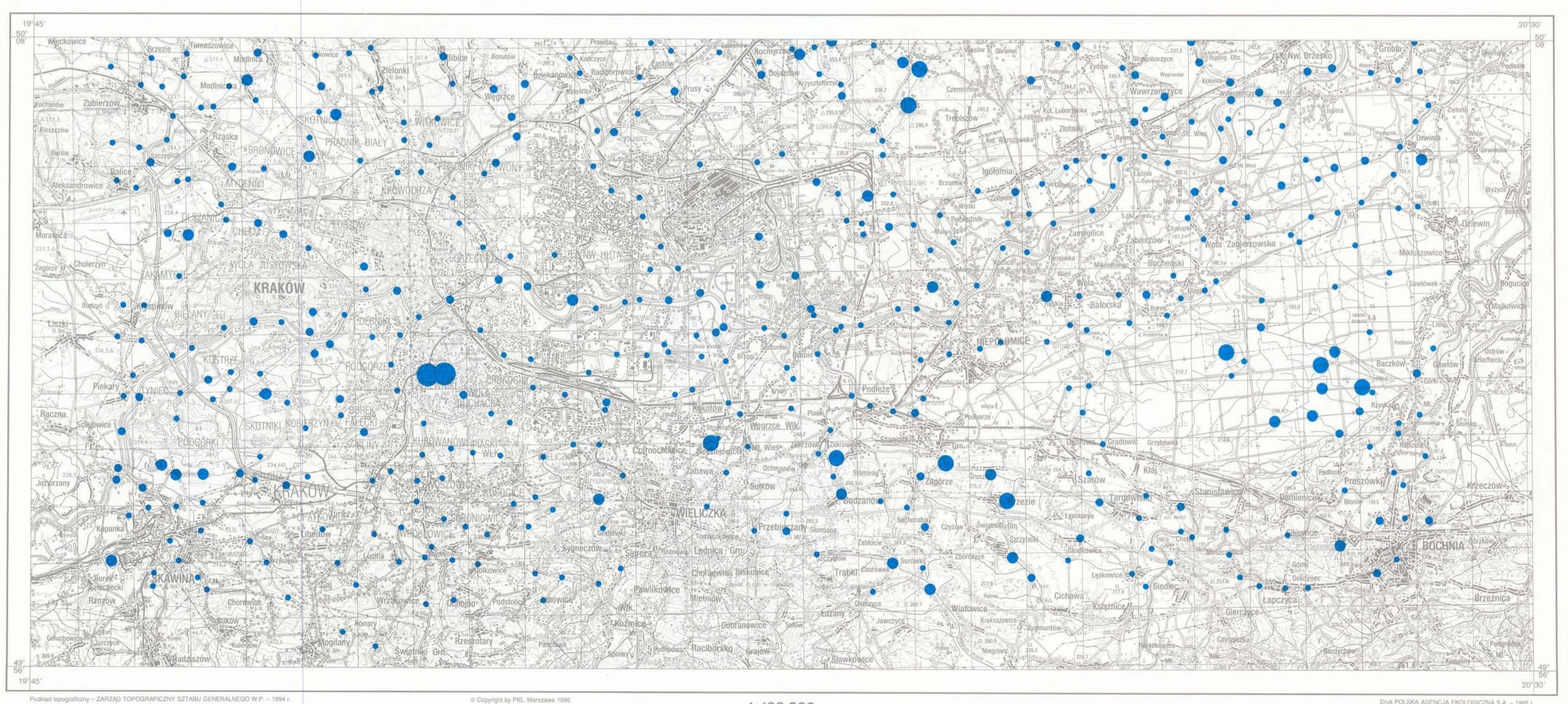












OMISNAGO GEOLOGICZNY

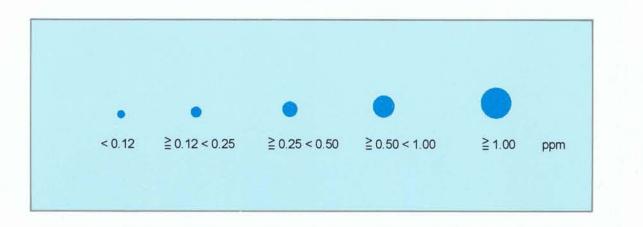
TOTAL STATUT GEOLOGICZNY

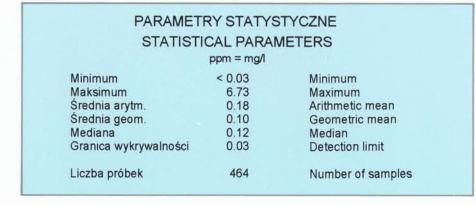
TOTAL STATUT GEOLOGICZNY

TOTAL STATUT GEOLOGICZNY

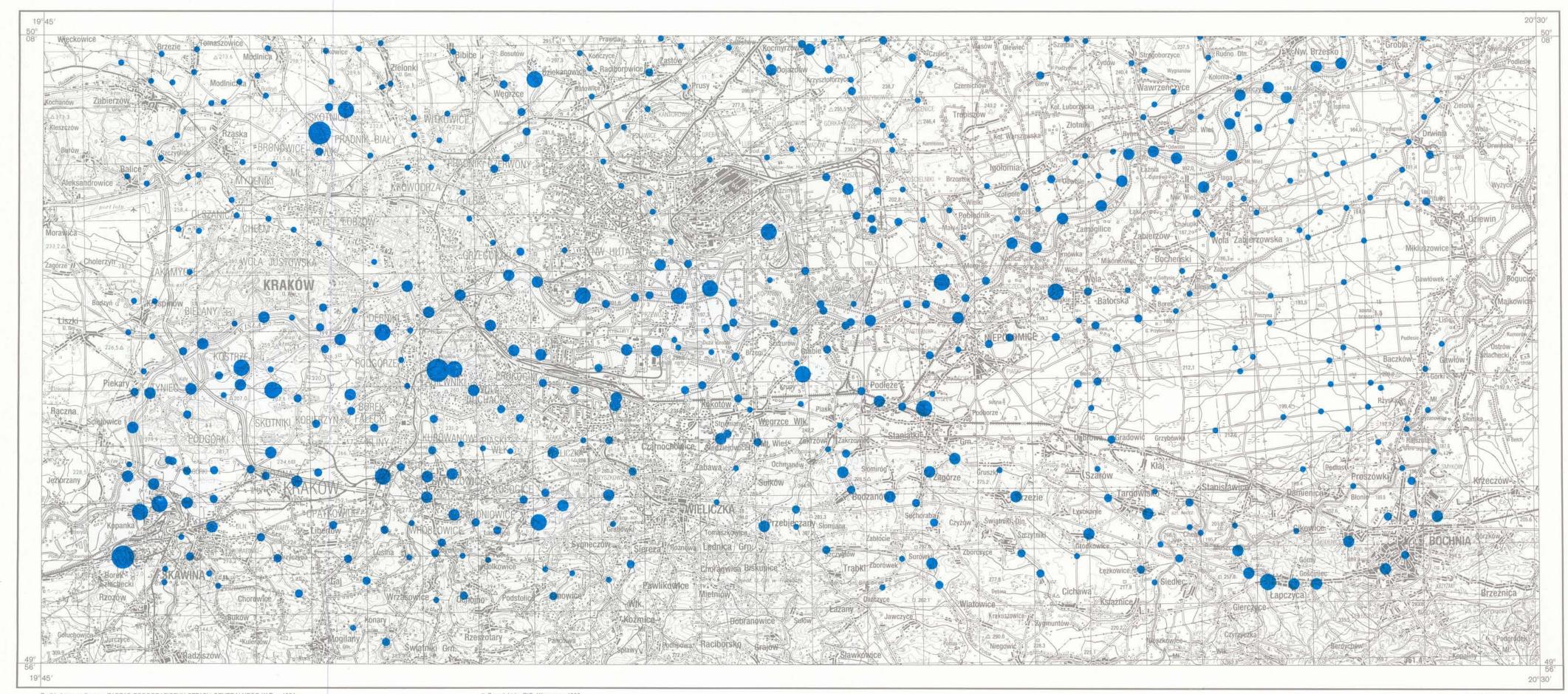
## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS

WODY POWIERZCHNIOWE SURFACE WATERS





B BOR BORON



100\_

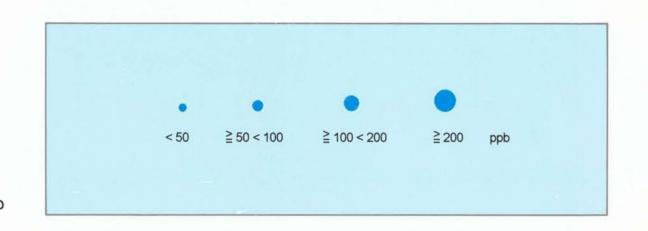
< 0.03

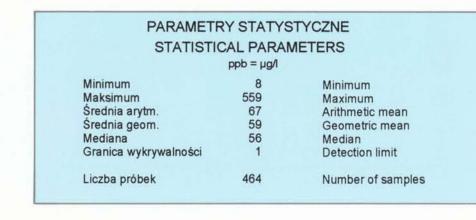
0.33

MALEO MALEO TOTAL TOTAL

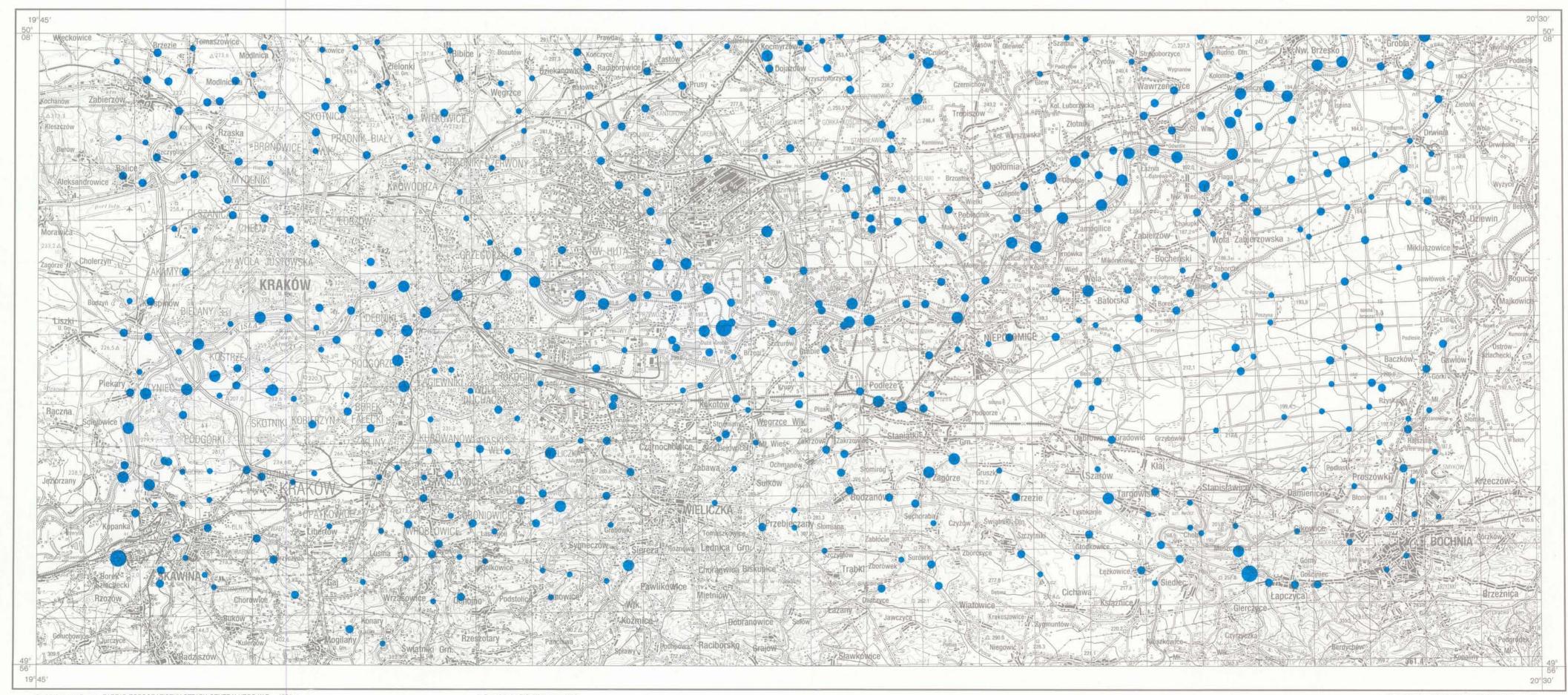
## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS

WODY POWIERZCHNIOWE SURFACE WATERS



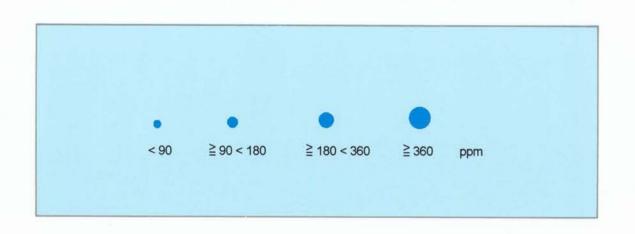


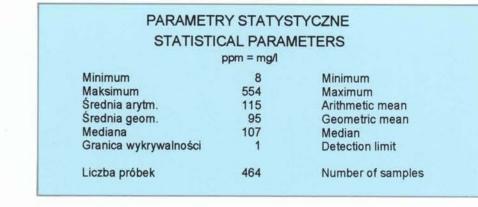
Ba BARIUM



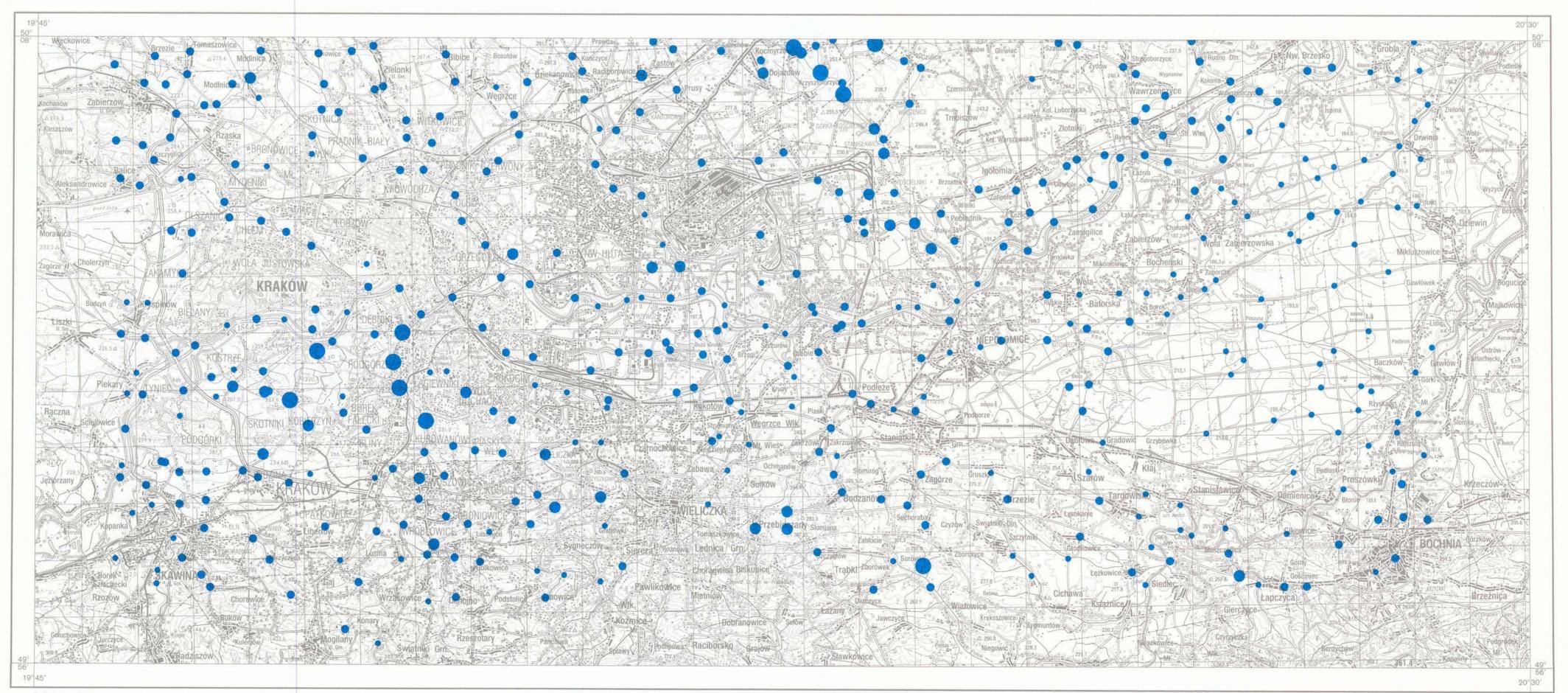


WODY POWIERZCHNIOWE SURFACE WATERS





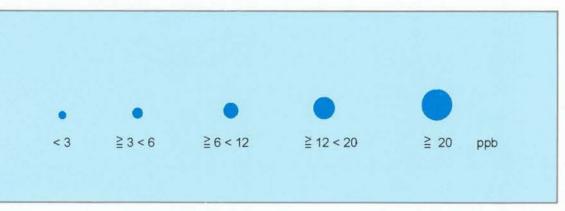
Ca WAPŃ CALCIUM

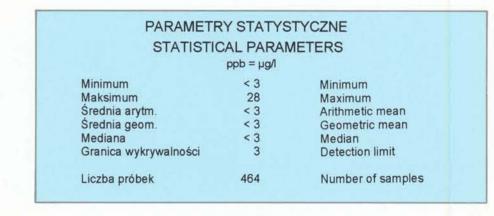




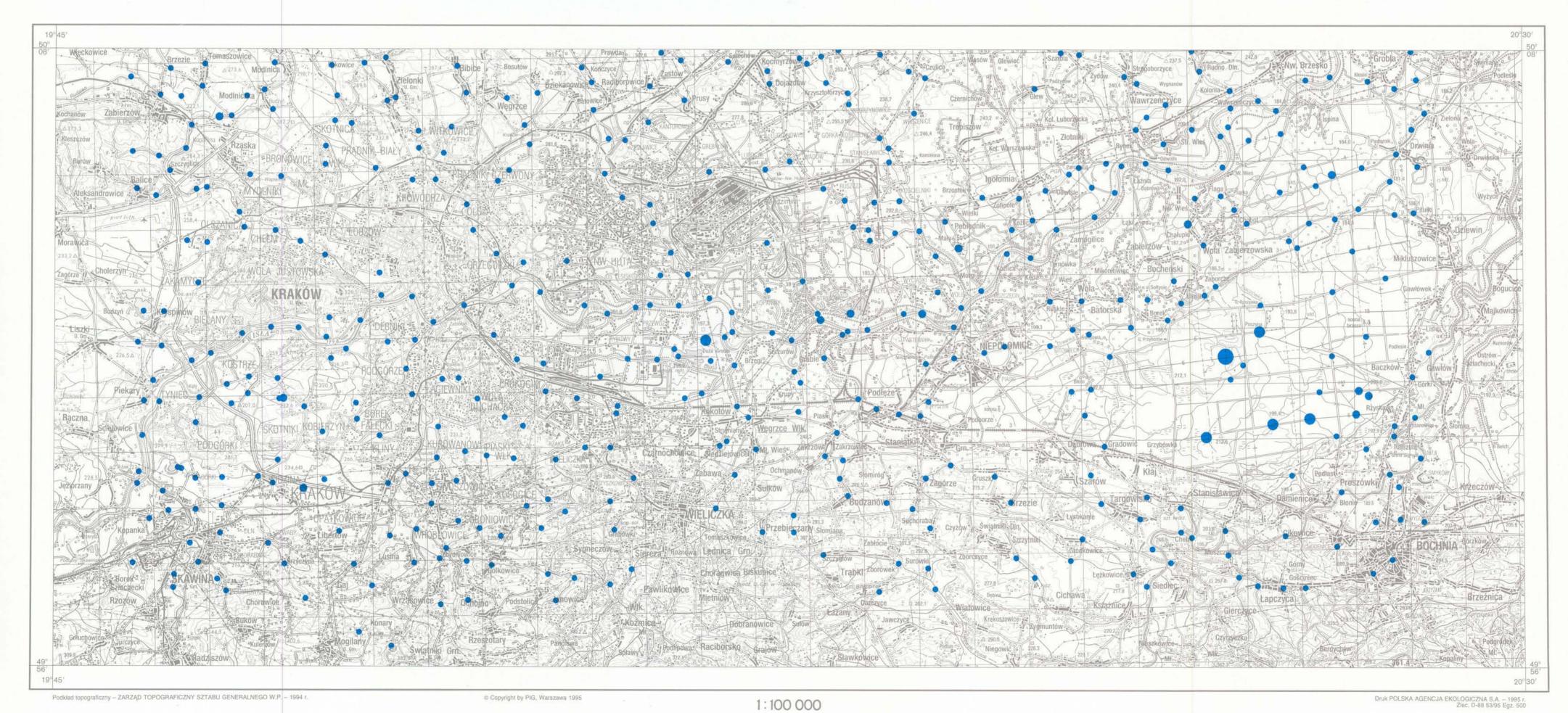
WODY POWIERZCHNIOWE SURFACE WATERS



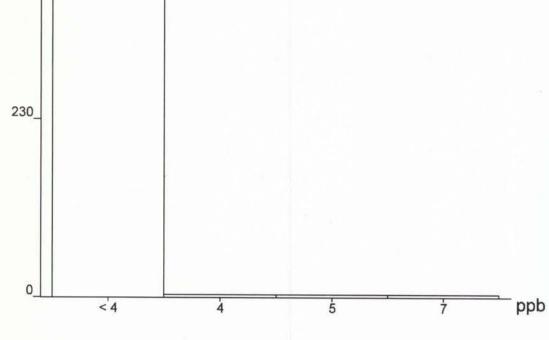


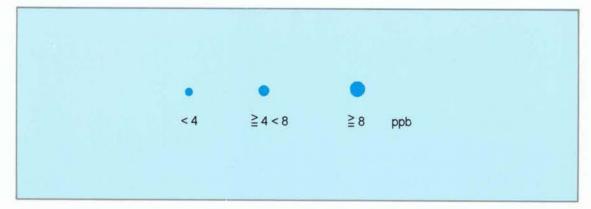


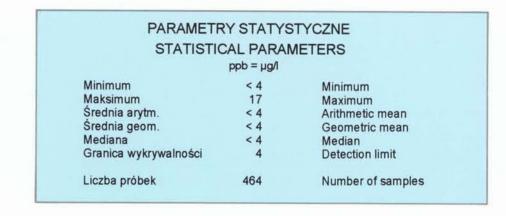


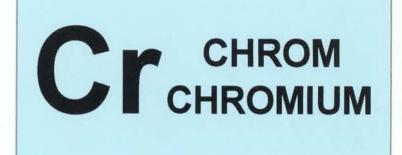


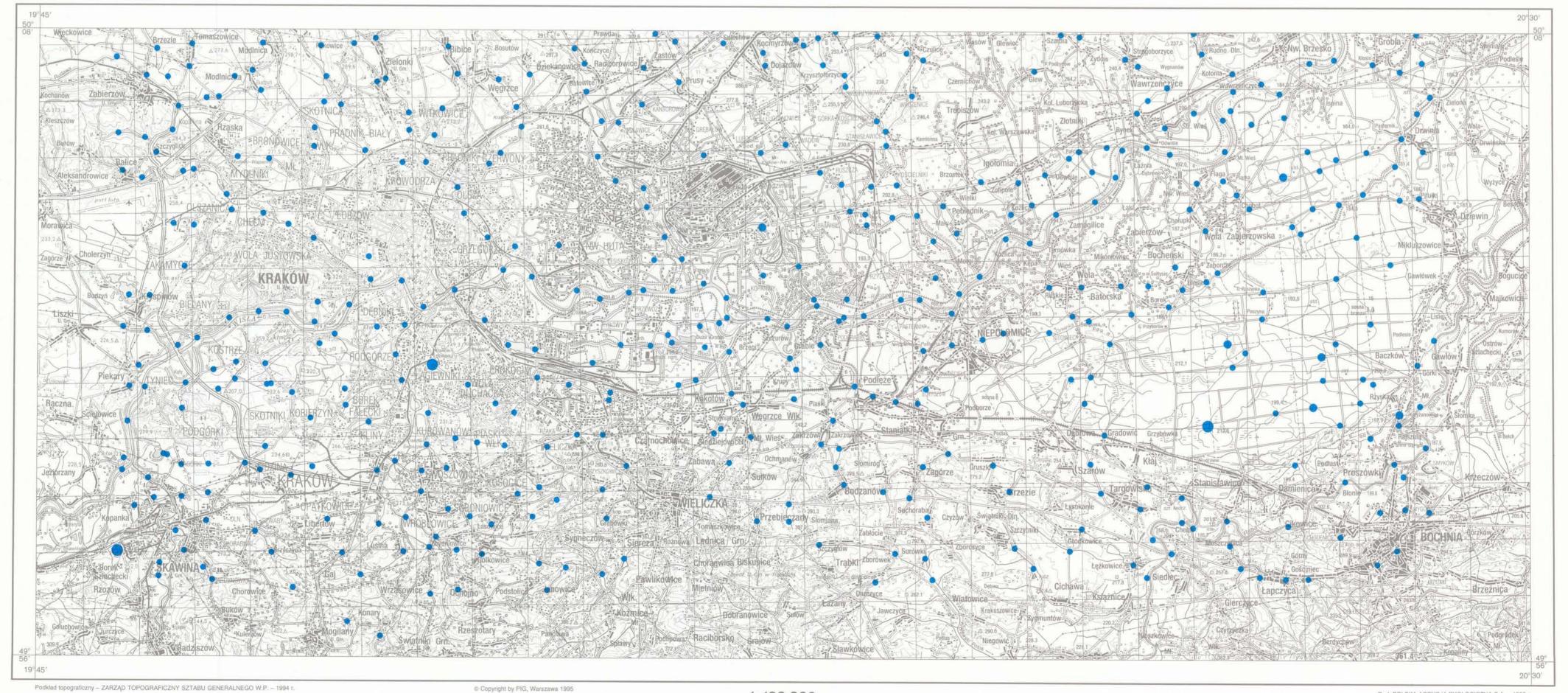
WODY POWIERZCHNIOWE **SURFACE WATERS** 









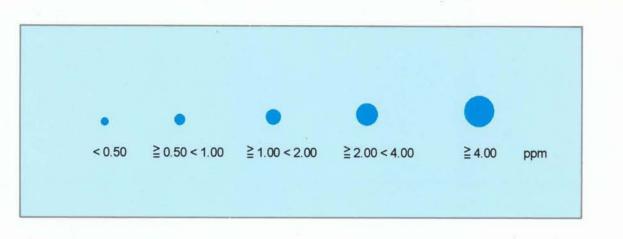


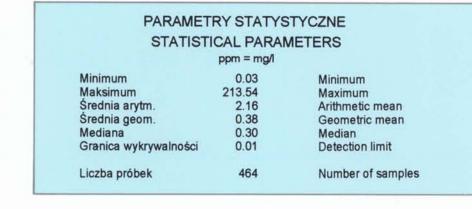
TABLICA 57



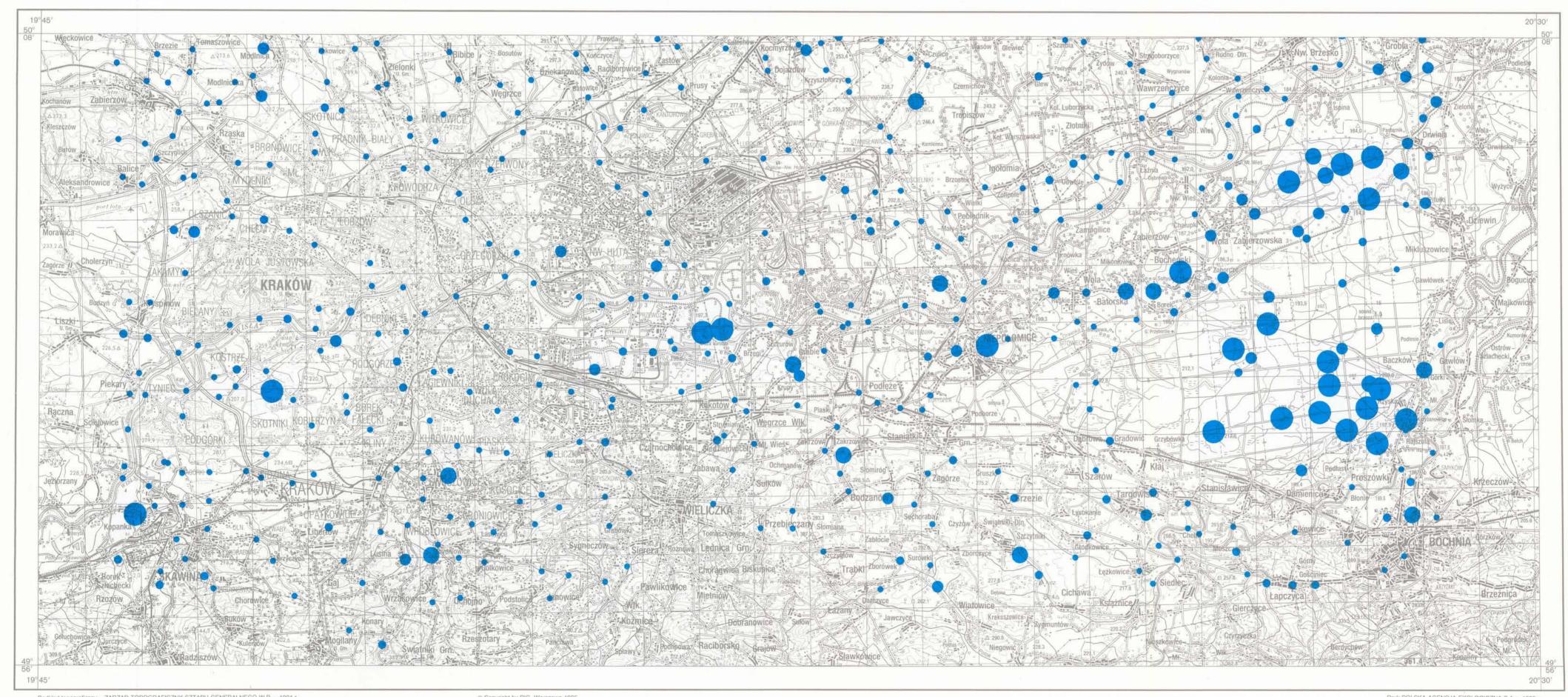
## ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS

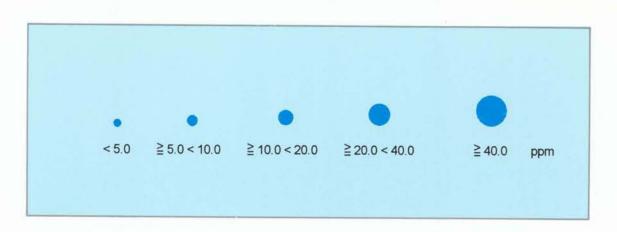
WODY POWIERZCHNIOWE SURFACE WATERS





Fe ŻELAZO IRON

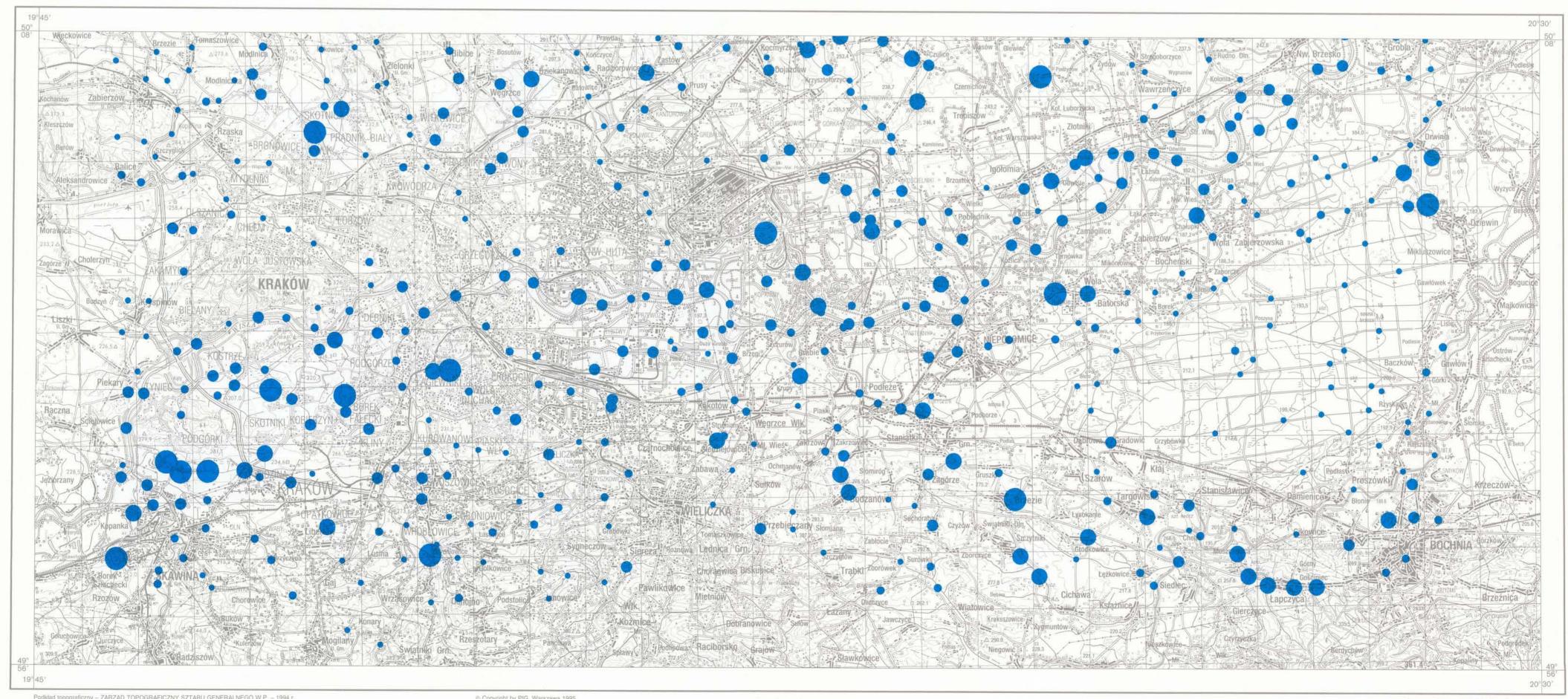




| PARAMET               | RY STATYS  | STYCZNE           |
|-----------------------|------------|-------------------|
| STATISTI              | CAL PARAM  | METERS            |
|                       | ppm = mg/l |                   |
| Minimum               | < 0.5      | Minimum           |
| Maksimum              | 178.1      | Maximum           |
| Średnia arytm.        | 11.4       | Arithmetic mean   |
| Średnia geom.         | 7.0        | Geometric mean    |
| Mediana               | 6.8        | Median            |
| Granica wykrywalności | 0.5        | Detection limit   |
| Liczba próbek         | 464        | Number of samples |

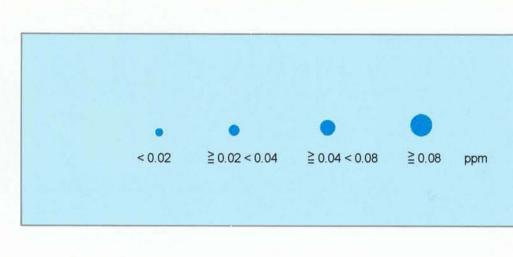
**WODY POWIERZCHNIOWE SURFACE WATERS** 

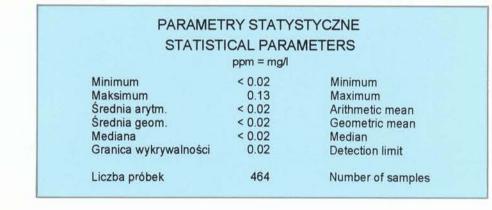




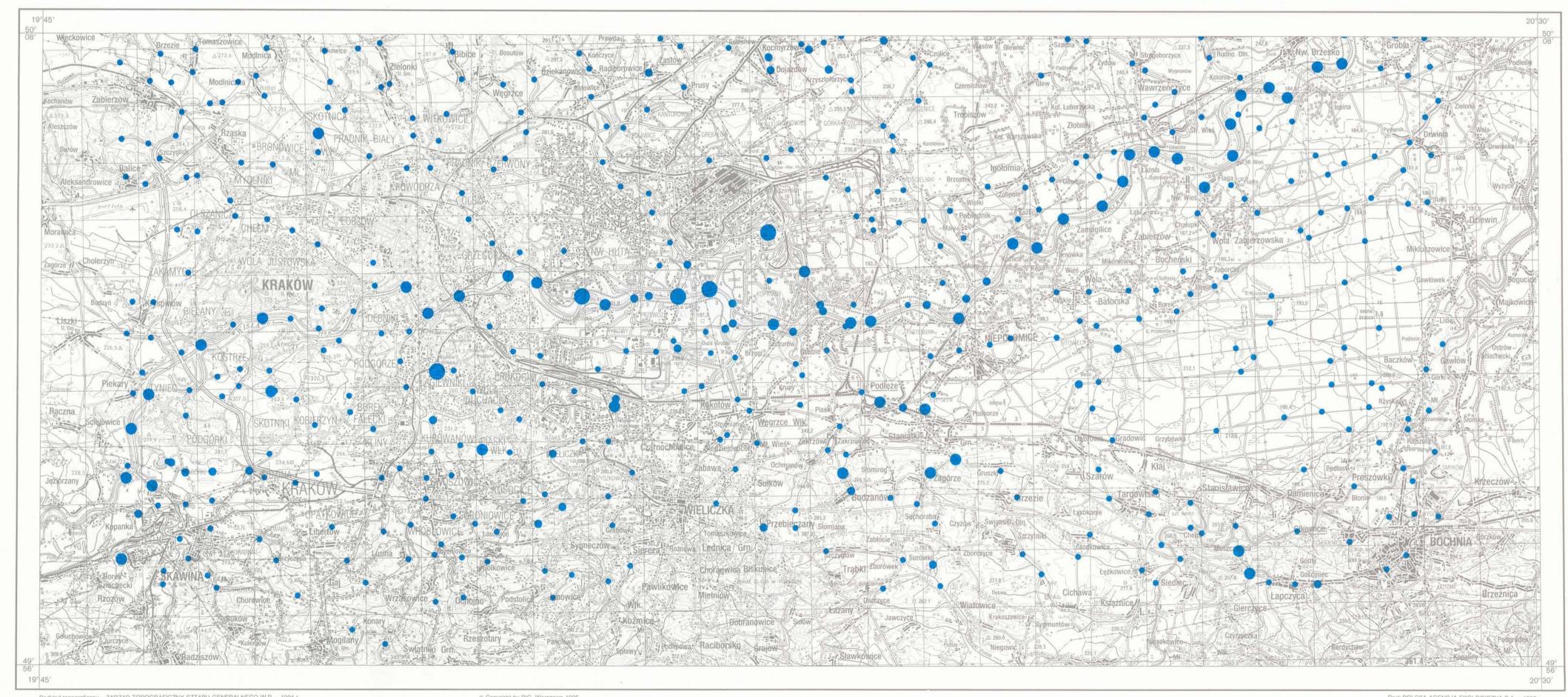


WODY POWIERZCHNIOWE SURFACE WATERS









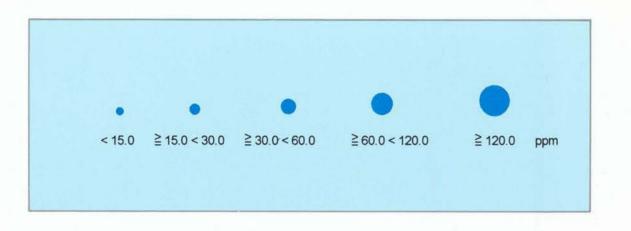
< 0.02

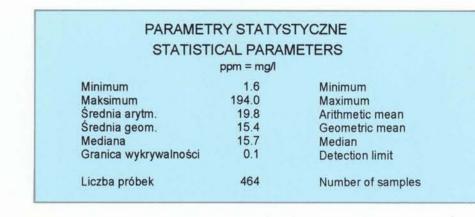
TABLICA 60



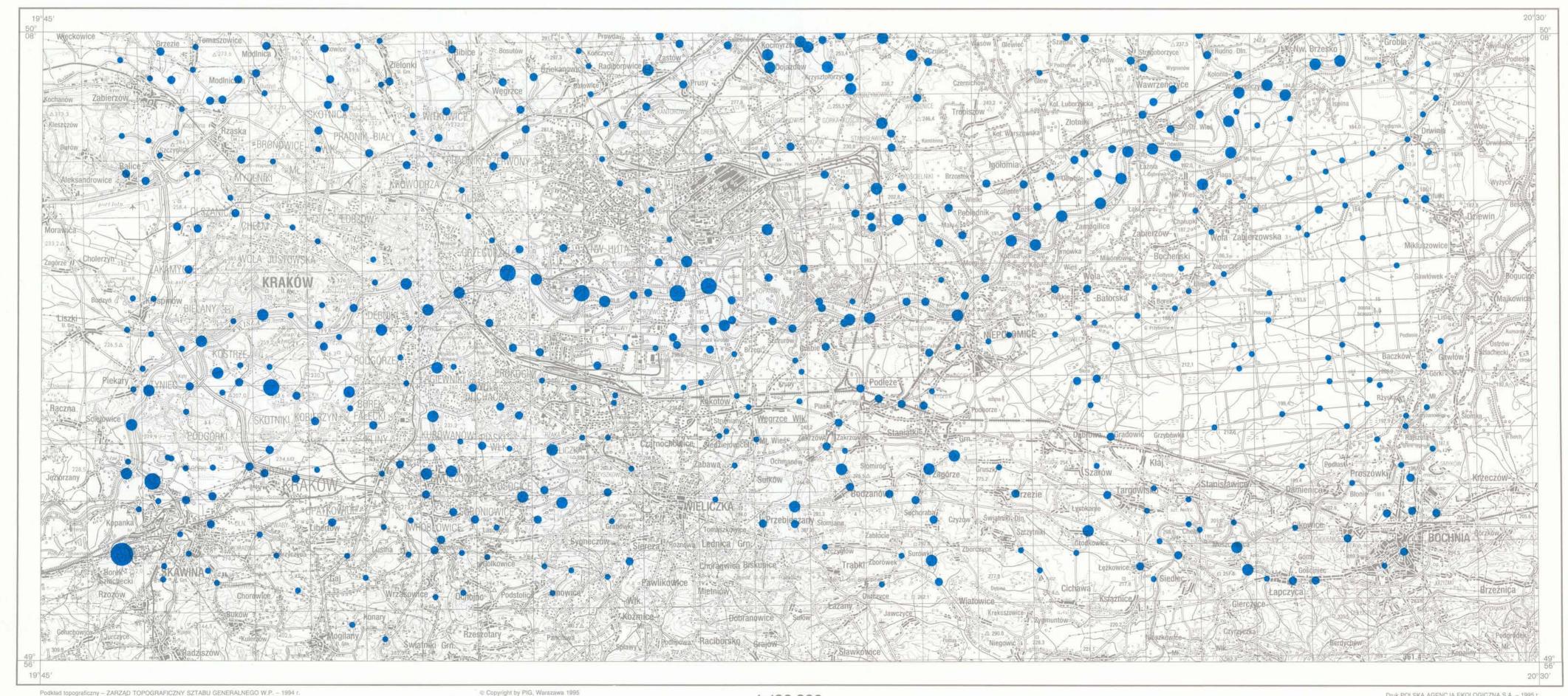
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

WODY POWIERZCHNIOWE **SURFACE WATERS** 





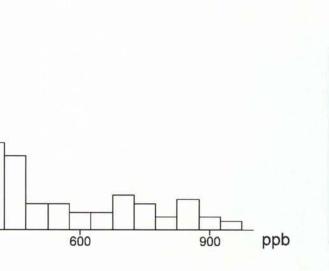


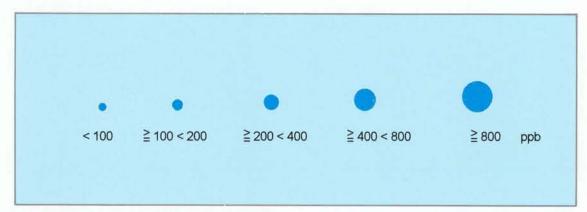


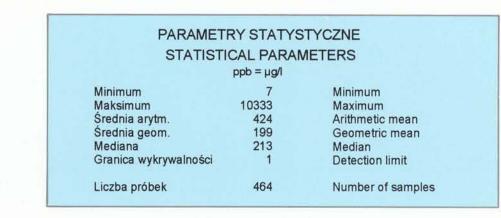
TABLICA 61

### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

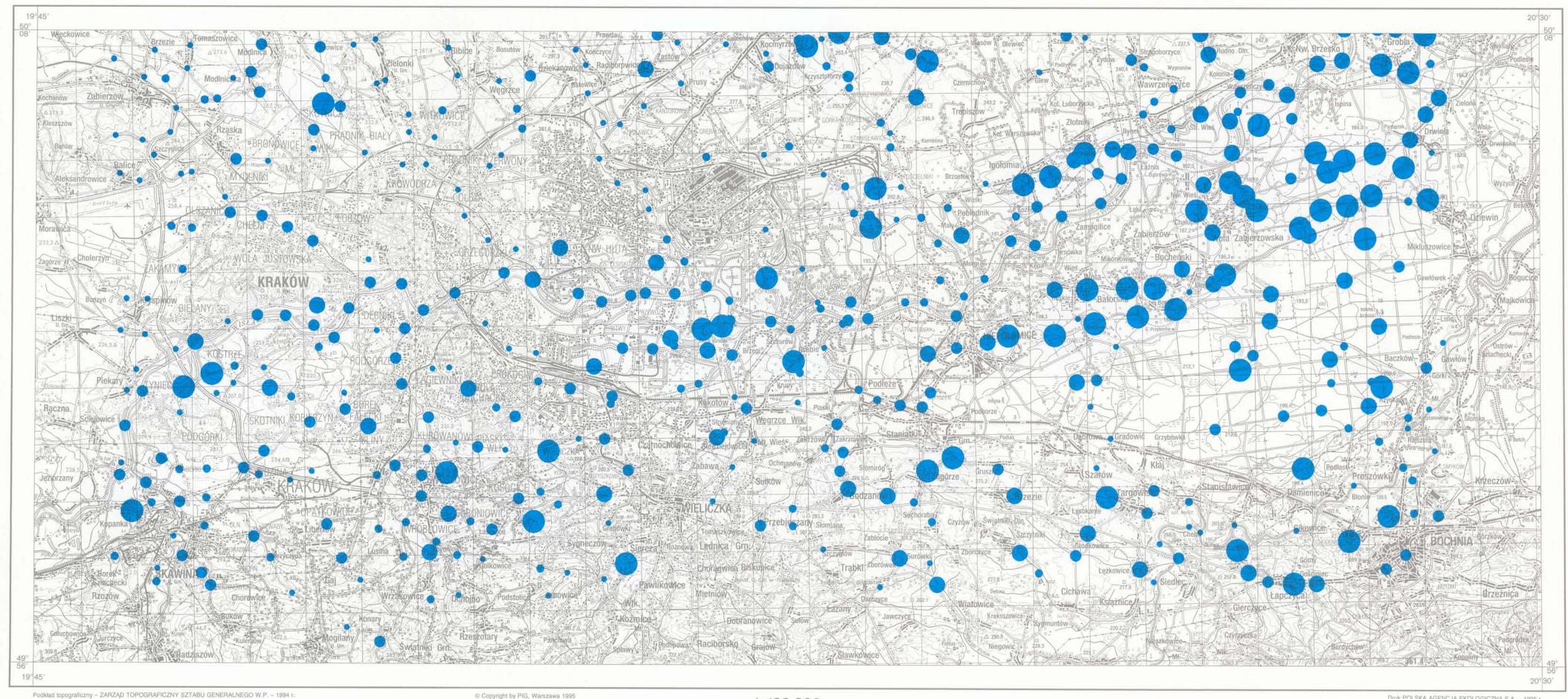


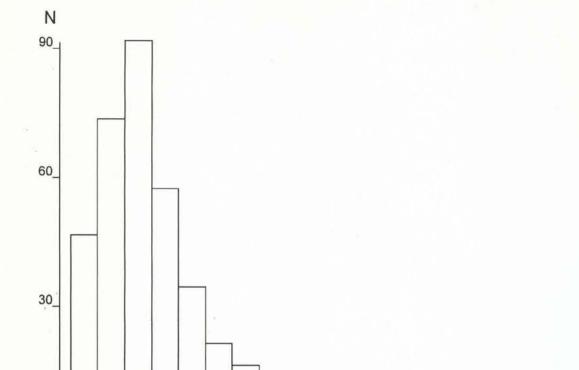




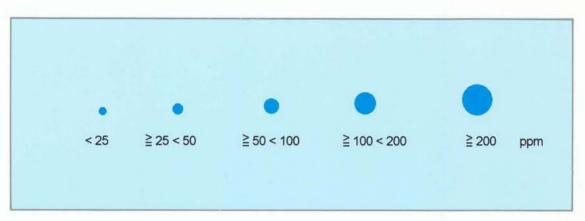


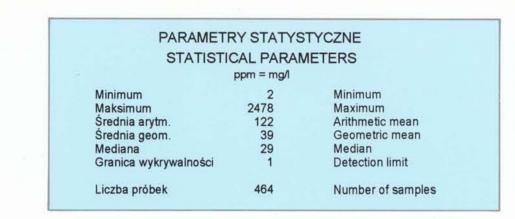






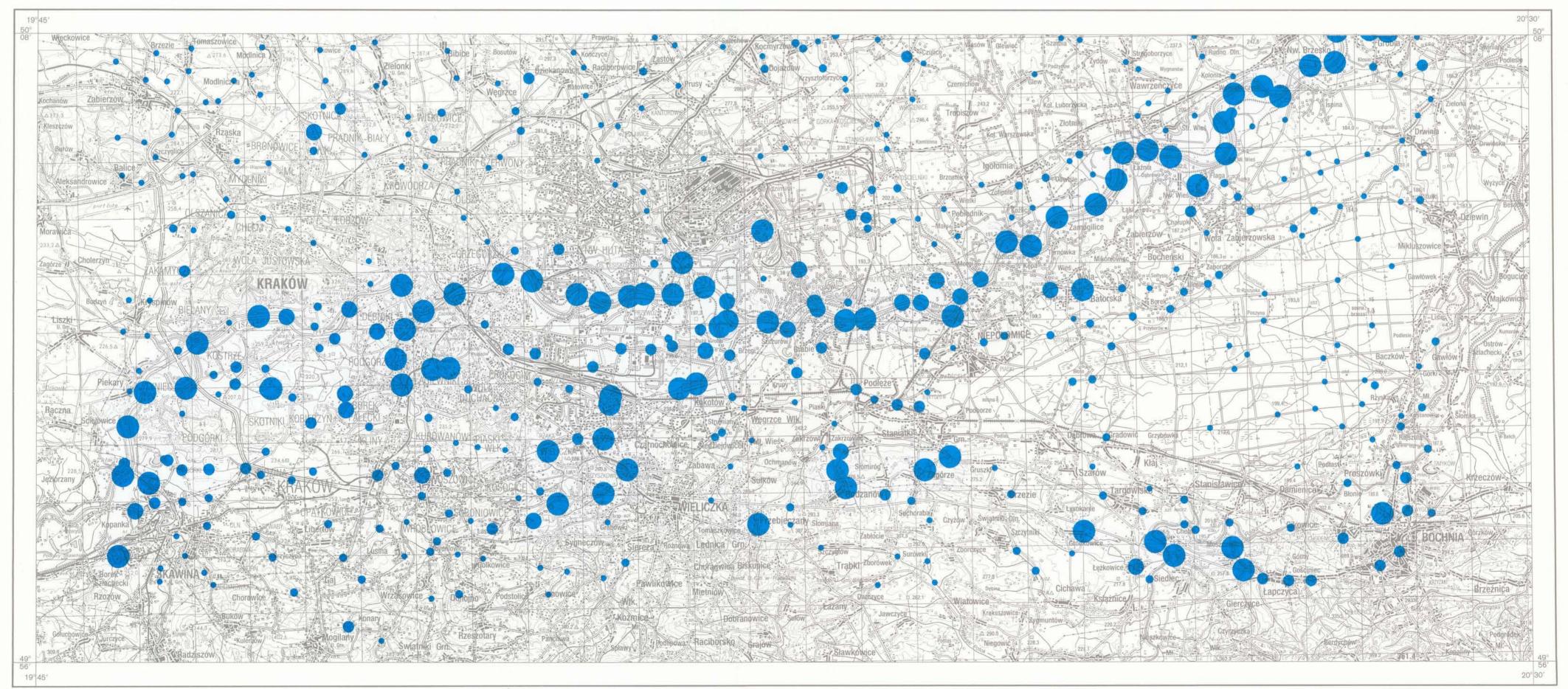




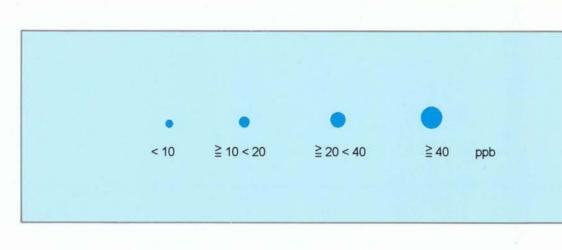


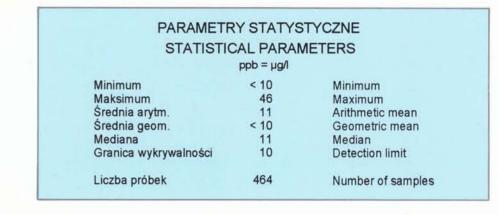
WODY POWIERZCHNIOWE SURFACE WATERS

Na sód sodium

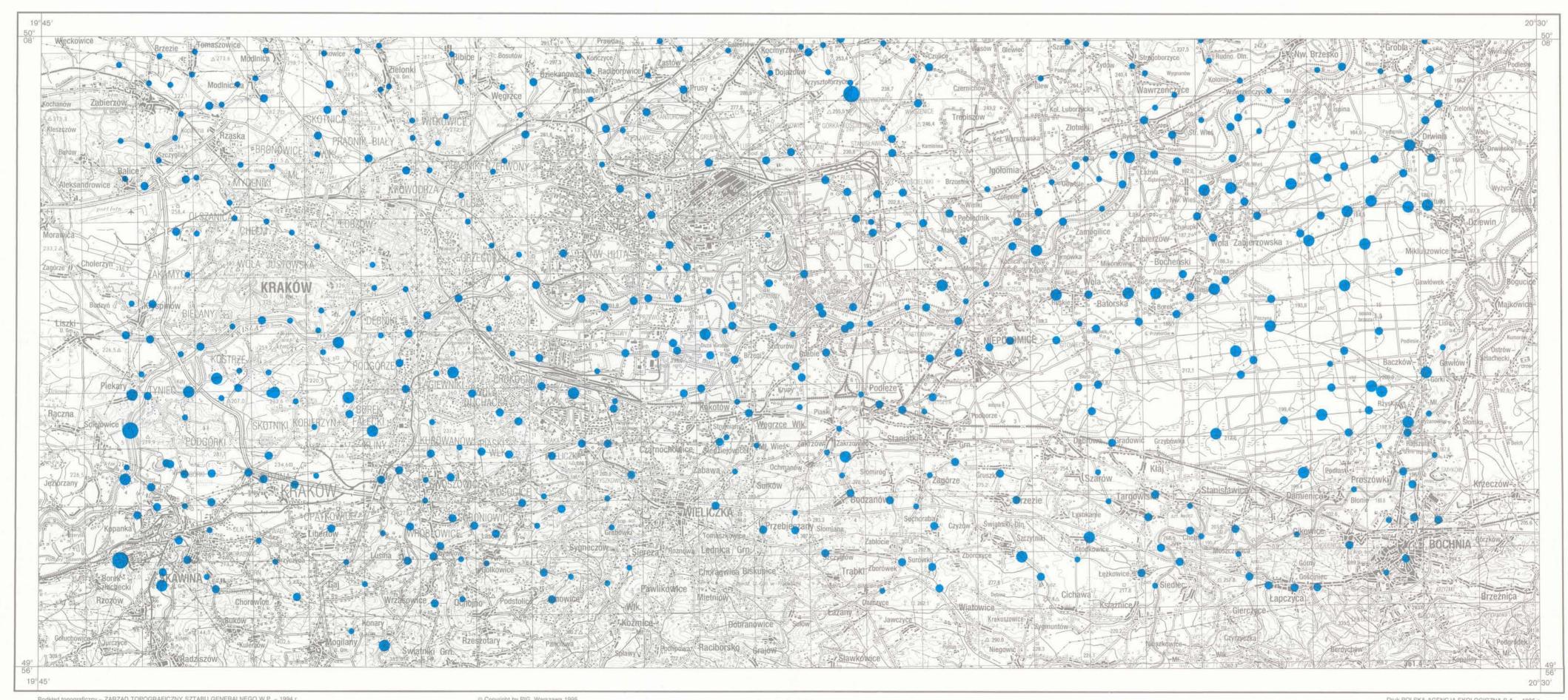


WODY POWIERZCHNIOWE **SURFACE WATERS** 

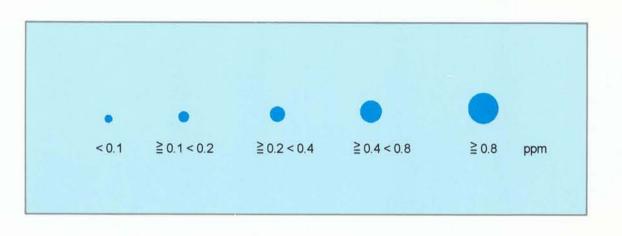


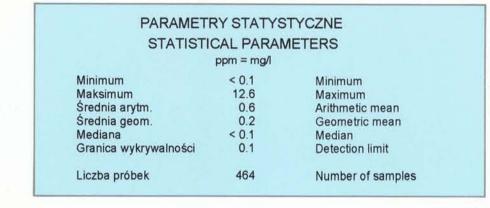




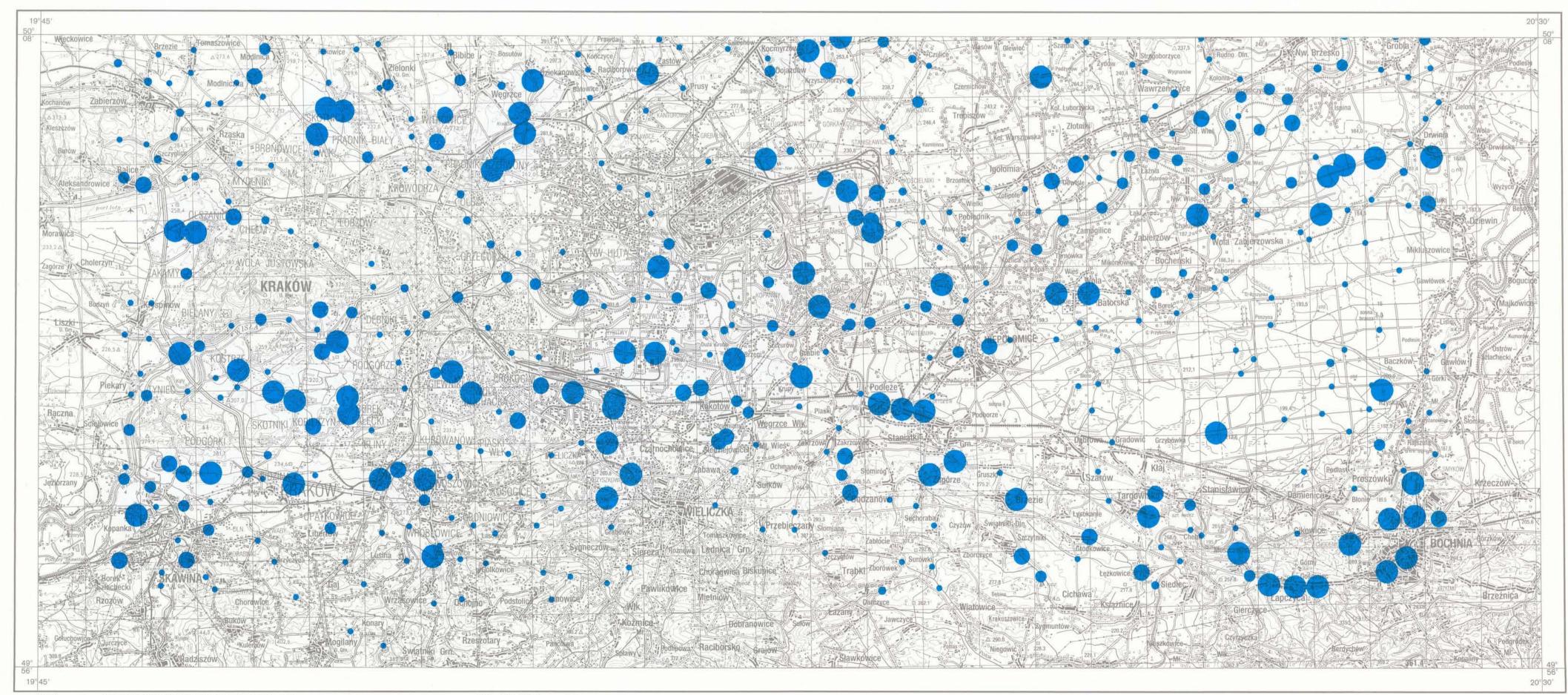


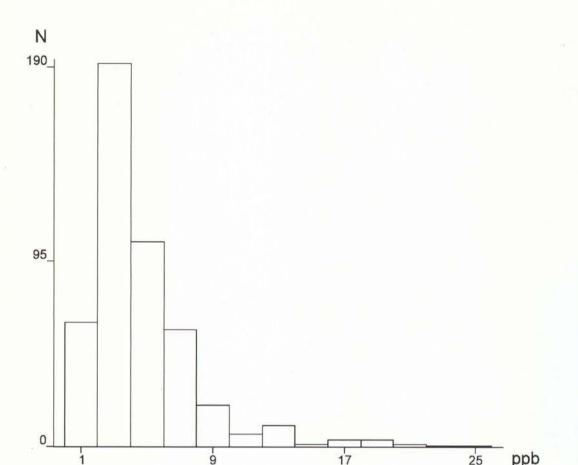
WODY POWIERZCHNIOWE **SURFACE WATERS** 

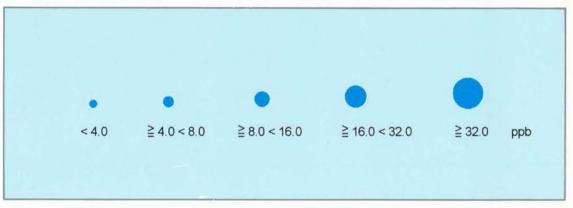




**FOSFOR PHOSPHORUS** 



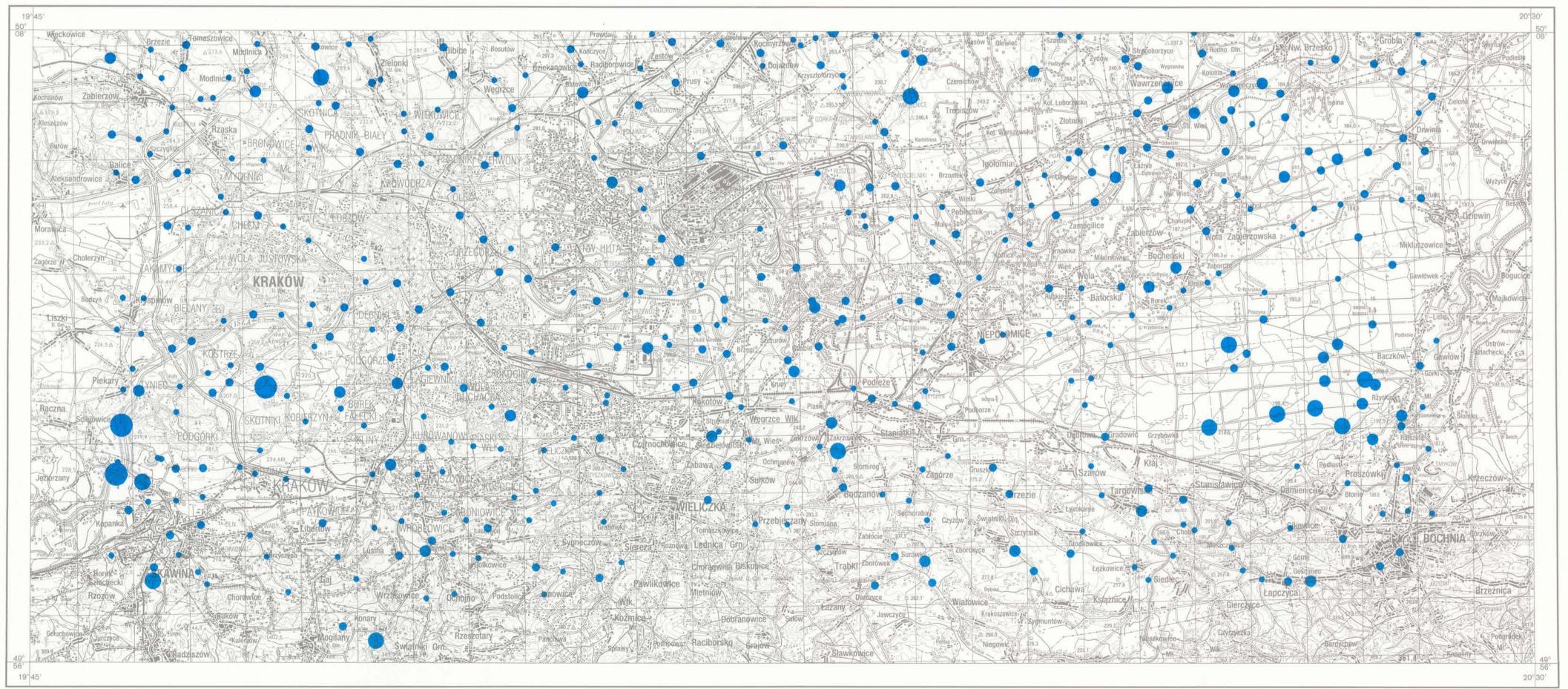




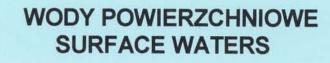
| STATISTI              | CAL PARAM       | METERS           |
|-----------------------|-----------------|------------------|
|                       | $ppb = \mu g/l$ |                  |
| Minimum               | 0.2             | Minimum          |
| Maksimum              | 47.9            | Maximum          |
| Średnia arytm.        | 4.9             | Arithmetic mean  |
| Średnia geom.         | 3.7             | Geometric mean   |
| Mediana               | 3.7             | Median           |
| Granica wykrywalności | 0.1             | Detection limit  |
| Liczba próbek         | 464             | Number of sample |

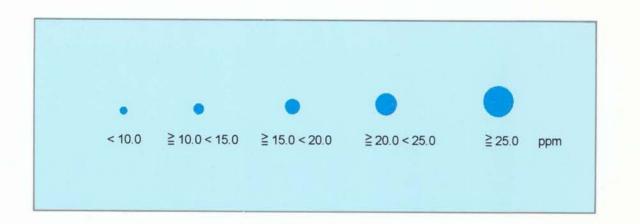
WODY POWIERZCHNIOWE **SURFACE WATERS** 

Po oŁów LEAD



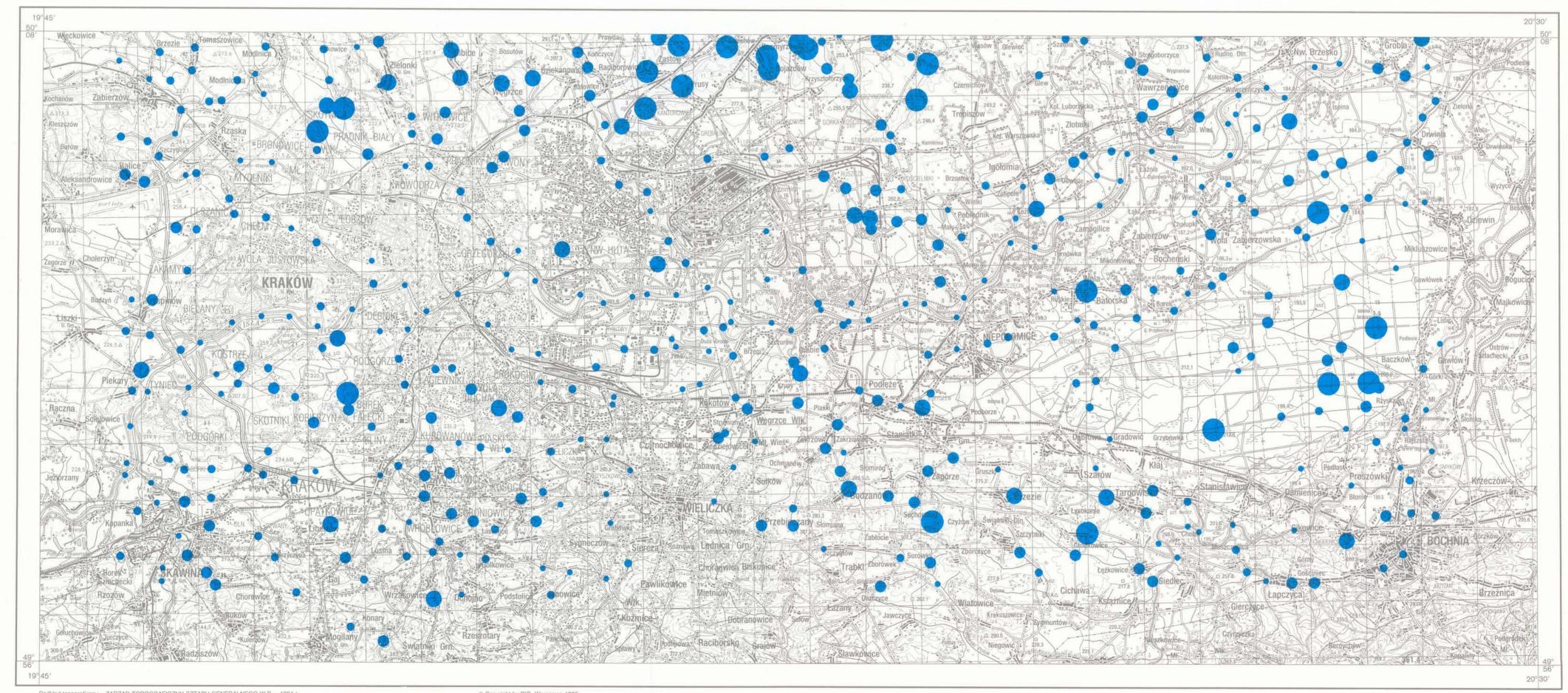






| PARAMETI              | RY STATYS  | STYCZNE           |
|-----------------------|------------|-------------------|
| STATISTI              | CAL PARA   | METERS            |
|                       | ppm = mg/l |                   |
| Minimum               | < 0.1      | Minimum           |
| Maksimum              | 37.1       | Maximum           |
| Średnia arytm.        | 12.5       | Arithmetic mean   |
| Średnia geom.         | 10.0       | Geometric mean    |
| Mediana               | 12.5       | Median            |
| Granica wykrywalności | 0.1        | Detection limit   |
| Liczba próbek         | 464        | Number of samples |

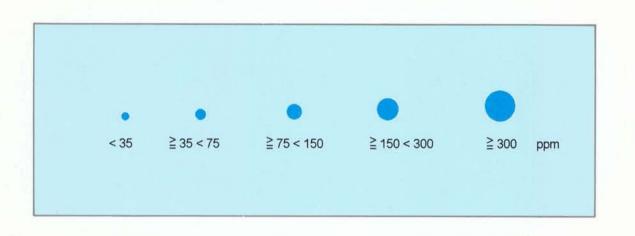


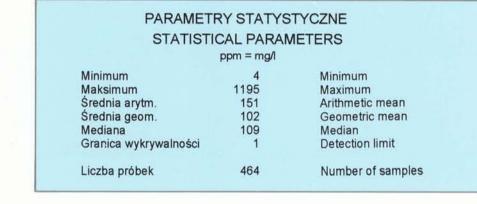


TABLICA 67

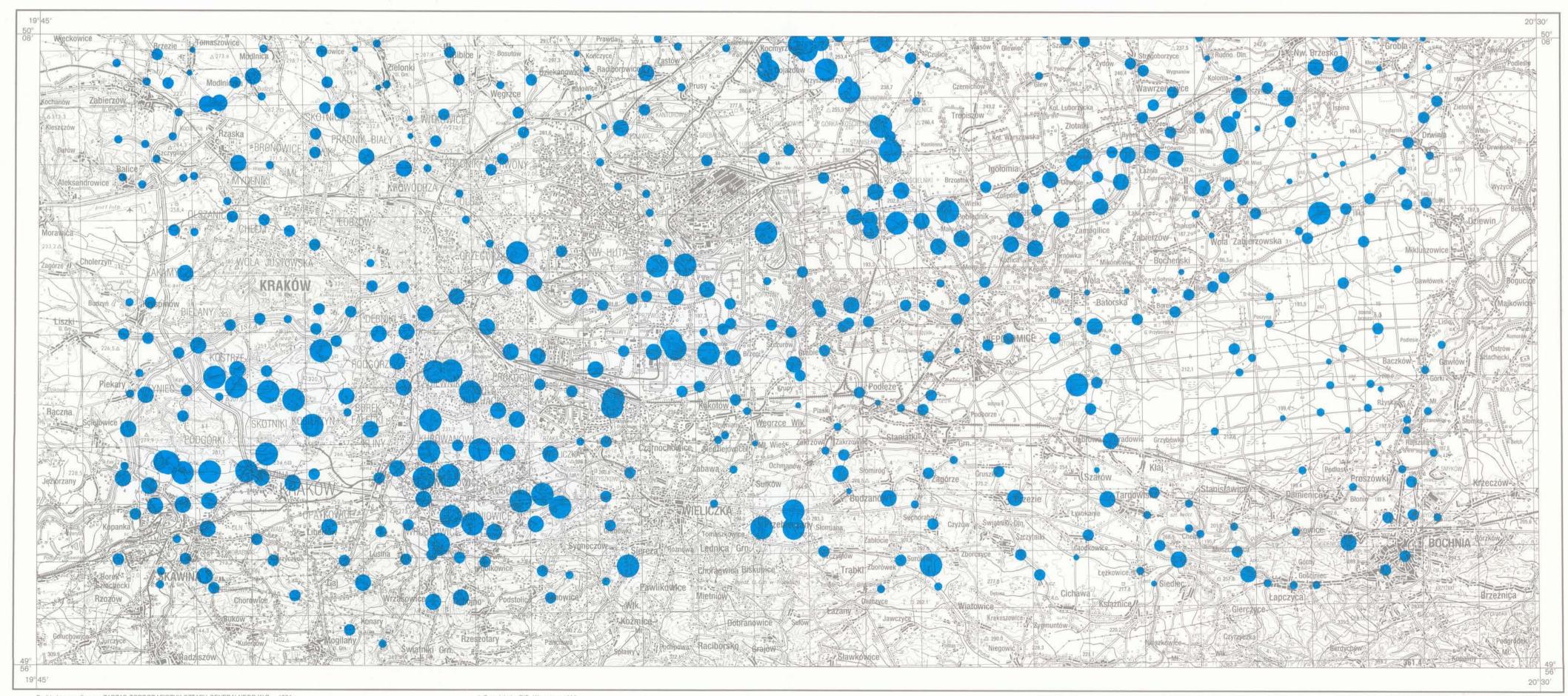
### ATLAS GEOCHEMICZNY KRAKOWA I OKOLIC **GEOCHEMICAL ATLAS OF CRACOW AND ENVIRONS**

**WODY POWIERZCHNIOWE SURFACE WATERS** 

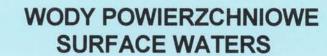


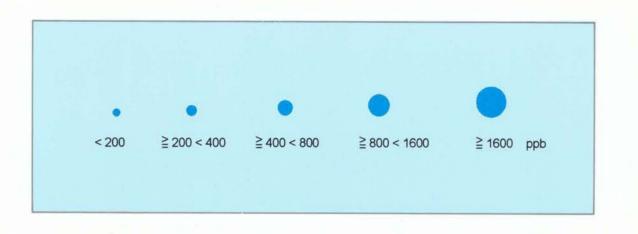


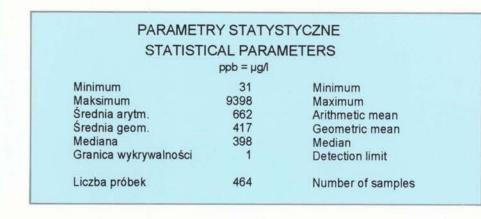
SO<sub>4</sub> SIARCZANY SULPHATES



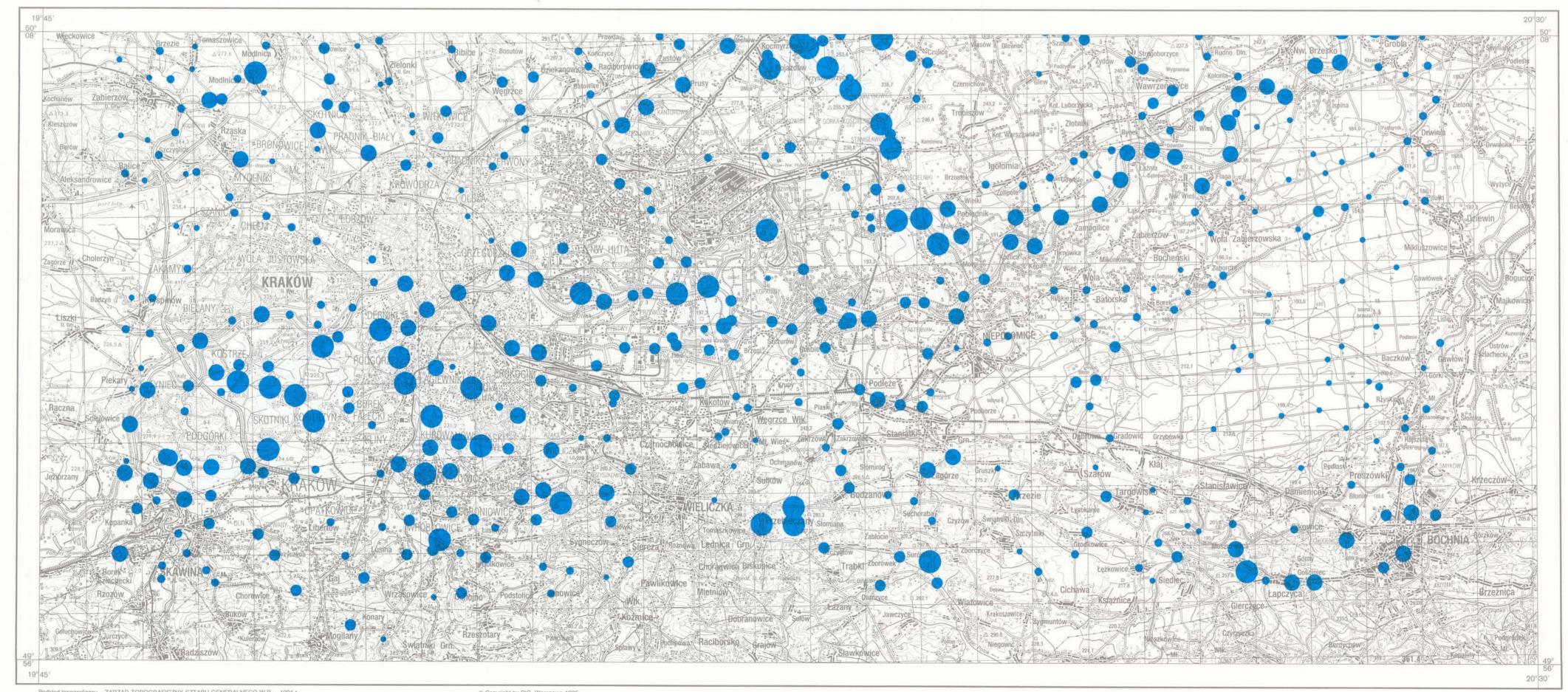






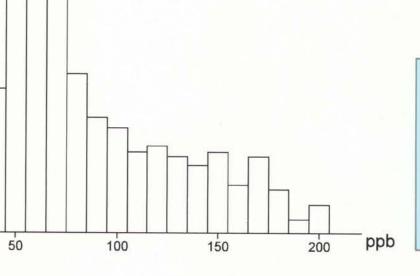


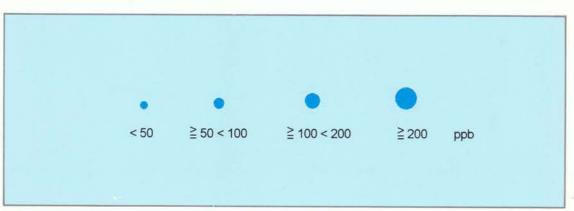


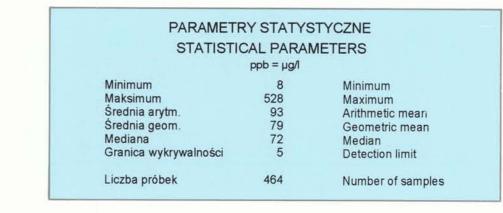




WODY POWIERZCHNIOWE SURFACE WATERS







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