INTRODUCTION

Since the 1990s, the European geological surveys have collected joint data on the occurrence of chemical elements and compounds in the Earth's surface environments and on the risks posed by their excessive concentration or deficit. The aim of the work is, on the one hand, to determine the geochemical background of the elements in soil, subsoil, stream sediments and surface waters on the European scale, and, on the other hand – to attempt developing a uniform international standards for the assessment of pollution of these environments. Earlier data cannot be comparable because the geological surveys of individual countries applied different sampling and analytical methods, and different criteria for interpretation of results and assessment of health risk.

As a result of several-year progress in the FOREGS project (**Fo**rum of **E**uropean **G**eological **S**urveys), an international group of geochemists has developed Geochemical Atlas of Europe (Salminen, ed., 2005; De Vos, Tarvainen, ed., 2006) containing basic information about the geochemical characteristics of soils, surface waters and stream sediments throughout the continent. The study of agricultural soils have been conducted only in the Baltic countries (Reimann et al., 2003).

The GEMAS (**GE**ochemical **M**apping of **A**gricultural **S**oils and Grazing Lands in Europe) project focuses on the study of agricultural soils and is another common presentation of a group of EuroGeoSurveys experts, conducted in 2008–2013 in cooperation with external organizations (Alterra from the Netherlands, Norwegian Forest and Landscape Institute, CSIRO Land and Water from Australia, as well as with the environment ministries and university departments of earth sciences in several countries).

Soil samples from the area of Poland in the frame of GEMAS project were collected by: **Przemysław Dobek, Aleksandra Dusza-Dobek, Tomasz Gliwicz, Piotr Kaszycki, Paweł Kwecko, Joanna Szymborska-Kaszycka**.

PURPOSE OF THE PROJECT

Our knowledge of the soils condition in agricultural areas is very important because it affects, on the one hand, the quantity and quality of food production, and, on the other hand, all legal decisions concerning land use. Information on the chemical condition of soils are also used for other purposes, for example, for determining the source of contaminants in food.

The aim of the project was to determine the concentrations of several tens of chemical elements (and selected physicochemical parameters) in soils of arable fields and grazing land (meadows and pastures) of Europe. Geochemical background values of individual chemical elements in soils of the European continent vary widely (even several orders of magnitude). In many areas, the soils contain anomalous concentrations of pollutants that pose environmental and health hazard. However, also the shortages of elements, just like their excess, often have an equally serious effect on plants and animals as well as human health.

The project made it possible to gather information about the concentrations of many substances in soils across Europe, and their collection in the form of a single database will help in the development and implementation of the EU Soil Protection Directive.

The present report is devoted to the analysis of spatial distribution of selected elements and parameters in Poland, which were not examined during earlier geochemical surveys. The study does not include elements and parameters that were previously determined during the development of "Geochemical Atlas of Poland" (Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V, Y, Zn and pH), and the enclosed geochemical maps were produced on the basis of 10,840 soil samples (with the sampling density of 1 sample/25 km^2). The results of GEMAS project study on these elements are summarized in Table 1 only. Due to the very low contents, maps of spatial distribution of the noble metals and all rare earth metals have not been constructed.

METHODS

The scope and terms of the GEMAS project realization were agreed on several meetings of the EGS working groups. Geological surveys of all countries covered the costs of field work in their territories and the costs of transport of samples to the laboratory of the Geological Survey of Slovakia. Chemical analyses were financed by the industrial consortium Eurometaux – European Association of Metals, based in Brussels.

Sampling. At the workshop in Berlin in March 2008, details of the project (field work procedure, data recording) were settled, and a sampling training was conducted in accordance with the Field Manual (2008).

Soil sampling from all over Europe was carried out in summer 2008, with a regular density of 1 sample/2500 km^2 (Fig. 1A). In this area, 50 x 50 km size polygons were created.

Samples, which were taken closest to the centre of the polygon, represented the predominant soil type. Arable field or grazing land soils selected for sampling were characterized by dimensions not smaller than 25 x 50 m, and the area was as flat as possible (except in valleys and depressions) and least vulnerable to anthropogenic factors. The following features disqualified the site from sampling:

– anthropogenic changes of land (areas of landfills and sewage discharge visible or detectable by smell);

– industrial installations and infrastructure (minimum distance 2 km);

– motorways and roads (minimum distance 200 m);

– power lines (minimum distance 100 m).

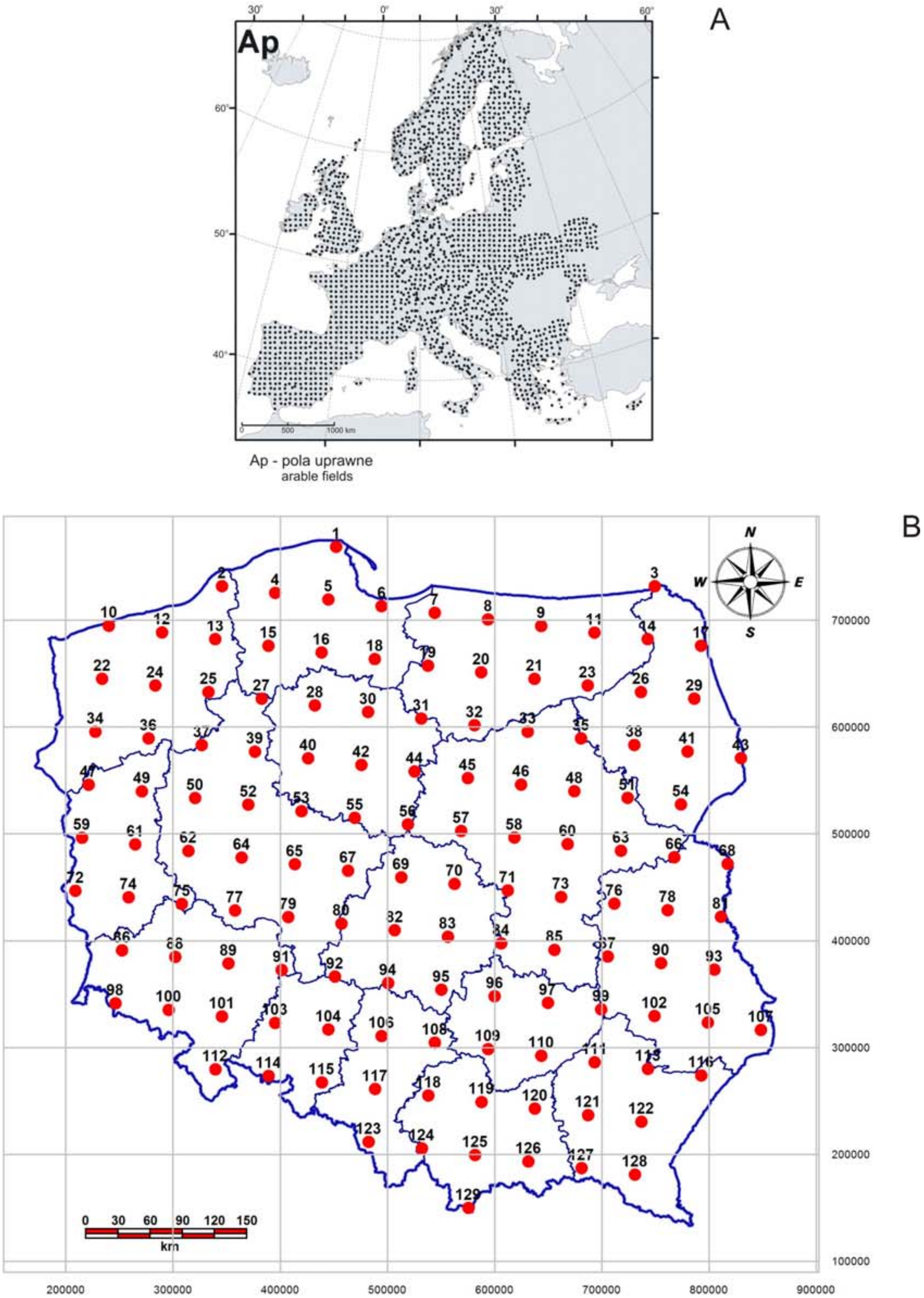

Fig. 1. Miejsca opróbowania gleb Europy (A) i Polski (B)
Sampling points of soils in Europe (A) and in Poland (B)

Soil samples were placed in *Rilsan* bags (teflon coated) and labeled providing a country code, sample number and land use type (Fig. 2A). The first three letters on the label denote country, the digits – sample number, and the last letters – land use: arable fields (Ap) or grazing land (Gr). In addition, the soil profile was documented photographically (Fig. 2B).

Two samples were collected from each polygon:

– sample from arable field (0–20 cm); and if the thickness of arable field was greater – from the profile at its lower limit;

– sample from grazing land (0–10 cm), devoid of plant roots.

At each sampling site, a 10 x 10 m square was marked out and a cumulative sample was collected from the four corners and from the centre of the square (subsamples, Fig. 3), using an unpainted steel spade. Then, the subsamples were averaged by mixing them, and by removing gravel, stones and roots. After taking the cumulative sample (2–2.5 kg), a foiled tagged (sample number) card was placed inside the plastic bag which was then closed with a special zip-lock.

After collecting twenty samples, control samples (duplicates) were taken from the same polygon. Duplicate sampling sites were slightly modified: the corners and the centre of the polygon were shifted by about 1–2 m in relation to the original square.

In the area of Poland, the samples were taken from 129 polygons (Fig. 1B) (after Pasieczna, Kwecko, 2010).

After sampling, each sample card was filled in with data on the date of sampling, description of the sampling site (sample No, field size, crop type, bedrock type) and coordinates (in WGS 84).

Fig. 2. Numeracja próbki (A) i profil glebowy (B)
Sample number (A) and soil profile (B)

Preparation of samples for analysis. After drying, the samples were delivered to the laboratory of the Geological Survey of Slovakia, where they were sieved through a <2 mm mesh nylon sieve, homogenized and divided into subsamples:

- 4 subsamples, 200 ml each, assigned for archival purposes;
- 2 subsamples, 100 ml each, and 4 subsamples, 50 ml each, for chemical analysis.

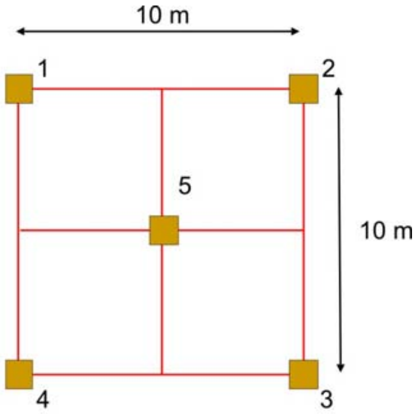

Fig. 3. Schemat pobierania próbki zbiorczej
Composite soil sampling scheme

Chemical analysis. The determinations of concentrations of Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr were performed at the ACME Analytical Laboratories (Vancouver) in Canada. Samples of weighing 15 g were digested in 90 mL of aqua regia and held for 1 hour in a water bath (95◦C). After cooling, the solution was made up to a final volume of 300 mL with 5% HCl. The sample weight to volume ratio was 1 g per 20 mL. Analyses were made by the ICP-AES and ICP-MS methods (Reimann et al., 2010, Reimann et al., eds., 2014). This sample digestion method is used in soil studies conducted by geological surveys for the purpose of developing the geochemical atlases covering the whole continent or its substantial part (Reimann et al., 1998, 2003; Salminen, ed. 2005; De Vos, Tarvainen, eds., 2006; Evaluation..., 2009).

Soil pH (in 0.01 M $CaCl_2$) and TOC content (high-temperature combustion method with IR detection) were determined at the laboratory of the Geological Survey of Norway, and the CEC value at the laboratory of the Geological Survey of Slovakia.

The ranges of concentrations of the analysed elements and parameters in the soils of Poland, their average concentrations (expressed as medians) and the determination limits are summarized in Table 1, and the comparison of their statistical parameters in soils of arable fields and grazing land are shown in Figures 4–25.

Quality control. Correctness of the chemical determinations was tested by analysing certified reference materials (Australian soil ORIS and American soil SONE-1) with certified concentrations of the elements, as well as by analysing laboratory's control samples, confirming correct instrument measurements, and control samples of the GEMAS project (prepared separately for arable field soils and grazing land soils). Control samples (every 20th sample) of the GEMAS project were tested at several laboratories of the European geological surveys prior to incorporating them into the analytic series (Evaluation..., 2009; Reimann et al., eds., 2014).

Development of geochemical maps. The development of geochemical maps was based on sets of sampling points with known geographical coordinates, and with assigned attributes of elemental concentrations. Geochemical maps of the concentrations of B, Be, Bi, Ce, Cs, Ga, Hf, In, La, Mo, Nb, Rb, Sb, Sc, Se, Sn, Te, Th, Tl, TOC, U, W, Y and Zr from the area of Poland are shown in Plates 1–25. Geochemical data are presented as combined point maps (which reflect the elements contents at sampling sites) with contour maps showing the spatial trends in their distribution. The concentration classes on contour maps were adjusted using the percentile values (> 90%), which allowed the identification of areas with anomalous elements concentrations.

The contour maps are the result of mathematical operations in the adopted interpretation model and do not always comply in details with the actual elements concentration at a given point. Precise visualization of the elements concentrations depends on the density of observations (sampling sites), and is a consequence of the map scale. The presented geochemical maps should be regarded only as a signal to take a more detailed study and to determine the actual extent of natural or anthropogenic anomalies. Detailed studies in an appropriate scale can show that the geochemical image is more complex.

RESULTS

B Boron

General information

Boron is a trace element in rocks of the Earth's crust, where its average concentration ranges from 10 to 17 mg/kg (Reimann et al., 1998; Kabata-Pendias, Mukherjee, 2007). It accumulates in acidic igneous rocks (10–30 mg/kg) and in marine sediments and bioliths (50–70 mg/kg in coal). The enrichment of boron in coals causes its concentration in the ashes of up to 9000 mg/kg (De Vos, Tarvainen, ed., 2006). During weathering processes, boron compounds are readily soluble, and the resulting ions are sorbed by clay minerals, micas and organic matter.

Anthropogenic sources

Boron is used as an additive in the production of hardened steel, glass, semiconductors, washing agents (borax), pharmaceutical preparations (boric acid) and cosmetics, and as a dye in signal rockets. Boron carbide (B_4C) is used as a material for making tools, and as a neutron absorber in the nuclear energy sector. High concentrations of boron are also found in sewage, municipal and mining landfills as well as dumping grounds of power and chemical plants (Tomaszewska, 2010).

Soils

The boron content in world’s soils varies mostly in the range of 10–100 mg/kg (Tab. 2). Light sandy soils exhibit low contents (5–20 mg/kg) as compared with clay and humic soils (30–80 mg/kg) that better absorb this element. The quoted contents are much greater than those from the GEMAS project data (Tab. 2), where only that portion of the element, which is very slightly soluble in aqua regia, was determined.

Boron is an essential microelement for plant life and affects many metabolic processes. It goes into the soil solution as a result of weathering of minerals (micas, tourmaline) in the form of boric acid (H_3BO_3). At the pH above 6.3, boric acid is dissociated and the resulting anion is combined with positively charged iron and aluminum oxides, clay minerals and organic matter. Boric acid is also absorbed from the soil solution by plant roots.

The boron content in most of Poland’s soils (90% of the samples) studied by the GEMAS project does not exceed 5 mg/kg (Plate 1). The soils of arable fields contain slightly less boron (median 2 mg/kg) than the soils of grazing land (median 2.4 mg/kg) (Fig. 4). In the southeast of the country, there are local enrichments (5–8 mg/kg) with a maximum of 10–11 mg/kg in the grazing land soils found in the valleys of the upper Wieprz, Bug and middle San rivers. Parent rocks of these soils are Holocene alluvial muds, peats and silts rich in organic matter (3–5.8% TOC) that can sorb boron which is sourced probably from Cretaceous carbonates and overlying Quaternary loess and tills occurring in this region.

Boron anomalies (up to 15 mg/kg) in soils of the lower Bug and Noteć river valleys (up to 22 mg/kg) are presumably of similar origin. In both these areas, the boron enrichment is associated with extremely high contents of total organic carbon (25% and 20%, respectively) sorbing many elements.

In the Płonia River valley and near Sępopol in the Masurian Lake District, boron anomalies occur in soils developed on Quaternary ice-dammed lake deposits.

Tabela 2
Table

Zawartość boru w glebach (mg/kg)
Boron content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		10–100			Kabata-Pendias, Mukherjee, 2007
Słowacja Slovakia	5189	<3–1622	61	t.	Čurlik, Šefčik, 1999
Litwa Lithuania	696	9–122	27,8	t.	Kadūnas et al., 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,5–49	2,5	a.r.	Reimann et al.,eds., 2014
Polska – projekt GEMAS Poland – GEMAS project	258	<1–22	2	a.r.	Obecna praca This study

n – liczba próbek; number of samples, a.r. – woda królewska; aqua regia, t.– zawartość całkowita; total content

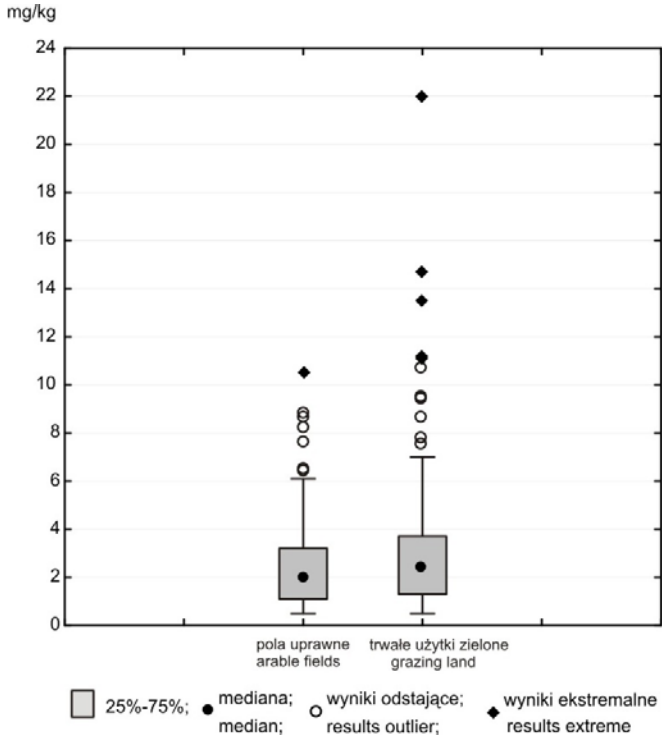

Fig. 4. Porównanie parametrów statystycznych zawartości boru w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of boron content in arable fields and grazing land soils

Be Beryllium

General information

Beryllium (along with strontium and barium) belongs to the group of alkali metals. It exhibits oxyphilic properties, and connections with the carbon circulation, which affects its distribution in terrestrial environments (Kabata-Pendias, Mukherjee, 2007). The beryllium concentration in igneous rocks of the Earth's crust is 1–3 mg/kg (De Vos, Tarvainen, eds. , 2006). Most of this element accumulate in acidic volcanic rocks and clay deposits (up to 6 mg/kg). Among the components of sedimentary rocks, increased beryllium content is typical of micas and clay minerals (especially montmorillonite). The characteristic feature is its accumulation in loess (up to 2 mg/kg). Because of the ease of beryllium sorption by organic matter, it can concentrate in lignites (up to 6.9 mg/kg) and coal – up to several hundred mg/kg (Veselý et al., 2002).

Anthropogenic sources

Beryllium is used in various industries – to harden light metal alloys, in the production of X-ray, fluorescent and neon tubes, radiation detectors, transistors, coil cores, lasers and microwave device components. Beryllium alloys of copper, nickel and aluminum are the materials for the construction of aircraft engines, for the manufacture of springs in precision mechanisms, electrical relays and switches. Beryllium-copper alloys are used in the manufacture of non-sparking tools necessary in the petrochemical industry and in the electronics industry for the manufacture of integrated circuits and electronic connectors. This metal is also used in the production of computers, highly chemical-resistant ceramic tubes, and crucibles for melting chemically active metals, such as chromium, zirconium and uranium.

Soils

Beryllium compounds are highly soluble in acidic environments, which often causes them to be washed out of the surface layer to accumulate in deeper parts of the soil profile. The average concentration of beryllium in various soils worldwide is in the range of 0.1–4.9 mg/kg (Tab. 3). In sandy soils of Poland, the average beryllium concentration is 0.33 mg/kg, and in loamy soils – 0.73 mg/kg (Kabata-Pendias, Mukherjee, 2007).

The soils of arable fields of Poland contain slightly less beryllium than the soils of grazing land (Fig. 5). The distribution of beryllium in the soils of Poland (Plate 2) is conspicuous by increased concentrations in the south and in some localities near the northern state border. Over most of the area of Poland, the beryllium concentration does not exceed 0.5 mg/kg. There are also concentrations above 0.7 mg/kg in soils of some regions of the Sudetes and Cieszyn Silesia, near Kraków, in the Warta River upstream catchment area, in the Wisłok and San river valleys, in the Żuławy region and near Sępopol in the Masurian Lakeland.

In the Sudetes (Biała Lądecka River valley), soil's parent rocks are represented by Proterozoic and Cambrian crystalline schists, gneisses and amphibolites (Marks et al., 2006), which can show naturally elevated beryllium concentrations. In the region of Stara Kamienica, slight beryllium enrichment in soils (up to 0.8 mg/kg) is probably due to their development from Cambrian-Ordovician granitogneisses which can contain beryllium accumulations locally up to 15 mg/kg (Lis, Sylwestrzak, 1986; Veselý et al., 2002).

Local increase in the beryllium content in the Godziszów region, the Carpathians, results presumably from the chemical composition of the Carpathian Flysch rocks. The most likely sources of beryllium (and molybdenum, vanadium and zinc) are siliceous-clayey-marly rocks of the Menilite Beds, rich in bitumen and pyroclastic material (Gucwa, Wieser, 1980).

Beryllium enrichment in soils in the vicinity of Kraków, between the Warta and Pilica river valleys, can be attributed to industrial emissions from metallurgical plants. The maximum beryllium concentration (1.3 mg/kg) recorded in grazing land soils of the Vistula River valley may be the result of emissions of industrial dust from the Sendzimir Steelworks, as may be the case with the anomaly observed in the region affected for above a hundred-years by dust emissions from the Zawiercie Steelworks.

Beryllium concentrations exceeding the value of geochemical background (0.7–0.9 mg/kg), found in the soils of the Wisłok and San river valleys and in the Żuławy region, result presumably from the fact of its binding by organic matter and clay minerals of soils developed on river muds, and the emission sources can be considerably distant.

In the Sępopol region, Masurian Lakeland, slight beryllium enrichment in soils (up to 0.7 mg/kg) can be explained by its sorption in organic matter of soils that developed on Quaternary ice-dammed lake deposits (Kondracki, 2000).

Tabela 3
Table

Zawartość berylu w glebach (mg/kg)
Beryllium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,1–4,9			Kabata-Pendias, Mukherjee, 2007
Europa – BSS projekt Europe – BSS project	743	<0,01–0,19	0,02	ammonium acetate	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	747	<0,5–3,9	1,2	t.	Reimann et al., 2003
Słowacja Slovakia	5189	<0,2–7,7	1,3	t.	Čurlik, Šefčik, 1999
Europa – projekt GEMAS Europe – GEMAS project	4132	<0,05–11	0,50	a.r.	Reimann et al., eds., 2014
Polska – projekt GEMAS Poland – GEMAS project	258	<0,1–1,3	0,2	a.r.	Obecna praca This study

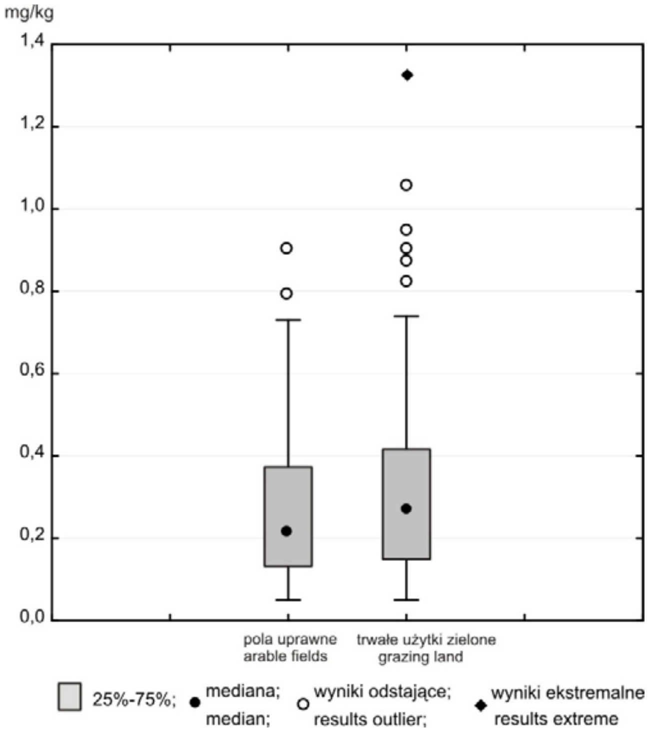

Fig. 5. Porównanie parametrów statystycznych zawartości berylu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of beryllium content in arable fields and grazing land soils

Bi Bismuth

General information

Bismuth is dispersed in rocks of the Earth's crust. Estimates of its average concentration in the lithosphere are based on a small number of very disparate data, and range from 0.002 to 0.3 mg/kg (Polański, Smulikowski, 1969; Paulo, Strzelska-Smakowska, 2001; Reimann et al., 2003; Kabata-Pendias, Mukherjee, 2007). The bismuth average concentration in acid rocks is estimated at 0.14–0.66 mg/kg and decreases to 0.014 mg/kg in ultramafic rocks (Fedorczuk, Mincer, 1990; Paulo, Strzelska-Smakowska, 2001). Particularly high bismuth enrichment is observed in rhyolites (0.9 mg/kg) and some types of granites (0.27 mg/kg) (Lueth, 1999).

In near-surface environments, bismuth is poorly mobile. It is a constituent of insoluble compounds retained by iron and manganese hydroxides and by organic matter. Among sedimentary rocks, the most abundant in bismuth are clayey deposits (0.05–0.50 mg/kg), and the smallest amounts are found in carbonates (0.1–0.2 mg/kg). Bismuth enrichments were reported from some types of coal – up to 5 mg/kg, bauxites – 2.15 mg/kg, and copper-bearing shales and apatites – up to 100 mg/kg (Fedorczuk, Mincer, 1990; Kabata-Pendias, Pendias, 1999).

Bismuth occurs as a native metal and in about 120 minerals (Paulo, Strzelska-Smakowska, 2001). It forms its major mineral – bismuthine (Bi_2S_3), and occurs in tellurides, sulphides, selenides and sulphosalts found in polymetallic Mo-Sn-W-Cu-Pb-Ag-Au deposits. The bismuth content in galena grains can be up to 8%, while in copper concentrates up to 0.07% (Paulo, Strzelska-Smakowska, 2001). In hypergenic conditions, carbonates are formed – bismuthite $(BiO)_2CO_3$ and bismuth ocher (Bi_2O_3).

Anthropogenic sources

The most common source of contamination by bismuth is metallurgy of lead, copper, silver and gold (Reimann et al., 1998). Commercially bismuth is extracted as a byproduct of copper and lead metallurgy (Paulo, Strzelska-Smakowska, 2001). It also originates from waste and sewage of factories producing fusible alloys, plastics, pharmaceuticals, batteries, electric fuses, electronic devices, dental materials, magnets and pigments for cosmetics, and of those using it as a catalyst in polymerization processes (Leonard et al., 2002; De Vos, Tarvainen, eds., 2006; Kabata-Pendias, Mukherjee, 2007; Yang, Sun, 2007). Bismuth, as a non-toxic element, replaces lead in the equipment used in the food processing industry.

Soils

The concentration of this element in worldwide soils is estimated at 0.03–13 mg/kg (Tab. 4), but most often it ranges from 0.04 to 1.5 mg/kg. Near copper smelters and metal mining areas, the value can attain several hundred mg/kg (Kabata-Pendias, Mukherjee, 2007). Soil contamination by bismuth is sometimes found in areas of intense fertilization, especially with sewage sludge and wastewater rich in phosphates, and with mineral fertilizers (Senesi et al., 1999). Bismuth enters into the soil together with dust from areas of mining and smelting of metal ores, from combustion of coal and wastes, and from chemical plants.

The geochemical background of bismuth in the soils of Europe does not exceed 0.5 mg/kg (De Vos, Tarvainen, eds., 2006). Agricultural soils of the Baltic countries contain an average of 0.069 mg/kg of bismuth: from 0.057 mg/kg in Belarus to 0.111 mg/kg in Sweden (Reimann et al., 2003). The soils of Saxony contain an average of 0.10 mg/kg of bismuth, and there are also anomalies (up to 24 mg/kg) in the Ore Mountains (Rank et al., 1999). In the soils of Slovakia, the geochemical background of bismuth is 0.3 mg/kg, and anomalies (up to 37.2 mg/kg) are observed in the Spiš ore mining area and in areas of volcanic rocks in the central part of the country (Čurlik, Šefĉik, 1999). Comparison of the spatial distribution of this element in A and C horizons of Slovakian soils indicates that its main anthropogenic sources are metal smelters and coal-fired heating plants.

Results of the GEMAS project from Poland allow to conclude that the geochemical background of bismuth clearly differentiates into two distinct geochemical provinces of the country, as determined from previous studies (Pasieczna, 2011). In the northern province (Polish Lowlands), the concentration of this element is below 0.20 mg/kg (Plate 3). In the southern province (the Sudetes and the Western Carpathians), the bismuth concentration is mostly in the range of 0.20–0.25 mg/kg, and anomalous concentrations (>0.25 mg/kg) were recorded in several locations near the southern border of the country, where they are associated with mineralization in soil's parent rocks. The median value of bismuth is 0.07 mg/kg in soils of arable fields and 0.09 mg/kg in grazing land soils (Fig. 6).

In the Sudetes, elevated bismuth concentrations (in soils of the Karkonosze-Izera Block) can be associated with mineralization in quartzite-mica-chlorite schists and granites. The enrichment (up to 0.34 mg/kg of bismuth) is most distinct near Stara Kamienica, where there is arsenic, copper, iron, molybdenum and tin mineralization (Jaskólski, 1960; Lis, Sylwestrzak, 1986; Madziarz, Sztuk, 2006). Ore veins can also be a source of bismuth in the Kaczawskie Mountains (Paulo, 1970) and Rudawy Janowickie Mountains (Parafiniuk, Domańska, 2002).

Local bismuth anomalies in the Carpathians can be explained by the chemical composition of sedimentary rocks of the Carpathian Flysch. The most likely source of bismuth (and molybdenum, vanadium and zinc) are siliceous-clayey-marly layers of the Menilite Beds rich in bitumen and pyroclastic material (Gucwa, Wieser, 1980). The maximum bismuth concentration (0.45 mg/kg) was recorded in the Białka region and near Skoczów (0.37 mg/kg) in soils developed on the Podhale Flysch (Marks et al., 2006).

Tabela 4
Table

Zawartość bizmutu w glebach (mg/kg)
Bismuth content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,03–13			Kabata-Pendias, Mukherjee, 2007
Europa – BSS projekt Europe – BSS project	744	0,005–1,210	0,069	a.r.	Reimann et al., 2003
Słowacja Slovakia	5189	<0,1–37,2	0,3	t.	Čurlik, Šefčik, 1999
Europa – FOREGS projekt Europe – FOREGS project	840	<0,5–9,57	<0,5	t.	Salminen, ed., 2005
Europa – GEMAS projekt Europe – GEMAS project	4132	<3–17	13	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,005–18	0,17	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,02–0,45	0,08	a.r.	Obecna praca This study

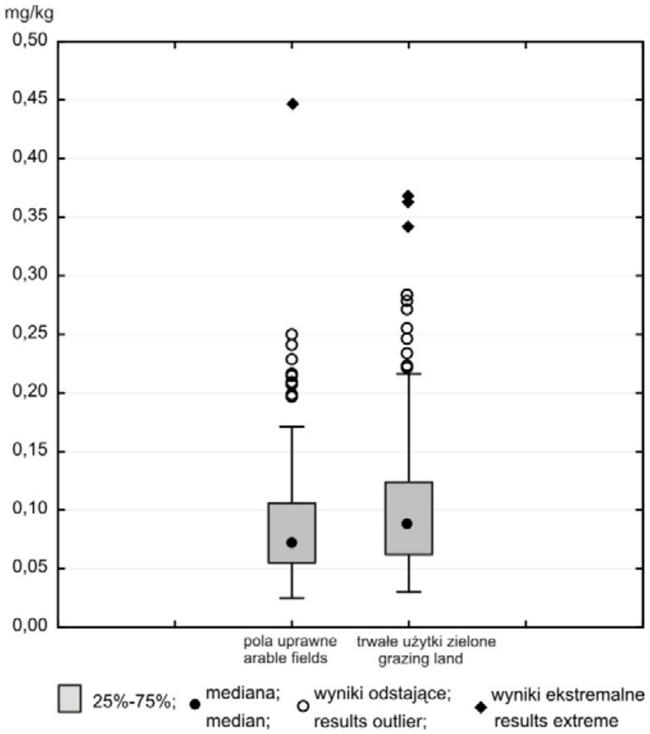

Fig. 6. Porównanie parametrów statystycznych zawartości bizmutu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of bismuth content in arable fields and grazing land soils

Ce Cerium

General information

Cerium is an element distinguishing by the highest frequency among the rare earth elements (De Vos, Tarvainen, ed., 2006), and by the ability to form a number of minerals including monazite, cerite, cerianite, xenotime, bastnaside and others (Polański, Smulikowski, 1969). Acidic igneous rocks contain more cerium (90 mg/kg in granites) than mafic rocks (3 mg/kg). Its concentration in sedimentary rocks varies from 3 to 90 mg/kg, and the least abundant in cerium are carbonates (Kabata-Pendias, Mukherjee, 2007). In recent lake sediments of Poland, the average cerium concentration is 16–21 mg/kg (Małecka, 2007).

Anthropogenic sources

Cerium is used in carbon electrodes of gas-lighting arc lamps, and serves as a hardening additive in aluminum and stainless steel production. In the form of iron alloys, it is used for the production of sparkling stone lighters. Cerium oxide is a component of catalysts used for the purification of vehicle exhaust gases, as an additive to polishing materials. Its other compounds are used as dye porcelain (Cerium ..., 2013). Due to the increasingly widespread use of cerium in household appliances (TVs, lamps, glass), its anthropogenic dispersal in the environment also increases (mainly from landfill leachates, effluents and emissions of combustion engines).

Soils

The cerium concentration in worldwide soils is 15.8–97.4 mg/kg; with an average of 48.7 (De Vos, Tarvainen, ed., 2006). The average total cerium concentration in European soils, determined by the study within the framework of FOREGS project, is almost identical (48.2 mg/kg) (Tab. 5). The same study on Poland's soils yielded an estimated value of the cerium geochemical background at 19.65 mg/kg (Kwecko, 2012). The analysis also shows that sandy soils contain less cerium compared with loamy ones and those developed on carbonates. It confirmed the results of previous studies on cerium concentration in clayey soils and loess, amounting to 20–21 mg/kg (Kabata-Pendias, Pendias, 1999).

The cerium concentration in arable and grazing land soils, determined within the framework of GEMAS project, varies from 2.2 to 44.9 mg/kg (median 15.2 mg/kg). Values of the concentration range and median in arable field and grazing land soils are similar (Tab. 1, Fig. 7). Over almost the whole area of Poland, the cerium concentration in soils does not exceed 30.3 mg/kg (Plate 4).

Cerium anomalies in soils due to enrichment of this element in their parent rocks were observed in the southern geochemical province of Poland. A local anomaly (with a maximum cerium concentration of 44.9 mg/kg) is observed in grazing land soils developed on Holocene alluvial muds of a small stream (between the valleys of the Wisłoka and Wisłok rivers) and in soils developed on flysch deposits (SE of Rzeszów).

Near Godziszów, Cieszyn Silesia, elevated cerium concentrations (up to 40.1 mg/kg) are found in arable field soils developed on alluvial muds of a stream eroding carbonate-shale deposits of the Carpathian Flysch, which is probably the source of cerium. Sorption of cerium in soils is facilitated by the abundance of the clay fraction in the alluvial muds. Its significant role in the accumulation of cerium is indicated by the positive correlation of this element and the <0.002 mm fraction in the Vistula valley soils (Chojnicki, 2000).

Soils of the Sudetes, Opawskie Mountains and upper Odra River valley are conspicuous by both a high value of the cerium geochemical background (30–34 mg/kg) and the presence of anomalies in the western margin of the Golden Mountains, in the Prudnik Stream valley east of Głuchołazy, and near the village of Polska Cerkiew. In the former two localities, outcrops of Carboniferous granites and granodiorites with well-known occurrences of monacite and xenotime in pegmatite veins are supposed to be the cerium sources (Lis, Sylwestrzak, 1986). In other Sudetic regions, enrichment of cerium (and other REE) is associated with tin-bearing mineralization that also caused mobilization of REE and enrichment of these elements in micas, chlorites and garnets (Mayer et al., 1997).

Soils of the Odra River valley are developed on loess naturally enriched in REE. A similar origin is interpreted for the cerium enrichment in soils from the area located south of Kraśnik, which are also developed on loess.

Tabela 5
Table

Zawartość ceru w glebach (mg/kg)
Cerium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		15,8–97,4	48,7	t.	De Vos, Tarvainen, eds., 2006
Europa – FOREGS projekt Europe – FOREGS project	843	2,45–267	48,2	t.	Salminen, ed., 2005
Europa – BSS projekt Europe – BSS project	747	3,7–167	37	t. (HF)	Reimann et al., 2003
Słowacja Slovakia	5189	<5–335	65	t.	Čurlik, Šefčik, 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<20–317	57	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	1,6–272	28	a.r	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	2,2–44,9	15,2	a.r.	Obecna praca This study

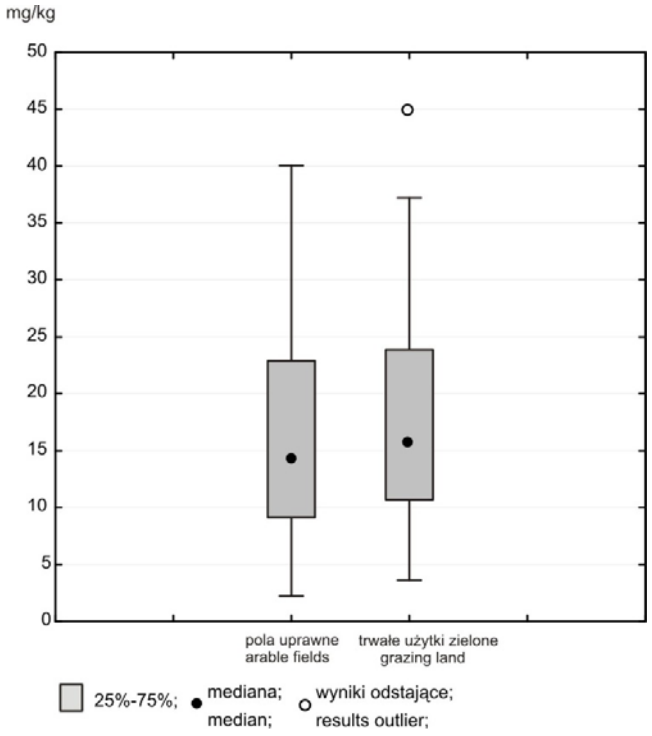

Fig. 7. Porównanie parametrów statystycznych zawartości ceru w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of cerium content in arable fields and grazing land soils

Cs Cesium

General information

The cesium concentration in the Earth's crust is 1–6 mg/kg (Reimann et al., 1998; Kabata-Pendias, Szteke, 2012). Cesium ions have limited opportunities to enter into the structure of rock-forming minerals due to their large size. However, some micas and potassium feldspars have the ability to accumulate this element. The largest quantities of cesium (up to a few percent) accumulate in the minerals that formed in the pegmatite stage of magma crystallization – in lepidolites and beryllium. In acidic igneous rocks, the cesium concentration reaches 2–6 mg/kg, whereas in alkaline rocks – 0.1 mg/kg (De Vos, Tarvainen, eds., 2006). Cesium released during weathering processes is readily adsorbed by clay minerals in soils, mainly by illites. The ease with which cesium is incorporated into interchangeable positions in the structures of clay minerals results in its accumulation in shales (approx. 5 mg/kg). While in sandstones and carbonates, cesium accumulates in quantities not exceeding 1 mg/kg.

Anthropogenic sources

The industrial significance of cesium is small. It is used as a catalyst in organic synthesis, and in the production of photoelectric cells and infrared radiation sensors. Manufacture of these devices and their storage causes cesium to be disseminated in the environment, do does the combustion of coal that can contain up to 1.5 mg/kg of cesium. The toxic isotope ^{137}Cs is hazardous to the environment. It is released during nuclear reactions and from landfills of nuclear materials.

Soils

The average cesium concentration in European soils, determined during FOREGS investigations, is 3.71 mg/kg, ranging from <0.5 to 69.1 mg/kg, whereas that determined during GEMAS investigations vary between 0.03 and 56 mg/kg (Tab. 6).

In Polish soils, the cesium concentration ranges from 0.11 to 1.86 mg/kg (Fig. 8). For most of the samples (90%), the cesium geochemical background value does not exceed 1 mg/kg (Plate 5).

In the Gdańsk Coast and the Żuławy region, some of the soils contain up to 1.60 mg/kg of cesium.

In the Sudetes and the Western Carpathians, the cesium geochemical background is slightly greater (1–1.24 mg/kg). Anomalous concentrations (>1.32 mg/kg) in the Sudetes were found in soils developed on Carboniferous conglomerates, mudstones and claystones near

Kamienna Góra and on granites and granodiorites in the Nysa Kłodzka River valley. In the Western Carpathians, the cesium geochemical background varies from 1 to 1.32 mg/kg. Local anomalies with the cesium concentrations of 1.41–1.86 mg/kg are found in the Dunajec and Wisłoka river valleys.

Tabela 6
Table

Zawartość cezu w glebach (mg/kg)
Cesium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		<1–30			Kabata-Pendias, Mukherjee, 2007
Europa – FOREGS projekt Europe – FOREGS project	840	<0,5–69,1	3,71	t.	De Vos, Tarvainen, eds., 2006
Europa – BSS projekt Europe – BSS project	747	<0,1–20	1,5	t. (HF)	Reimann et al., 2003
Słowacja Slovakia	5094	<1–100	5	t.	Čurlik, Šefčik, 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<3–56	5	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	0,03–43	1	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,02–1,86	0,42	a.r.	Obecna praca This study

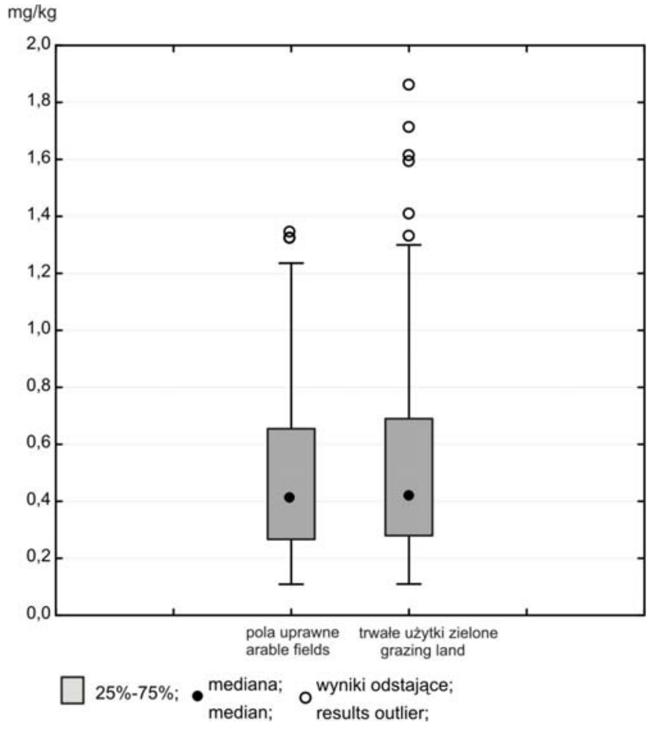

Fig. 8. Porównanie parametrów statystycznych zawartości cezu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of cesium content in arable fields and grazing land soils

Ga Gallium

General information

In the Earth's crust, gallium is a typical dispersed element with the concentration ranging from 14 to 19 mg/kg (Wedepohl, 1995; De Vos, Tarvainen, eds., 2006). Crystallochemically and geochemically, gallium is related to aluminum and iron, which results from a similar size of ionic radii of Al^{3+}, Fe^{3+} and Ga^{3+} (Polański, Smulikowski, 1969). In igneous rocks, gallium is found in plagioclases, micas, amphiboles and magnetite. Its concentrations in granites and basalts are similar (about 17 mg/kg). In hydrothermal environments, it exhibits sulfophilic properties and occurs in association with zinc, accumulating in sphalerite and wurtzite which may contain up to 1000 mg/kg of gallium. In weathering processes, gallium accompanies aluminum and accumulates in clay minerals of clays and shales. Particularly rich in gallium are bauxites (20–100 mg/kg) and some types of coal (100–500 mg/kg).

Anthropogenic sources

Surface environments of the Earth may be enriched with gallium in areas remaining under the influence of emissions from aluminum and zinc smelters and those located close to power and heating plants. Particularly abundant in gallium are mining waters from zinc sulphide mines (Shiller, Frilot, 1996), leachates from landfills, and waste combustion residues (Kabata-Pendias, Mukherjee, 2007). Commercially, gallium is extracted from bauxite. It is used in the production of high-temperature thermometers, elements of nuclear weapons, low-melting alloys and solders. Gallium arsenide, phosphide and fluoride are used as semiconductors.

Soils

In soils of the world, the gallium concentration ranges from <1 to 70 mg/kg and is closely related to the contents of clay fraction, ferric and manganese hydroxides, and organic matter (Kabata-Pendias, Pendias, 1999). The FOREGS investigations determined the gallium geochemical background in European soils as 13.5 mg/kg. The average gallium concentration in Slovakian soils is 12 mg/kg, and in Lithuania – 6.3 mg/kg (Tab. 7).

The presented analysis of soils in Poland shows that the gallium concentration varies between 0.3 and 5.7 mg/kg (Plate 6) and the element tends to accumulate in grazing land soils rather than in arable fields (Fig. 9), which confirms the previous studies and the thesis of its accumulation in soil’s organic fraction (Połedniok, 2008).

The gallium geochemical background is highly variable in Poland. Over most of the country's area, the soils contain less than 3.2 mg/kg of this element. A regional increase in the gallium concentration (4.2–5.7 mg/kg) is observed in the Sudetes where the greatest values were found in soils developed on Carboniferous conglomerates, greywackes, mudstones and claystones (upper Bóbr River valley and north of Kamienna Góra), suggesting plagioclases and micas of these deposits as a source of gallium. A gallium anomaly detected in the upper Nysa Kłodzka River basin undoubtedly originates from granodiorites and granites composing this area.

In the Carpathians, local anomalies exceed 4–5 mg/kg of gallium. These (in the Raba River valley east of Rabka, and in the Kamienica River valley east of Nowy Sącz) could develop due to the chemical composition of parent rocks – Paleogene clayey deposits of the Carpathian Flysch. These are variously coloured clay shales, locally sideritic (Paul, 1991, 1993), and the enrichment of gallium can be associated with its elevated content in iron minerals.

Tabela 7
Table

Zawartość galu w glebach (mg/kg)
Gallium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		<1–70			Kabata-Pendias, Mukherjee, 2007
Europa – FOREGS projekt Europe – FOREGS project	843	0,54–34,3	13,5	t.	De Vos, Tarvainen, eds., 2006
Europa – BSS projekt Europe – BSS project	748	<3–25	10	t.	Reimann et al., 2003
Słowacja Slovakia	5189	<2–43	12	t.	Čurlik, Šefčik, 1999
Litwa Lithuania	696	1,5–33,7	6,3	t.	Kadūnas et al., 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<2–38	12	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	0,14–23	3,4	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,31–5,7	1,3	a.r.	Obecna praca This study

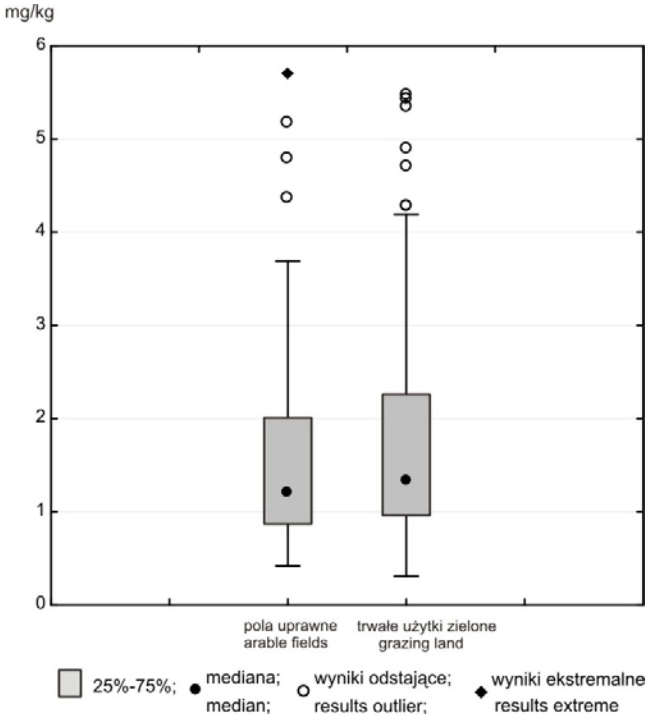

Fig. 9. Porównanie parametrów statystycznych zawartości galu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of gallium content in arable fields and grazing land soils

Hf Hafnium

General information

The hafnium concentration in rocks of the Earth's crust is estimated at 5.8 mg/kg (Wedepohl, 1995). Hafnium shows associations with zirconium, having similar properties and occurring in its minerals, in particular in zircon and baddeleyite. In some zircons from Norway, the hafnium content reaches several percent (De Vos, Tarvainen, eds., 2006). Among igneous rocks, alkaline rock intrusions are most abundant in hafnium (>100 mg/kg). Sedimentary rocks contain 0.3–6 mg/kg of hafnium (Kabata-Pendias, Mukherjee, 2007), and the highest concentrations are found in loess, which is associated with the presence of weathering-resistant zircon in this sediment (Buggle et al., 2008).

Anthropogenic sources

The main anthropogenic source of hafnium is the discharge of industrial wastewater from the sectors including production of light bulbs, fluorescent lamps, parts of nuclear reactors and metallic alloys.

Soils

In soils from different regions of the world, the hafnium concentration varies from 0.0X to 20.8 mg/kg (Tab. 8). Similar values of the medians of hafnium from the topsoil in Europe (5.55 mg/kg) and from soil horizon C (5.30 mg/kg) indicate that its origin is associated primarily with the composition of parent rocks (Salminen, ed., 2005). The hafnium-richest soils developed on pre-Quaternary crystalline rocks and on Quaternary loess covers.

In the majority of Polish soils analysed in this study, the hafnium concentration was <0.07 mg/kg (Plate 7, Fig.10). A slightly higher concentration of this element (0.07–0.12 mg/kg) were measured in north-eastern Poland (Kętrzyn and Giżycko region) and near Nowogard in soils developed on glacial deposits of the youngest glaciation (glacial tills, sands and gravels), and on Holocene alluvial muds of the Vistula Delta.

Hafnium enrichments above 0.12 mg/kg in southern Poland are associated with two types of sources. In soils of the southern Lublin region, hafnium originates probably from loess rich in weathering-resistant minerals, mainly zircon. The maximum hafnium concentration (0.18 mg/kg) in alluvial soils of the Vistula River valley east of Kraków may be due to industrial sewage discharges from the ArcelorMittal steelworks. Sewage discharges from metal processing plants may also be a reason for its increased content in soils of the Pilica and Radomka river valleys.

Local enrichment of hafnium (up to 0.17 mg/kg) is also present in soils developed on alluvial sediments of the Bug River (downstream of the confluence with the Nurzec River).

Tabela 8
Table

Zawartość hafnu w glebach (mg/kg)
Hafnium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,0X–20,8			Kabata-Pendias, Mukherjee, 2007
Europa – FOREGS projekt Europe – FOREGS project	843	<0,2–21,2	5,55	a.r.	Salminen, ed., 2005
Europa – GEMAS projekt Europe – GEMAS project	4132	<5–28	8	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,01–6,73	0,05	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,02–0,18	0,02	a.r.	Obecna praca This study

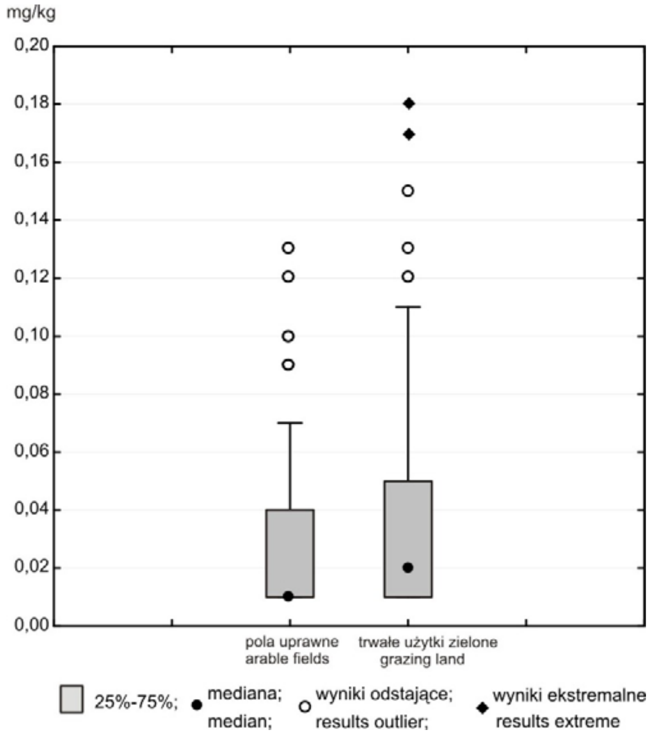

Fig. 10. Porównanie parametrów statystycznych zawartości hafnu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of hafnium content in arable fields and grazing land soils

In Indium

General information

The indium concentration in rocks of the Earth's crust is 0.11–0.25 mg/kg, with a trend of slightly greater contents in granites compared with mafic rocks, and in clay rocks compared with sandy ones (Kabat-Pendias, Mukherjee, 2007). Due to its chalcophylic nature, indium easily accumulates in the amount of 1–2% not only in sphalerite, galena, chalcopyrite and sulphides of other metals, but also in cassiterite. However, it is very rare in rock-forming minerals. This element has the ability to concentrate in coal, bituminous shales and crude oil. In hypergenic conditions, indium occurs mainly as a trivalent ion easily precipitating with ferric and manganese hydroxides.

Anthropogenic sources

The main pollution outbreaks of indium are lead and zinc ore processing plants, emissions from the combustion of coal and oil, and wastewater of many industries. In the 20th century, indium was used mainly in aircraft engine components. In the first decade of the 21th century, its production began to rise due to the application in the electronics industry, particularly in the manufacture of liquid crystal displays, solar panels and optical waveguides. Indium is used as an alloying additive increasing steel hardness and corrosion resistance, and as a component of anticorrosive metal coatings. Some indium alloys have superconducting properties.

Soils

In soils, indium is bound by organic matter and ferric oxides. Its concentration in worldwide soils is in the range of 0.01–0.50 mg/kg (Tab. 9). In areas contaminated by mining of zinc, lead and tin ores, its concentration may reach 1.92 mg/kg (Asami et al., 1990).

Previous studies on European soils determined the average indium concentration (expressed as a median value) to 0.05 mg/kg. The highest concentrations of this element were found, inter alia, in areas of tin mineralization in Portugal and Spain, in the Massif Central in France and in the Ore Mountains (Erzgebirge) on the Czech-German border (Salminen, ed., 2005; De Vos, Tarvainen, eds., 2006). According to the GEMAS project data, the median of indium concentration in arable fields soils of Europe is much lower (0.018 mg/kg).

Soils of Poland contain little indium; the median of its concentration is less than the detection limit (0.003 mg/kg), hence the difficulty in determining the geochemical background in most of the country. Only in the Sudetes, Cieszyn Silesia and the Western Carpathians, there are elevated indium concentrations up to 0.02–0.03 mg/kg, and locally to 0.05 mg/kg (Plate 8). Due to the very low variability in the indium content and the impossibility of calculating the median (the values are below the detection limit), comparison of its variability in arable field and grazing land soils is not presented.

Tabela 9
Table

Zawartość indu w glebach (mg/kg)
Indium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,01–0,50			Kabata-Pendias, Mukherjee, 2007
Europa – FOREGS projekt Europe – FOREGS project	840	<0,01–0,41	0,05	a.r.	Salminen, ed., 2005
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,003–0,35	0,018	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,003–0,05	<0,003	a.r.	Obecna praca This study

La Lanthanum

General information

Lanthanum, as well as cerium and other elements of the cerium group, accumulates in rock-forming minerals (biotite, apatite, pyroxene and feldspar), and in less common minerals such as monazite, cerite and bastnasite. Acidic igneous rocks are much richer in lanthanum (45–55 mg/kg) compared with mafic rocks (6–15 mg/kg) (Reimann et al., 1998; Sadeghi et al., 2013). Among sedimentary rocks, the most abundant in lanthanum are claystones and shales (50 mg/kg), poorer is loess (35 mg/kg), and its smallest concentration is found in sandstones (20 mg/kg). In carbonates, the lanthanum content results from the presence of monazite, zirconium and other clastic admixtures (De Vos, Tarvainen, eds., 2006). Under hypergenic conditions, lanthanum shows very low mobility due to the sorption by clay minerals, metal hydroxides and organic matter.

Anthropogenic sources

Lanthanum is introduced into the environment in the process of extraction and processing of rocks containing its minerals. This element and its compounds are used in many modern technologies – in metallurgy, production of automotive catalytic converters, hybrid batteries, many household appliances, optical glass, lamps, polishing powders, dyes and fertilizers (Całus-Moszko, Białecka, 2012; Podbiera-Matysik et al., 2012).

Soils

Lanthanum content in soils is related to its content in parent rocks. Studies of soils conducted across Europe revealed from 1.10 to 143 mg/kg of lanthanum (Salminen, ed., 2005). The average lanthanum concentration in different types of Europe's soils was estimated at 26.1 mg/kg (Kabata-Pendias, Mukherjee, 2007),. According to the GEMAS project, the lanthanum concentration variability is in the range of 1–269 mg/kg (Tab. 10). Soils of Slovakia contain an average of 38 mg/kg of lanthanum (Čurlik Šefčík, 1999). Previous studies from Poland determined its concentration at 11.9 mg/kg (Dudka, 1992).

The results of analysis of the lanthanum concentration in Polish soils, performed in this study, vary from 1.3 to 20.7 mg/kg, and the spatial distribution is similar to the distribution of cerium. The ranges of concentration and the median values in soils of arable fields and grazing land soils are similar (Tab. 1, Fig. 11).

In most the soils, the lanthanum concentration is below 14.7 mg/kg (Plate 9). Elevated concentrations up to 14.7–16.9 mg/kg are found in several locations: in peat soils developed on ice-dammed lake deposits near Sępopol, Masurian Lake District, in soils developed on loess south of Kraśnik, and in soils developed on flysch deposits southeast of Rzeszów.

Greater values of the geochemical background are observed in southern Poland. In the Sudetes and Opawskie Mountains, they are in excess of 14.7 mg/kg, and there are also anomalies exceeding 17.2 mg/kg at some localities. Elevated concentrations are found in areas of cerium anomalies, where they probably have a similar origin being related to both pre-Quaternary mineralization and loess occurrences. Areas of increased lanthanum concentration (49–58 mg/kg) in the Sudetes are associated with occurrences of tin-bearing mica schists of the Stara Kamienica belt, mineralized during the tin and sulphide stage (Mayer et al., 1997).

Tabela 10
Table

Zawartość lantanu w glebach (mg/kg)
Lanthanum content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data			35	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	748	<20–193	33	t.	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	843	1,10–143	23,5	t.	Salminen, ed., 2005
Słowacja Slovakia	5189	4–220	38	t.	Čurlik, Šefčik, 1999
Litwa Lithuania	696	0,3–59,7	13,4	t.	Kadūnas et al., 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<20–269	23	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	1–230	14	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	1,3–20,7	7,5	a.r.	Obecna praca This study

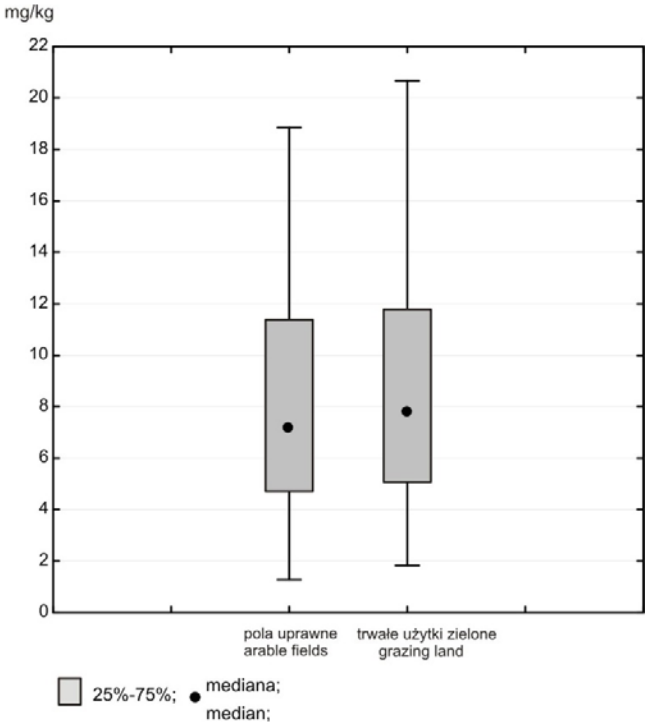

Fig. 11. Porównanie parametrów statystycznych zawartości lantanu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of lanthanum content in arable fields and grazing land soils

Mo Molybdenum

General information

In the lithosphere, molybdenum is associated mainly with acidic magmatic rocks and clayey deposits. It shows different geochemical trends, concentrating in both sulphide parageneses and oxides. It usually occurs in the form of molybdenite (MoS_2), which is dispersed in granites, but may also accompany tin ores (Kabata-Pendias, Pendias, 1999). Zones of molybdenite oxidation are areas of powellite ($CaMoO_4$) occurrence. Wulfenite ($PbMoO_4$) is found in areas of lead ore oxidation, in paragenesis with galena and cerussite. The average molybdenum concentration in igneous rocks is determined at 0.3–2 mg/kg, and in clayey sedimentary rocks – 3 mg/kg (Kabata-Pendias, Pendias, 1999, Reimann et al., 1998). High molybdenum concentrations are present in copper-bearing shales, bituminous shales (up to 200 mg/kg) and biolites (up to 2%) (Enzmann, 1972; Migaszewski, Gałuszka, 2003).

Anthropogenic sources

Molybdenum is a component of steel alloys, increasing their hardness and strength. As an additive in acid-resistant steel, it improves its resistance to corrosion. Molybdenum wires are used in light bulbs, electronic lamps and heating elements of electric furnaces. Molybdenum compounds are applied as catalysts in the petroleum industry, in the manufacture of paints, inks and plastics, and as additives for high-temperature-resistant lubricants.

To the natural environment, molybdenum can be introduced too with the emissions from mining and metallurgy plants, coal burning and sewage discharge.

Soils

In soils, molybdenum readily forms complex anionic compounds, mobile under neutral and alkaline pH. In acidic environments, it is bound by aluminum, iron and manganese hydroxides, and by organic matter and clay minerals, thereby limiting its availability to plants. Molybdenum is a microelement essential for the proper development of plants. Its deficiency results in the appearance of bright spots on leaves, bud dieback, and difficulty in maturing of leaf lamina. Particularly sensitive to the lack of molybdenum are plants of the Brassicaceae family.

The molybdenum concentration in worldwide soils is estimated at 0.1–7 mg/kg (Tab. 11). In the topsoil of Europe, its concentration is in the range of <0.1–17.2 mg/kg (De Vos, Tarvainen, eds., 2006). In general, the soils containing greater amounts of clay fraction (<0.02 mm) are enriched in this element.

In most of the territory of Poland, the molybdenum concentration in soils is <0.45 mg/kg (Plate 10, Fig. 12). A regional increase in the concentration (0.45–0.75 mg/kg) occurs in the Carpathians and their foreland. Locally in the Carpathians, there are also concentrations exceeding 0.75 mg/kg. The anomalies are related to the chemical composition of soil's parent rocks. Detailed geochemical studies of sedimentary rocks of the Carpathian Flysch (Gucwa, Wieser, 1980) indicate that the most likely sources of molybdenum are siliceous-clayey-marly Menilite Beds containing the greatest amount of bitumens among the Carpathian Flysch rocks, and rich in pyroclastic material and metals (manganese, vanadium, copper and zinc). The molybdenum concentration in these layers may be up to 144 mg/kg; with an average of 35 mg/kg, and the values of correlation coefficients Mo/C_{org} and Mo/bitumens indicate biogenic origin of this element and its accumulation due to the activity of calcareous nannoplankton. Molybdenum concentrations in the Menilite Beds (0.1–22.1, average 1.25 mg/kg) have also been proven by a regional geochemical survey of stream sediments in the Western Bieszczady Mountains and Beskid Niski Mountains (Bojakowska, Borucki, 1994).

Soil enrichment of molybdenum in the Wałbrzyskie Mountains (0.54–0.64 mg/kg) can be attributed, as in the Carpathian Mountains, to the abundance of organic matter in the bedrock represented mainly by Carboniferous deposits of the Culm facies (Cwojdziński, 2012; Sawicki, ed., 1965).

In the Polish Lowlands, local molybdenum anomalies are observed in soils developed on alluvial sediments of the Warta River, in the area of Poznań (up to 1.57 mg/kg), and of the Bug River near the village of Nur (up to 1.03 mg/kg). These enrichments are of anthropogenic origin and the accumulation of molybdenum and other metals in soils formed from floodplain muds is favoured by an abundance of organic matter and clay minerals composing the alluvial muds.

Downriver of Poznań, near Międzychód, the soil enrichment of molybdenum originates from the waters and sediments transported by the Warta River, even from distant areas. Industrial activities (especially drainage in the open-pit lignite mining area in the Konin and Bełchatów regions, and sewage discharges from metallurgical plants of the Kłobuck-Częstochowa region), runoff and sewage discharge from urban areas of Częstochowa and Poznań, as well as agricultural activities cause the water and sediment degradation in the Warta River catchment area. In this region, the soils contaminated with molybdenum abounds also in sulphur (1100 mg/kg) and uranium (1.9 mg/kg), which as well originate from anthropogenic outbreaks.

Near the village of Nur, soils enriched with molybdenum are characterised by an abundance of sulphur (4000 mg/kg), too. In addition, they also show a significant concentration of uranium (11.2 mg/kg) and other elements. In soils developed on alluvial sediments, the metals originate from the waters and sediments of the Bug River carrying harmful substances from sewage discharged in southern Poland and neighbouring countries.

In the north, near Strzelno, there are local enrichments of molybdenum (up to 1 mg/kg), as well as chromium, rubidium and thallium in the soils developed on glacial tills. The likely source of these metals can be weathering fragments of mineralized igneous rocks of Scandinavian origin, occurring in the tills (Bohdziewicz et al., 1980; Skompski, 2000).

Tabela 11
Table

Zawartość molibdenu w glebach (mg/kg)
Molybdenum content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,1–7	1,2	t.	Kabata-Pendias,Mukherjee, 2007; Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	747	<0,6–72	<0,6	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	840	<0,1–21,3	0,62	t.	Salminen, ed., 2005
Słowacja Slovakia	5189	<0,2–48,6	0,5	t.	Čurlik, Šefčik, 1999
Litwa Lithuania	696	0,24–3,13	0,68	t.	Kadūnas et al., 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<2–33	<2	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	0,03–14	0,42	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,05–1,71	0,19	a.r.	Obecna praca This study

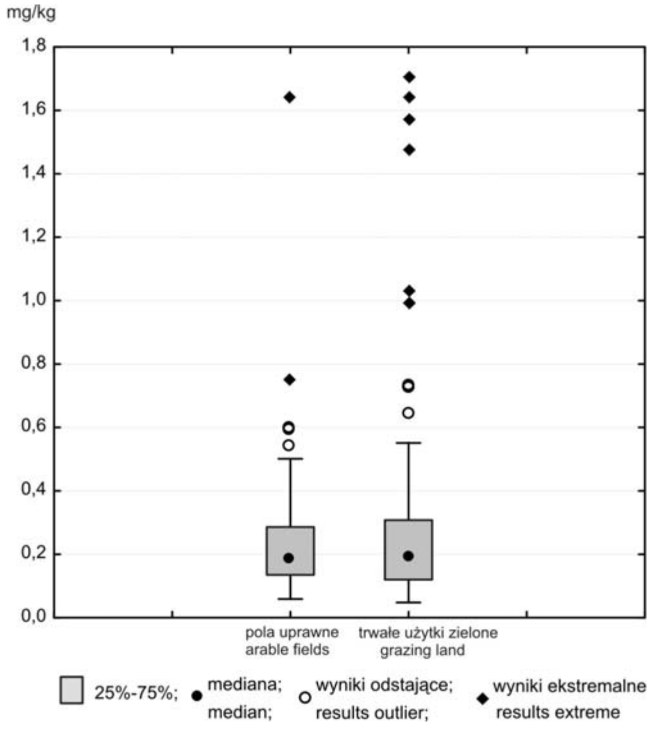

Fig. 12. Porównanie parametrów statystycznych zawartości molibdenu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of molybdenum content in arable fields and grazing land soils

Nb Niobium

General information

Niobium is among the dispersed elements in the lithosphere. Its concentration in acidic igneous rocks is 15–60 mg/kg (Kabata-Pendias, Mukherjee, 2007). It accompanies titanium and zirconium; hence niobium is found in ilmenite, titanite, zircon, pyroxenes and amphibolites. Granite pegmatites contain the most common niobium minerals – niobite, columbite, fergusonite, samarskite and other oxides. Among sedimentary rocks, clayey deposits are most abundant in niobium (up to 20 mg/kg).

Both the major niobium minerals and niobium-containing rock-forming minerals are resistant at the hypergenic stage, allowing them to accumulate in clastic deposits. Niobium is characterised by very low mobility in all surface environments, but it can be mobilized in the presence of complexing organic compounds (Kabata-Pendias, Pendias, 1999).

Anthropogenic sources

The most important use of niobium is the production of highly corrosion-resistant iron and nickel alloys, and tin and aluminum alloys of superconductive properties. Niobium alloys with tin or titanium are used in the manufacture of electronic devices, lasers and implants, as well as in the glass industry. Niobium carbide is used as an abrasive.

Soils

The average niobium concentration in different soils of the world was estimated at 12 mg/kg (Tab. 12), and the figures for various regions range from <4 to 8 mg/kg (Kabata-Pendias, Mukherjee, 2007). As regards Poland’s neighboring countries, niobium concentrations were determined only for Lithuanian soils, where its geochemical background was estimated at 12.7 mg/kg. The FOREGS project has shown that the low concentrations (<6.50 mg/kg) are typical of sandy soils of the European Lowlands, developed on glacial sediments (De Vos, Tarvainen, eds., 2006).

The map of niobium distribution in Poland’s soils, constructed based on GEMAS project data, provides a very striking image. Over most of the country, the niobium concentration does not exceed 0.50 mg/kg. Enrichments of >0.64 mg/kg, and locally >0.81 mg/kg, were observed in the Sudetes and in their foreland (Plate 11). The maximum niobium concentration (1.57 mg/kg) was measured in soils of the Bielawa and Dzierżoniów region, developed on gneisses and granodiorites containing ilmenite and rutile (Lis, Sylwestrzak, 1986). Anomalous concentrations (up to 1.37 mg/kg) are also found in the Nysa Kłodzka River catchment area (soils of the Biała Lądecka River valley), where crystalline schists and gneisses with ilmenite and titanite are the natural source of niobium (Marks et al., 2006). Another niobium anomaly (up to 1.20 mg/kg) is observed in the Góry Opawskie Mountains.

A greater range of niobium concentrations and a higher median value in grazing land soils, compared with data for arable fields (Tab. 1, Fig. 13), suggest the possibility of its accumulation in organic matter.

Tabela 12
Table

Zawartość niobu w glebach (mg/kg)
Niobium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data			12	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	748	<2–48	7	t.	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	843	0,45–134	9,68	t.	Salminen, ed., 2005
Litwa Lithuania	696	4,5–50,1	12,7	t.	Kadūnas et al., 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<2–174	13	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,02–21,1	0,50	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,05–1,57	0,22	a.r.	Obecna praca This study

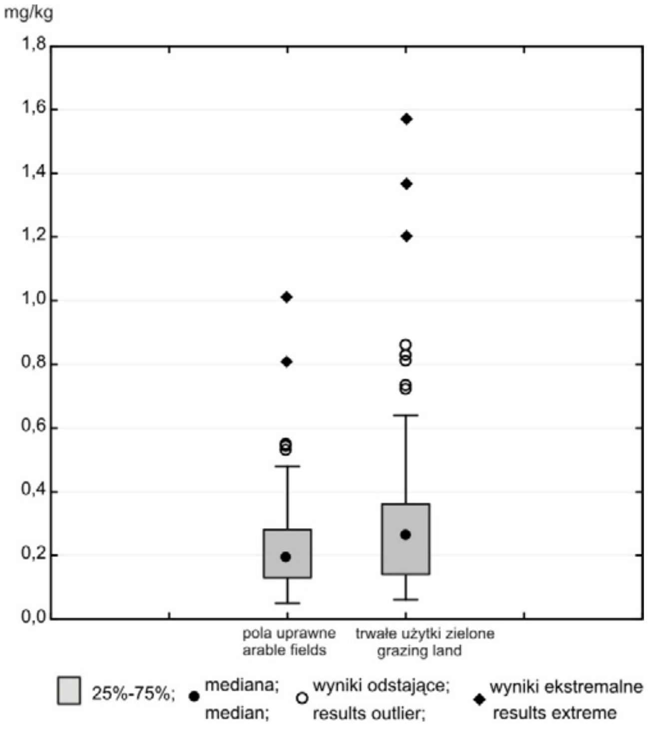

Fig. 13. Porównanie parametrów statystycznych zawartości niobu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of niobium content in arable fields and grazing land soils

Rb Rubidium

General information

Rubidium is a typical dispersed element; it does not create its own minerals, but is often accompanied by potassium (in feldspars, micas, chlorides and clay minerals), which is similar in the ionic radius. It is also dispersed in lithium and cesium minerals. The high rubidium concentrations (120–200 mg/kg) are found in acidic igneous rocks and clayey sediments, and the low concentrations (2–20 mg/kg) in carbonate rocks (Kabata-Pendias, Mukherjee, 2007). Clay raw materials of Poland (Poznań Clays) contain 118–132 mg/kg of rubidium (Bojakowska et al., 2010).

Anthropogenic sources

This element and its compounds are used in the production of phototubes, pharmaceuticals, fluorescent lamps and special grades of glass.

Soils

The main source of rubidium in soils is the weathering of rocks containing potassium and lithium minerals, therefore its high amounts are found in soils developed on granites and gneisses (120 mg/kg). Much lower contents of this element occur in soils formed from sandy sediments. Rubidium ions are released in the process of decomposition of rocks and are captured by silicate products of weathering processes (mainly clay minerals and mica) and by organic matter.

The FOREGS project shows that the rubidium concentration in European soils ranges from <2 to 390 mg/kg, and according to the GEMAS project, the concentration varies between 0.22 and 562 mg/kg (Tab. 13). In soils of some regions of Poland, the rubidium concentration previously reported was 7–28 mg/kg (Skibniewska, Kośla, 2007).

Analysis of the rubidium content in soils of Poland, performed within the framework of the GEMAS project, shows the concentration variations from 1 to 29 mg/kg. The ranges of concentrations and the median values for soils of arable fields and grazing land soils are similar (Tab. 1, Fig. 14). Over most of the country, the rubidium concentration does not exceed 15 mg/kg. In southern Poland, there are some areas of rubidium concentration above 18 mg/kg (Plate 12).

The maximum rubidium concentration (29 mg/kg) was recorded in soils developed on gneisses and granodiorites in the Sudetic foreland (Bielawa and Dzierżoniów area).

In the Carpathians, increased rubidium concentrations (up to 21 mg/kg) are found in soils of the Kamienica River valley (east of Nowy Sącz), which may be attributed to the chemical composition of parent rocks: Paleogene clay deposits of the Carpathian Flysch.

Other areas of elevated rubidium concentrations are located near Staszów, where the soils are developed on Miocene sulphur-bearing deposits (Marks et al., 2006). Intergrowths of clays or sulphate mineralization may be the source of rubidium in these sediments; rubidium is in fact one of the cations that occupy the positions of monovalent metals in the alunite group minerals (Bolewski, 1982).

Tabela 13
Table

Zawartość rubidu w glebach (mg/kg)
Rubidium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data			65	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	748	<2–194	65	t.	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	845	<2–390	80	t.	Salminen, ed., 2005
Litwa Lithuania	655	14–140	63	t.	Kadūnas et al., 1999
Słowacja Slovakia	5189	3–527	84	t.	Čurlik, Šefčik, 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<2–562	73	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	0,22–329	14	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	1–29	7	a.r.	Obecna praca This study

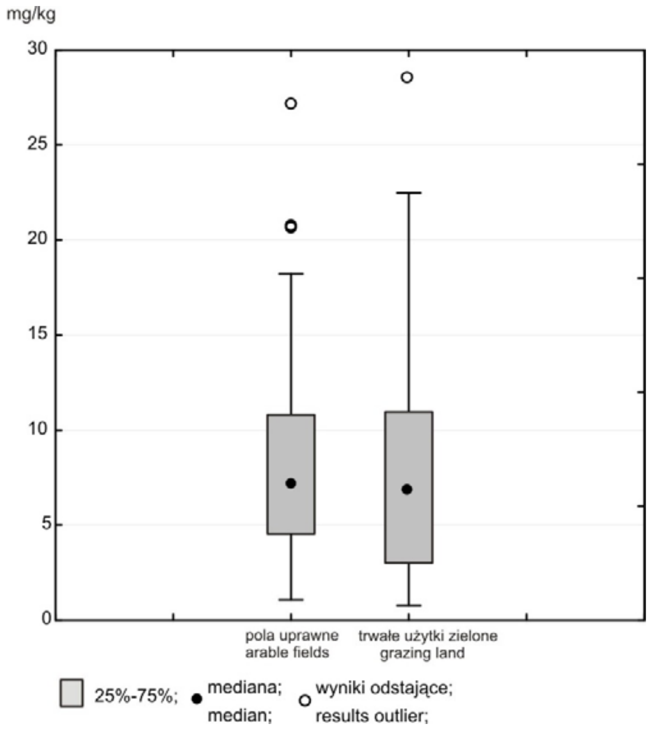

Fig. 14. Porównanie parametrów statystycznych zawartości rubidu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of rubidium content in arable fields and grazing land soils

Sb Antimony

General information

The average antimony concentration in rocks of the Earth's crust is 0.1–0.9 mg/kg. It has sulfophilic and amphoteric properties (Reimann et al., 1998; Paulo, Strzelska-Smakowska, 2000). In igneous rocks, its concentration is in the range of 0.1–2 mg/kg, however, clayey sedimentary rocks can contain up to 4 mg/kg of antimony (Kabata-Pendias, Mukherjee, 2007).

Due to the ease with which antimony can migrate to silicic hydrothermal solutions, it accumulates most commonly in polymetallic deposits, often in the form of fillings of vugs and cracks (Polański, Smulikowski, 1969). The most important minerals in antimony sulphide ore deposits are antimonite (Sb_2S_3) and berthierite ($FeSb_2S_4$); and in antimony oxide ore deposits – senarmontite and valentinite (Sb_2O_3). In hypergenic environments, antimony shows low mobility and easy binding by ferric and manganese oxides and hydroxides, by organic matter and by clay minerals.

Anthropogenic sources

The greatest pollution of Earth's surface environments by antimony is associated with the mining and processing of its ores as well as of gold, copper and lead ores containing a variety of minerals. Antimony enrichment in the surface environments is also caused by dust emissions from coal combustion (Karayigit et al., 2000), mining of mercury ores (Plouffe et al., 2004), vehicle exhaust emissions (Dietl et al., 1996), industrial sewage, municipal waste (Watanabe et al., 1999), and the production of solders, bearings, batteries, weapons, composites for the manufacture of car body and car console, electrical equipment, fire-resistant textiles and coatings of plastic objects, anti-corrosion coatings, semiconductors, paints, microbicides, ceramic materials and optical glass.

Soils

The concentrations of antimony in polluted soils of various regions of the world range from 0.05 to 2 mg/kg (Environment.., 2006; Kabata-Pendias, Mukherjee, 2007), and its accumulation occurs mainly in the topsoil (Ainsworth et al., 1990; Reimann et al., 2010). In areas of historical mining and metallurgy of antimony ores, the soils contain up to a few thousand mg/kg of antimony, and the plants – up to several hundred mg/kg of this element (Ainsworth et al., 1990; Hammel et al., 2000; Hiller et al., 2012).

Antimony concentrations in the topsoil of Europe are <0.02–31.1 mg/kg, and in the arable soils of Baltic countries <0.1–3.2 mg/kg (Reimann et al., 2003). The geochemical background determined for Slovakian soils is 0.7 mg/kg, and varies within the range of <0.1–247 mg/kg (Tab. 14). Soils of Sweden and the topsoil of Finland contain 0.07–0.41 and <0.2–0.9 mg/kg of antimony, respectively (Koljonen, ed., 1992; Eriksson, 2001).

According to the GEMAS project data, the antimony concentration in most soils of Poland does not exceed 0.52 mg/kg (Plate 13), and the average is 0.14 mg/kg in arable soils and 0.17 mg/kg in grazing land soils (Fig. 15).

Antimony enrichments (0.42–0.60 mg/kg) are found in some areas of the Sudetes and the Carpathians. The antimony concentrations of 0.52–0.61 mg/kg were found in the vicinity of Dobra near Bolesławiec, in the area of placer gold deposits – gold-bearing sands and gravels on Upper Cretaceous sandstones (Dziekoński, 1972). The material from waste piles of historical gold mining in this area (12th to 14th centuries) also contained native silver, magnetite, ilmenite, titanite and other minerals that can show overgrowths of antimony minerals or antimony admixture in the crystal lattices of sulphides and oxides of other metals. Antimony enrichment (0.52–0.60 mg/kg) in soils from the Sędzisław region near Kamienna Góra can be related to bedrock mineralization. Copper mineralization that occurs in this area (Lis, Sylwestrzak, 1986) is probably associated with Carboniferous and Permian volcanic rocks and may be accompanied by antimony minerals.

In the Carpathians, elevated antimony contents were observed in soils developed on Paleogene deposits of the Podhale Flysch (shales, mudstones and sandstones). Near Rzepiska (east of Białka Tatrzańska), the concentrations of this element reach 1 mg/kg. In this area, antimony (as well as molybdenum, iron, nickel, tellurium and bismuth) probably comes from flysch deposits containing material of magmatic origin – tuffite interbed. Similar antimony enrichment was found in the topsoil near Pszczyna, where the concentration was determined at 0.34–2.26 mg/kg (Loska et al., 2004).

A local antimony anomaly (up to 1.03 mg/kg) occurs in the vicinity of the village of Kamionka, near Czersk (outskirts of the Tuchola Forest). Near the sampled area, there is a large breeding farm. The likely source of antimony is sewage and breeding waste of veterinary products containing antimony pentasulphide (Sb_2S_5) used in the treatment of animals (Customs, 2012).

Point antimony anomalies are also found in grazing land soils developed on alluvial deposits in the valleys of the Noteć River (up to 0.71 mg/kg) and the Bug River (up to 0.66 mg/kg).

Tabela 14
Table

Zawartość antymonu w glebach (mg/kg)
Antimony content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data			0,5		Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	747	<0,1–3,2	0,24	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	840	0,02–31,1	0,60	t.	Salminen, ed., 2005
Słowacja Slovakia	5189	<0,1–247	0,7		Čurlik, Šefčik, 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<5–36	<5	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,02–25	0,26	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,06–1,03	0,16	a.r.	Obecna praca This study

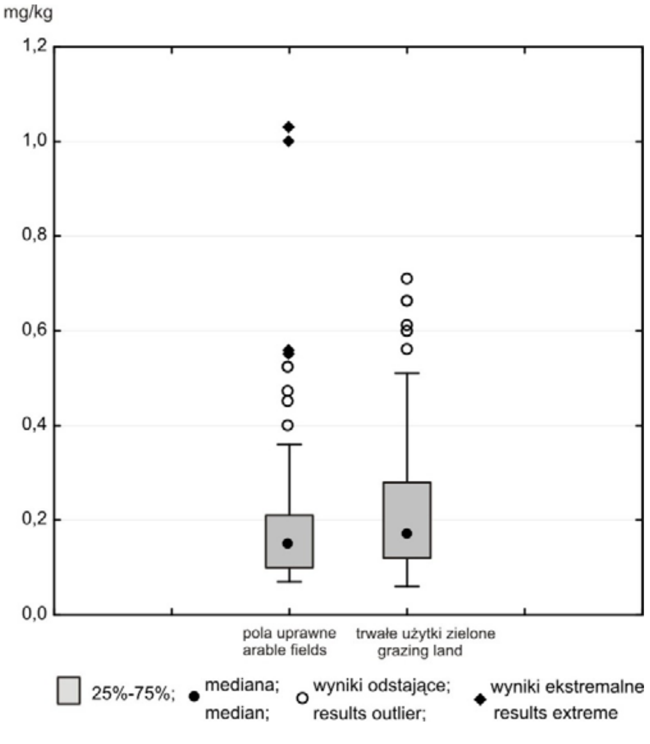

Fig. 15. Porównanie parametrów statystycznych zawartości antymonu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of antimony content in arable fields and grazing land soils

Sc Scandium

General information

Scandium is dispersed in minerals of other elements in the lithosphere. Its ionic radius size affects its relationship with iron and magnesium. In igneous rocks, where its concentration is 3–15 mg/kg (Kabata-Pendias, Mukherjee, 2007), scandium is present mainly in pyroxenes, amphiboles and biotite, but also in ilmenite and zircon. Basalts and gabbros are richer in scandium (30–40 mg/kg) compared with granites (<10 mg/kg). Among sedimentary rocks, clayey deposits, particularly shales rich in ferric compounds, as well as coal and oil, are most abundant in this element.

Anthropogenic sources

Earth's surface environments may be enriched in scandium in areas remaining under the influence of emissions from power and heating plants. It can also migrate into the soil, sediments and groundwater as a result of production of alloys, TV-sets, lasers, energy-efficient lighting products, and glass.

Soils

The scandium concentration in worldwide soils varies from 0.8 to 28 mg/kg and is associated with the presence of iron, aluminum and organic matter (Tab. 15). The geochemical background of the total amount of scandium in European soils, as determined in the studies of the FOREGS and GEMAS projects, is 8 mg/kg, and the average value after aqua regia digestion is 2 mg/kg.

In northern and central Poland (mostly covered with sandy soils), the scandium concentration does not exceed 2.4 mg/kg (Plate 14). Similar results were obtained during more detailed studies of forest sandy soils from the Opole region 1.9–3.1 mg/kg (Kłos, 2009). A regional increase in the scandium concentration (up to 3.5 mg/kg) is observed in the Sudetes, where scandium in soils originates likely from their parent rocks. In the valley of the upper Bóbr River (north of Kamienna Góra), the soils developed upon the bedrock of Carboniferous conglomerates, greywackes, siltstones and claystones, whose constituents are the source of scandium. In the Biała Lądecka region, the element is probably supplied from outcropping amphibolites. In Cieszyn Silesia (around Godziszów), the scandium concentration of 4.4 mg/kg was reported from soils developed on teschenites rich in pyroxenes and amphiboles.

In the Carpathians, local scandium enrichments (more than 3 mg/kg) in the Dunajec and Wisłoka River basins may be linked to the chemical composition of parent rocks – Paleogene clayey deposits of the Carpathian Flysch, represented by variegated clay shales, locally sideritic (Paul, 1991, 1993). It is likely that they are also enriched with scandium due to its increased content in iron minerals.

The average scandium concentrations in grazing land soils and arable fields are almost identical (Fig. 16).

Tabela 15
Table

Zawartość skandu w glebach (mg/kg)
Scandium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,8–28			Kabata-Pendias, Mukherjee, 2007
Europa – BSS projekt Europe – BSS project	747	<2–36	7	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	747	0,6–27	6	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	843	<0,5–54,1	8,21	t.	Salminen, ed., 2005
Litwa Lithuania	696	0,1–27,4	5,7	t.	Kadūnas et al., 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<2–42	8	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,05–22	2	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,1–4,4	0,8	a.r.	Obecna praca This study

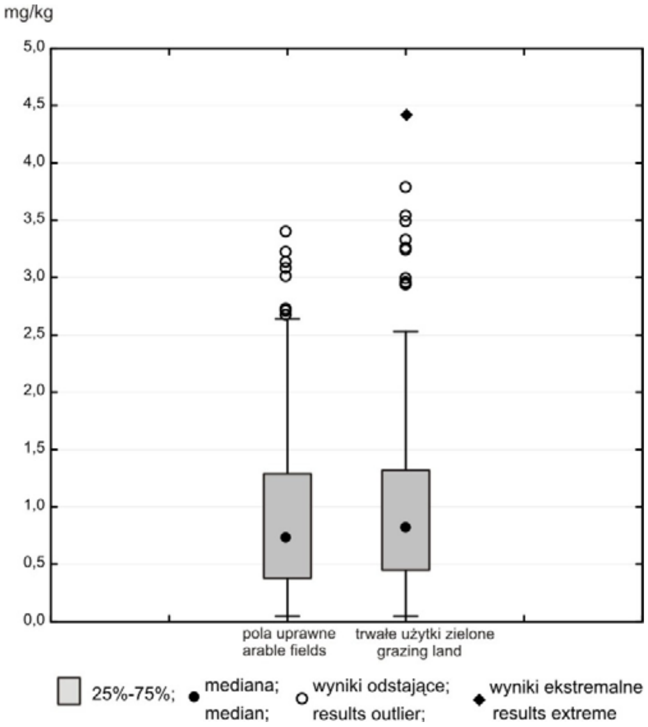

Fig. 16. Porównanie parametrów statystycznych zawartości skandu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of scandium content in arable fields and grazing land soils

Se Selenium

General information

Due to chalcophilic properties of selenium, it is accumulated along with sulphur in sulphide metal deposits, mostly in various simple sulphides (pyrite, galena, chalcopyrite, sphalerite, molybdenite) that may contain up to 20% of selenium. Mafic igneous rocks are slightly richer in this element (0.01–0.12 mg/kg) compared with acidic rocks (0.01–0.05 mg/kg) (Kabata-Pendias, Mukherjee, 2007). Among sedimentary rocks, elevated selenium concentrations are found in black shales (0.3–0.6 mg/kg), as well as coal and oil (up to 10 mg/kg). Uranium ore deposits, in which selenium accumulates in the form of sulphides and selenides, are also enriched with this element (Polański, 1974). In the weathering processes, selenium is quite mobile and it adsorbs to ferric hydroxides, organic matter and clay minerals.

Anthropogenic sources

Selenium pollution in the environment originates from the burning of fossil fuels, industrial wastewater discharges, copper and lead metallurgy, as well as from the activities of the petroleum industry. Selenium compounds are also used in the manufacture of semiconductors, pharmaceuticals, cosmetics and medicines, as well as an additives in fertilizers and insecticides. Selenium is produced as a byproduct of copper electrorefining process.

Soils

Selenium is an essential element necessary for many organisms, although it occurs in trace amounts in the plants and animals. Its presence determines the proper course of many physiological and biochemical processes, and both deficiency and excess result in disease. Sometimes, the role of selenium deficiency in soils is overestimated as regards disease induction, particularly human cancer incidence. Such an opinion is contradicted by a comprehensive study of selenium content in soil, drinking water, plants and human body tissues, carried out in eastern China, which demonstrated that much more dangerous to human health is, for example, an excess of nitrates in drinking water, and other ingredients in the diet (Appleton et al., 2006).

The natural concentration of selenium in worldwide soils ranges from 0.1 to 3.5 mg/kg (Tab. 16), and its primary sources are components of soil's parent rocks and atmospheric deposition. The median of selenium concentration in the soils of Europe (after aqua regia digestion) is seven times greater (2.1 mg/kg) compared with the median for Polish soils (0.3 mg/kg).

Earlier studies estimated the concentrations of this element in the soils of Poland to be 0.04–0.64 mg/kg (Borowska et al., 2007; Tomza-Marciniak et al., 2010), which was considered a deficit concentration. Results of the GEMAS project confirmed earlier observations, showing that the selenium concentration is in the range of <0.1–1.8 mg/kg. The spatial distribution of selenium in various regions seems to be controlled by the chemical composition of soil's parent rocks and soil-forming processes. In most of the soils, its concentration does not exceed 0.5 mg/kg (Fig. 17, Plate 15). Higher concentrations (>0.8 mg/kg) are found in only a few locations in grazing land soils rich in organic matter. Positive correlation between selenium and organic matter confirms the observations of other authors, indicating its accumulation in organic matter (Niedzielski et al., 2000; Borowska et al., 2007; Patorczyk-Pytlik, Kulczycki, 2009). The maximum selenium concentration (1.8 mg/kg) was found in grazing land soils in the valley of the lower Bug River, developed on Holocene alluvial muds and peats rich in organic matter (up to 25% TOC) that can sorb selenium. However, the source of selenium is difficult to determine. Similar enrichment of both selenium (1.1 mg/kg) and organic carbon (TOC to 20%) is found in the Noteć River valley soils. Increased concentration of selenium (1.2 mg/kg), accompanied by the abundance of organic matter, were also found in soils of the upper Wieprz River valley, developed on Holocene alluvial muds and peats.

The selenium concentrations of up to 0.8–0.9 mg/kg were reported at a number of locations, both in the north and south of the country. In the Wisłoka River valley, an elevated selenium concentration is found in soils developed on alluvial sediments deposited as a result of weathering of the Oligocene shales and conglomerates of the Outer Carpathians, and on the Quaternary loess covering their foreland.

In the Legnica-Głogów Copper District, there is a zone of soils containing 0.5–0.6 mg/kg of selenium, which is presumably associated with the emission of this element from copper smelters.

Tabela 16
Table

Zawartość selenu w glebach (mg/kg)
Selenium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,1–3,5			Kabata-Pendias, Mukherije, 2007
Europa – BSS projekt Europe – BSS project	743	0,02–7,6	0,14	a.r.	Reimann et al., 2003
Słowacja Slovakia	5189	<0,1–4,0	0,1	t.	Čurlik, Šefčik, 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<2–42	8	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,05–22	2,1	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,1–1,8	0,3	a.r.	Obecna praca This study

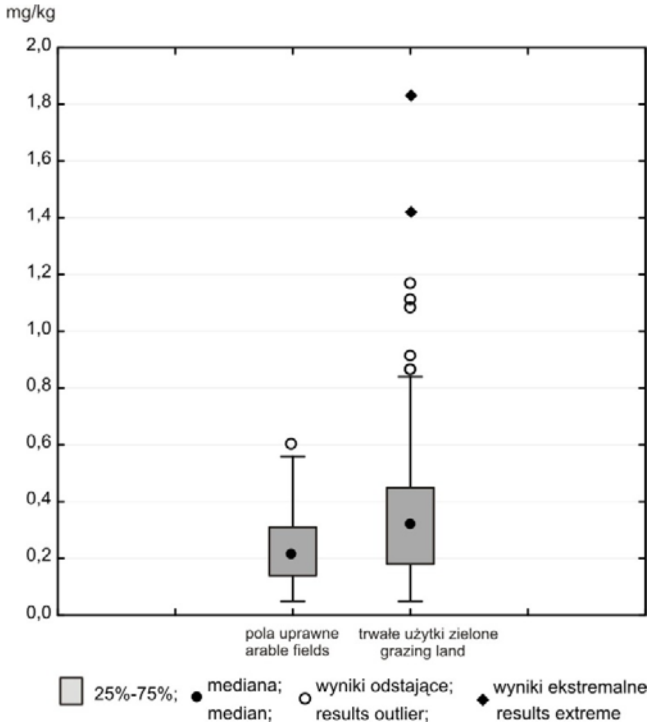

Fig. 17. Porównanie parametrów statystycznych zawartości selenu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of selenium content in arable fields and grazing land soils

Sn Tin

General information

Tin is a low mobile element in the environment. It is dispersed in rocks of the Earth's crust, and exhibits elevated concentrations is in acidic igneous rocks (1.3–3.6 mg/kg), fine-grained sedimentary rocks and coal (6–10 mg/kg) (Kabata-Pendias, Pendias, 1999; Reimann et al., 2003). Tin commonly forms weathering-resistant cassiterite (SnO_2). Released from the structures of minerals during the weathering process, tin forms complexes with organic matter and accumulate with clay minerals, ferric oxides and coal, where its concentration can be up to 2.3 mg/kg, (Llorens et al ., 2000).

Anthropogenic sources

Tin has been in use since ancient times; it is a component of bronze (with copper), alloyed with silver have been used for the manufacture of coins. Among major sources of environmental tin pollution are coal and waste burning, industrial wastewater discharges, production of tin metal-sheets and solder (Sn-Pb), plastics, dyes, pesticides and fungicides (Paulo, Strzelska-Smakowska, 1994). The tin concentration in fly ash may be up to 8.7 mg/kg (Llorens et al., 2000).

Tin may be present in aqueous solutions in forms variably mobile and variably toxic compounds that can accumulate in plant and animal tissues (Kabata-Pendias, Pendias, 1999). Naturally increased amounts of tin compounds in water and soil occur in areas of cassiterite deposits.

Soils

The average tin concentration in worldwide soils is estimated at 3.5–4.0 mg/kg (Tab. 17). In European soils, the concentrations range from <2 to 106 mg/kg, with the highest values recorded in soils developed on granites and in areas of tin-tungsten mineralization.

According to the GEMAS project data, the tin concentration in most soils of Poland does not exceed 1 mg/kg, and the average is 0.4 mg/kg (Tab. 17). Higher concentrations are found in soils from large areas of the Sudetes (1.0–1.3 mg/kg). Between the valleys of the Bóbr and Kwisa rivers, there is an anomaly with the tin concentration of 2.6 mg/kg (Plate 16). In this region, the anomalous contents are natural enrichments associated with the occurrence of cassiterite deposits in quartzite-mica-chlorite schists of the Izera Mountains (Jaskólski, 1960; Madziarz, Sztuk, 2006). These deposits were periodically mined at Gierczyn, Przecznica and Kamienica Mała

(Paulo, Strzelska-Smakowska, 1994). Gneisses and schists are very resistant to weathering, and secondary material from their breakdown can be transported in river sediments over a considerable distance. Studies of heavy minerals from alluvial sediments of this area showed <0.01% of SnO_2, and the average tin content in the Gierczyn deposit is up to 2% (Madziarz, Sztuk, 2006).

Grazing land soils developed on alluvial sediments of the Odra River (downriver of Wrocław and of the Bystrzyca River mouth) contain above 2 mg/kg of tin that may originate from either fluvial sediments of the rivers flowing across the Sudetes or industrial wastewater of the city of Wrocław. Occurrences of non-economic cassiterite deposits were reported from many areas of Lower Silesia (Jaskólski, 1960; Lis, Sylwestrzak, 1986), which may result in the enrichment of this mineral in the sediments. Wrocław is the area of chemical, metallurgical, automotive, and food industrial plants, as well as power and heating plants. Most of industrial wastewater is discharged to the urban sewage systems and then to the Odra River. Heating plants, scattering dust from coal combustion, are the major source of particulate emissions that can contain tin.

Local tin anomalies in the Polish Lowlands (in the valleys of the Obra, Gwda and Noteć rivers and in the Żuławy region) presumably are the result of industrial activities. The source of this element are sewage and waste from the metallurgical (mainly galvanization process), paint and electronics industries, and from the production of plastics and plant protection products. Another important source is dispersion of dust from coal burning. Identification of specific sources of tin pollution requires more detailed research.

Tabela 17
Table

Zawartość cyny w glebach (mg/kg)
Tin content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		3,5–4,0			Kabata-Pendias, Mukherjee, 2007
Europa – BSS projekt Europe – BSS project	747	<1–6,8	1,1	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	845	<2–106	3	t.	Salminen, ed., 2005
Słowacja Slovakia	5189	<1–227	5	t.	Čurlik, Šefčik, 1999
Litwa Lithuania	696	0,62–7,94	2,10	t.	Kadūnas et al., 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<4–809	<4	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,1–158	0,7	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,1–2,6	0,4	a.r.	Obecna praca This study

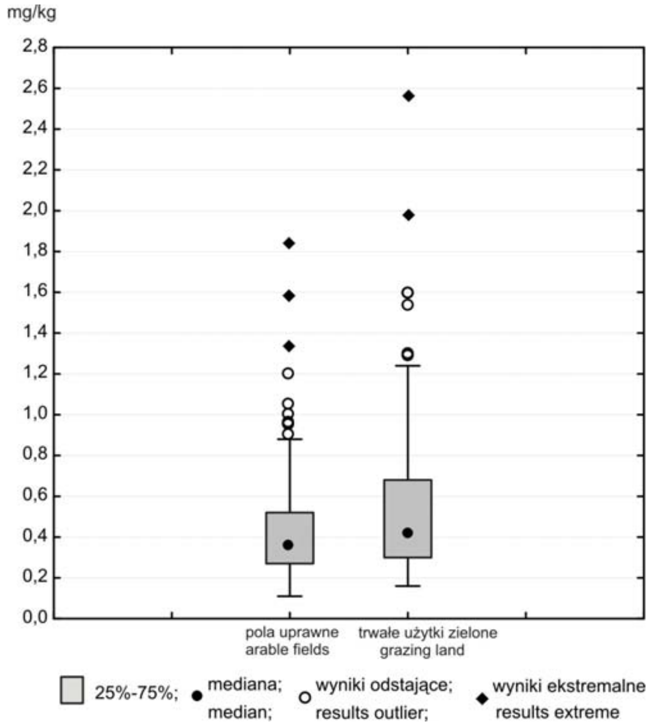

Fig. 18. Porównanie parametrów statystycznych zawartości cyny w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of tin content in arable fields and grazing land soils

Te Tellurium

General information

Despite its considerable dispersion in rocks of the Earth's crust (0.001–0.005 mg/kg), tellurium has the ability to form their own minerals (tellurides and telluro-sulphides) accumulating in sulphide deposits. Enrichment of tellurium is observed in greywackes and shales, where its concentration can be up to 1 mg/kg.Tellurium occurs also as a replacement for sulphur in sulphides. Pyrite, chalcopyrite, molybdenite may contain 70–430 mg/kg of tellurium (Dill, 2010). During weathering and oxidation of these minerals, sulphate ions are discharged and tellurium is accumulated with ferric hydroxides. Another possibility of accumulation is in organic matter, as evidenced by the tellurium concentration of 0.02–2 mg/kg in coal and fly ash (Kabata-Pendias, Mukherjee, 2007).

Anthropogenic sources

Tellurium is produced as a byproduct in the electrorefining of copper and other sulphides (e.g., lead). This element is used in a number of alloys to prevent their corrosion, and in rubber products to enhance their resistance to aging and high temperature. It is also used as a glass dye, a catalyst in some reactions, and a component of semiconductors. Tellurium is used in thermoelectric devices in refrigerators, in heat pumps, heat detectors, lasers, precision telescopic cameras, satellites, remote weather forecast stations, and space probes.

Soils

According to data of the FOREGS and GEMAS projects, the tellurium concentration in European soils varies from <0.02 to 0.95 mg/kg (Tab. 18). The lowest concentrations are typical of sandy soils of the European Lowlands, and positive anomalies occur in areas of polymetallic mineralization (including gold, antimony, silver, zinc and lead ores) as well as near metal smelters (De Vos, Tarvainen, eds., 2006; Perkins , 2011).

Soils of Poland, analysed within the framework of the GEMAS project, contain from <0.02 to 0.11 mg/kg of tellurium. The low determination limit of this element allows only the conclusion that its concentration does not exceed 0.02 mg/kg in most of the country (Plate 17). In southern Poland, there are a number of areas where the soils have higher contents of this element. Along the state border in the Carpathians, a prominent belt of soils enriched with tellurium (0.04–0.08 mg/kg) is observed. Flysch deposits are the likely source of this enrichment, especially the Oligocene sandstone-claystone series. Tellurium-bearing material probably originated from the weathering of older deposits in Slovakia and Ukraine, where metal ore deposits contain admixtures of tellurides (Řídkošil et al., 2001, Cook et al., 2005).

An area of soils with elevated tellurium concentrations (up to 0.11 mg/kg) extends between the river valleys of the upper Wieprz and the middle San. Soil's parent rocks are represented here mostly by the Quaternary loess and Cretaceous carbonate-clayey deposits. The general geochemical surveying of Poland revealed soil enrichments of cobalt, chromium, copper, nickel and iron in this area, which is likely associated with an admixture of volcanic material in these deposits (Lis, Pasieczna, 1995). The increased tellurium content may result from the same source. Research on recent volcanic emanations indicates their important role in both the transport of a number of metals (including tellurium) and the formation of their mineral deposits (Williams-Jones et al., 2002).

Local tellurium enrichment is also marked in the upper Pilica River valley, in soils developed on Cretaceous carbonates and glauconitic sandstones, covered with loess. The anomaly is probably of geogenic origin, although may be also related to long-term industrial dust emissions from the Zawiercie steelworks. Soils of this region are also enriched with beryllium, cerium, hafnium, lanthanum, zirconium, niobium and selenium. Another occurrence of tellurium concentration of up to 0.07 mg/kg is known from the region between Busko and Staszów, where soil's parent rocks are represented by sulphur-bearing organodetrital limestones and gypsum.

Due to the very low variability in tellurium concentrations, and the impossibility of calculating the median (values are below the determination limit), no comparison of tellurium data for arable field and grazing land soils is presented.

Tabela 18
Table

Zawartość telluru w glebach (mg/kg)
Tellurium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data			0,005	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	744	<0,005–0,07	0,008	a.r.	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	840	<0,02–0,93	0,03	t.	Salminen, ed., 2005
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,02–0,95	<0,02	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,02–0,11	<0,02	a.r.	Obecna praca This study

Th Thorium

General information

In igneous rocks, thorium, like uranium, is dispersed in accessory minerals such as monazite, xenotime and zircon. Post-magmatic rocks contain own thorium minerals (thorite, uraninite-thorianite series). At this stage, this element is also accompanied by the lanthanides, niobium, tantalum and titanium (Polański, 1974). Among igneous rocks, the most abundant in thorium are alkaline granites containing up to several tens of mg/kg of thorium, while in basalts, the concentrations are rarely in excess of 1 mg/kg (De Vos, Tarvainen, eds., 2006).

In sedimentary rocks, thorium is concentrated in weathering-resistant minerals (monazite, zircon in placer deposits) and clay minerals. Clay rocks contain 10–12 mg/kg of thorium; sandstone and carbonates 2–4 mg/kg (Kabata-Pendias, Mukherjee, 2007; Bojakowska et al., 2010). In lignite and coal, thorium is subjected to a significant concentration reaching a value of up to 30–35 mg/kg (Bojakowska et al., 2008).

Anthropogenic sources

Thorium is extracted from monacite sand deposits as a byproduct in the production of titanium and zirconium. It is used mainly as a fuel in nuclear reactors, where it is utilized in its entirety, without creating any problem of radioactive waste harmful to the environment. Such reactors also successfully burn radioactive waste from traditional uranium-based nuclear power plants. Thorium is also used in photoelectric sensors, lenses, and as an additive in some alloys.

Soils

The thorium concentration in worldwide soils varies from 3.4 to 10.5 mg/kg (Tab. 19); with the average of 9.4 mg/kg (Reimann et al., 2003). The average thorium concentration in European soils, determined during the FOREGS investigations is 7.24 mg/kg.

According to the GEMAS project analysis, the thorium concentration in Polish soils ranges from 0.1 to 5.3 mg/kg (median 1.0 mg/kg), and the degree of variability in arable field and grazing land soils is similar (Tab. 1, Fig. 19).

In most of the country, the thorium concentration is between 0.1 and 3.2 mg/kg (Plate 18). In northern Poland, the concentrations of up to 4 mg/kg are found only in the Żuławy region and near Sępopol in the Masurian Lake District.

Thorium-enriched soils occur at several locations in the south of the country. One of them is the Subcarpathian anomaly (with a maximum of 5.3 mg/kg of thorium in grazing land soils developed on Holocene alluvial muds between the Wisłoka and Wisłok river valleys), covering also the lower Dunajec River catchment area and a part of the Vistula River valley east of Kraków (up to 4.4 mg/kg). Near Godziszów, Cieszyn Silesia, thorium-enriched soils (4.4 mg/kg) have developed on alluvial muds of a stream dissecting carbonate-shale deposits of the Carpathian Flysch, rich in the clay fraction. Increased thorium contents are also observed in soil of the Nysa Kłodzka River valley. In this area, thorium probably originates from outcropping Carboniferous granites and granodiorites, which are known to contain monazite occurrences in pegmatite veins (Lis, Sylwestrzak, 1986).

Tabela 19
Table

Zawartość toru w glebach (mg/kg)
Thorium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		3,4–10,5			Kabata-Pendias, Mukherije, 2007
Europa – BSS projekt Europe – BSS project	748	<5–22	9	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	747	<0,4–20	4,9	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	843	0,3–75,9	7,24	t.	Salminen, ed., 2005
Litwa Lithuania	696	0,9–11,3	5,2	t.	Kadūnas et al.,1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<5–84	10	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	0,03–63	2,7	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,1–5,3	1,0	a.r.	Obecna praca This study

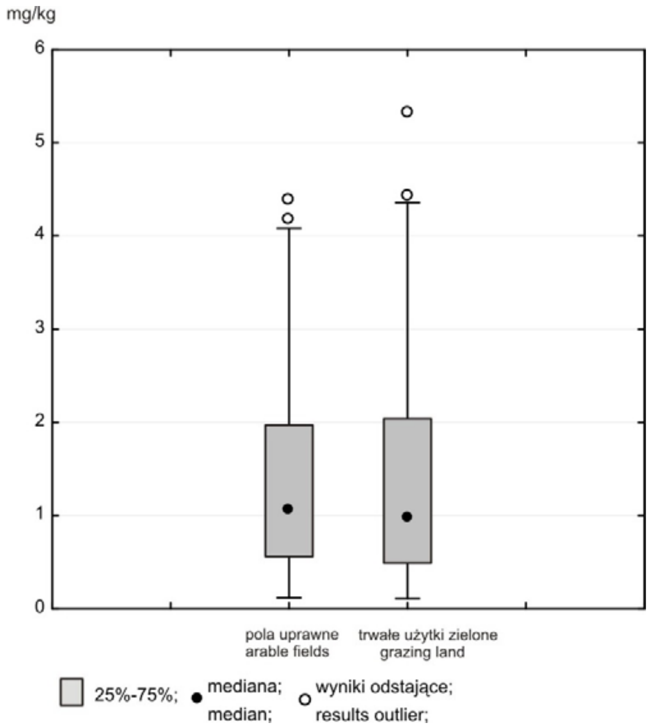

Fig. 19. Porównanie parametrów statystycznych zawartości toru w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of thorium content in arable fields and grazing land soils

Tl Thallium

General information

The ionic radius size of thallium, similar to that of potassium and rubidium, allows substitution of these metals by thallium in the structures of feldspars and micas, and its dispersion in the Earth's crust. The average thallium concentration in rocks of the Earth's crust is 0.85–1.00 mg/kg (Kabata-Pendias, Mukherjee, 2007) and ranges from 0.05 mg/kg in ultrmafic rocks to 3.5 mg/kg in granites and rhyolites (Reimann et al., 1998). In hydrothermal environments, thallium experiences a particularly strong concentration, and its carriers are sulphides (marcasite, pyrite, galena and sphalerite) and sulphosalts. Some of these minerals may contain up to 0.1% of thallium (Paulo et al., 2002). During the weathering process of sulphide ores, part of thallium is retained by ore metal sulphates and clay minerals, and its mobile part is transported and dispersed in sedimentary rocks containing from 0.01 mg/kg (carbonate rocks) to 2 mg/kg of the element (clay rocks, shales). The thallium concentration in coal, probably related to the admixture of sulphides, is 2–3 mg/kg.

Anthropogenic sources

Thallium is a very toxic element; many of its compounds have been classified as poisons. Poisoning of animal organisms is caused by absorption of thallium through digestion, inhalation or skin contact, and the characteristic poisoning symptom is loss of hair.

Into Earth's surface environments, thallium is introduced primarily as a result of emissions from metal smelters, cement plants and heating plants (Kazantzis, 2000). Until 1958, thallium compounds were used as a rat poison. Currently, it is used as a component of metallic alloys, optical glass, semiconductor materials, photovoltaic cells, wood preservation preparations and catalysts.

This element is produced as a by-product in the preparation of copper, zinc and lead concentrates, as well as in the processing of pyrites (Dill, 2010).

Soils

In soils, like in rocks, thallium occurs mainly in potassium minerals (micas and clay minerals). In various regions of the world, unpolluted soils contain 0.1–2.8 mg/kg of thallium (Takeda et al., 2004; Álvarez-Ayuso et al., 2013). In areas of long-time emissions of dust from zinc and lead smelters, thallium is accumulated in organic matter-rich soils.

According to the FOREGS project data, the concentration (total) of thallium in European soils varies from <0.05 to 24 mg/kg, and according to the GEMAS project data, its variability in aqua regia-digested samples ranges from <0.0005 to 2.5 mg/kg (Tab. 20). Regional studies have demonstrated that enrichment of thallium (0.56–2.06 mg/kg) is typical in soils developed on granites (Vaněk et al., 2009). The soils especially contaminated with this element are found in areas of mining and metallurgy of metals (Vaněk et al., 2009, 2013). In Poland, in the region of mining and processing of Zn-Pb ores, the soils developed on post-mining heaps in the calamine extraction area (near Bolesław) are heavily contaminated and contain an average of 43 mg/kg of thallium (Wierzbicka et al., 2004). Near a zinc smelter, the recorded thallium concentrations vary between 0.28 and 30.1 mg/kg (Vaněk et al., 2013), whereas in the area between Sławków, Bolesław and Bukowno, the thallium concentration ranges from 0.04 to 6.9 mg/kg (Lis et al., 2003; Jakubowska et al., 2007).

According to the GEMAS project analyses, the thallium concentration in 90% of soils studied in Poland is below 0.14 mg/kg (Plate 19), with the average of 0.07 mg/kg (Tab. 20). The average concentration (expressed by the median) is much lower than the average value calculated for the soils of Europe (0.12 mg/kg). The range of concentrations for the 25–75 percentile interval is slightly greater in grazing land soils (Fig. 20), which may indicate the binding of thallium mainly by organic matter.

A distinct anomaly of thallium concentrations (>0.18 mg/kg) is the area of mining and processing of Zn-Pb ores, Silesia-Cracow region. The maximum values (0.20–0.27 mg/kg) are found in soils developed on the ore-bearing Middle Triassic carbonates.

Thallium enrichment in soils (0.14–1.18 mg/kg) is also observed across much of the Western Carpathians and its foreland. At a number of locations in the Sudetes (Bóbr River valley east of Jelenia Góra, Nysa Kłodzka River valley near Biała Lądecka, and near Dzierżoniów), the thallium concentrations in soils are 0.14–0.22 mg/kg. All of these soils developed on granites and granodiorites which are certainly the source of thallium released form their minerals.

Tabela 20
Table

Zawartość talu w glebach (mg/kg)
Thallium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data			0,75	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	747	<0,1–2,5	0,4	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	840	0,05–24,0	0,66	t.	Salminen, ed., 2005
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,0005–2,5	0,12	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,02–0,27	0,07	a.r.	Obecna praca This study

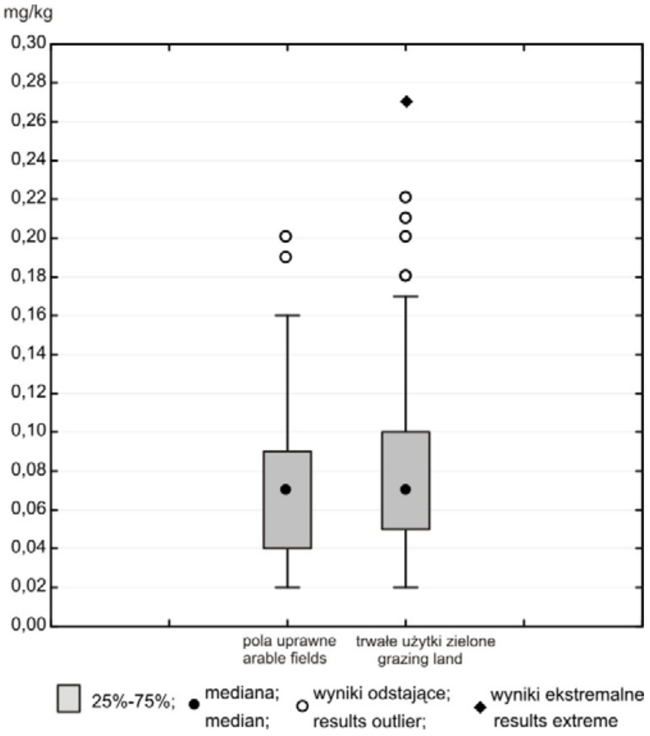

Fig. 20. Porównanie parametrów statystycznych zawartości talu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of thallium content in arable fields and grazing land soils

TOC Total Organic Carbon

General information

Carbon is an essential element for all living organisms. In the form of organic carbon, it is the most important component of soils and biosphere. Its content is an indirect indicator of the amount of organic matter in the soil, which determines its physical and chemical properties, such as sorption and buffering abilities, as well as biological processes. High content of organic matter makes the soil fertile, stabilizes its structure and reduces susceptibility to degradation by water and wind erosion. Retention of humus in the soil is important not only because of the maintenance of productive functions of the soil, but also in terms of the role of the soil in the sequestration (binding) of carbon from the atmosphere.

Anthropogenic sources

Carbon (in the form of CO_2) is emitted in large amounts into the atmosphere through the burning of coal in power, heating, cement and metallurgical plants, and as a result of emissions from car engines. These emissions adversely affect the Earth's climate, but they do not improve the quality of soils in which the humus content decreases over the years as a result of intense cultivation and lack of adequate fertilization. Land use (crops, meadow, forest), agricultural intensification, selection of crops and the level of organic fertilization are the main anthropogenic factors affecting the content of organic matter in soils.

Soils

The TOC value of the soil results from the amount of humic compounds, manure and peat. Their main component is carbon and its quantity is determined primarily by the content of humus which binds harmful elements in insoluble organic-mineral compounds, contributing to reducing their bioavailability.

Considerable differences in the amount organic carbon in soils depend on the nature of parent rock, soil type and land use. More organic carbon is retained in fine-grained, less aerated, and more humid soils. Organic soil (forest floor humus) can contain up to 45% of organic carbon (Reimann et al., 1998). The topsoil of podzols in Poland contains 0.35–1.33% of organic carbon, in cambisols its content is 0.87–1.45%, in rendzinas 1.16–3.50%, in alluvial muds 0.64–2.44% (Dobrzański, Zawadzki, ed., 1993).

The GEMAS project studies show that the total organic carbon content in Polish agricultural soils is clearly different in arable fields and grazing land areas (Fig. 21, Tab. 1). The

TOC value measured for arable fields is close to the value determined earlier for the territory of Poland (0.80–1.32%) during the general geochemical surveying of European soils (Salminen, ed., 2005). Soils of arable fields, abundant in organic carbon (>2%), occur only locally in the valleys of the Noteć (2.8–3.7%), Pisa (up to 3.4%), Krzna (up to 4.9%) and Barycz (up to 3.1%)(Plate 20) river. The high TOC values are probably due to the accumulation of plant tissues in soils developed on alluvial muds. In grazing land soils of the Noteć and Bug river valleys, as well as in the Suwałki region, the TOC value is up to 25% (Plate 21). Due to the very high variability in the ranges of TOC in the soils of arable fields (0.4–4.9%) and grazing land areas (0.5–25%), the spatial distribution of TOC is presented in separate maps.

Tabela 21
Table

Zawartość TOC w glebach (%)
TOC content in soils (%)

	n	Zakres Range	Mediana Median	Użytkowanie Land use	Źródło Source
Europa – FOREGS projekt Europe – FOREGS project	819	0,07–46,6	1,73		Salminen, ed., 2005
Europa – GEMAS projekt Europe – GEMAS project	2095	0,4–46,0	1,8	Pola uprawne Arable fields	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	2023	0,4–49,0	2,7	Trwałe użytki zielone Grazing land	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,4–25,0	1,4	Pola uprawne i trwałe użytki zielone Arable fields and grazing land	Obecna praca This study

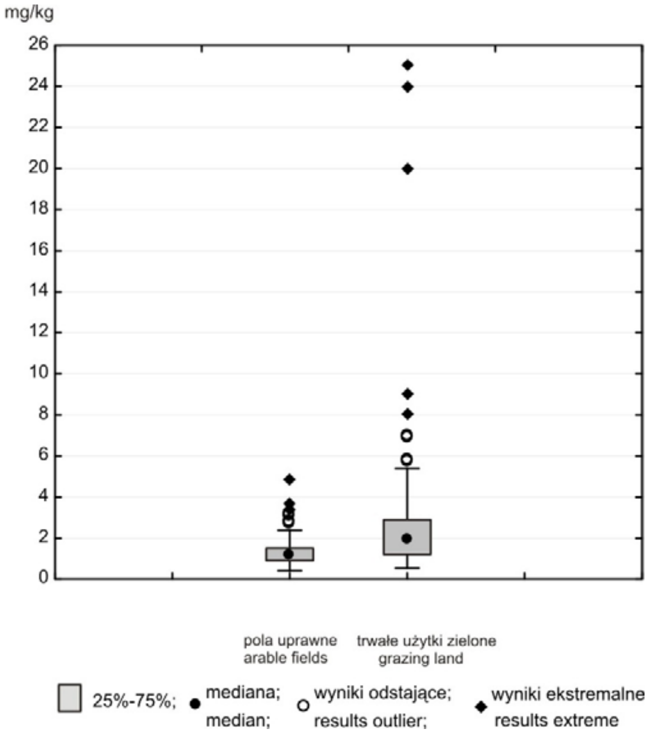

Fig. 21. Porównanie parametrów statystycznych zawartości TOC w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of TOC content in arable fields and grazing land soils

U Uranium

General information

In the Earth's crust, uranium is dispersed in accessory minerals (monazite, xenotime and zircon). Its primary minerals can be formed during the post-magmatic stage: e.g., uraninite, brannerite and carnotite. Acidic igneous rocks contain more uranium (2.5–6 mg/kg) than mafic rocks (0.1–0.5 mg/kg) (Reimann et al., eds., 2014).

Uranium gets into sedimentary rocks in mineral crumbs resistant to degradation, or in the form of suspensions and ions, as a result of weathering processes. From its primary minerals, uranium can be easily released and transported in the ionic form under oxidizing conditions (Polański, 1979). In reducing environments, U^{6+} is reduced to U^{4+}, which leads to its concentration in deposits rich in organic matter (up to several hundred mg/kg in bituminous shales and up to a few mg/kg in coal), as well as in phosphorites. In other sedimentary rocks, the uranium concentration ranges from 0.5 to 4 mg/kg (Kabat-Pendias, Mukherjee, 2007). The lignite and bituminous coal of Poland contain uranium usually in the range of 1.0–4.4 mg/kg (Bojakowska et al., 2008). Uranium-rich ores contain from 1000 to 5000 mg/kg of this element. In Poland, in the 1960s, uranium deposits containing 200 mg/kg of this element were extracted in the Sudetes (Wydobycie...).

Anthropogenic sources

Anthropogenic sources of uranium include the mining and mineral processing of its ores. The ^{235}U isotope is used as fissile material in nuclear bombs, reactors and submarines. Uranium is also used in the production of nuclear weapons, in radiotherapy, in the manufacture of luminescent paints, and in the ceramic and photographic industries.

In the natural environment, its occurrence is also an effect of dust emission from the metallurgical and petroleum industries, and of the production and use of phosphate fertilizers.

Soils

Uranium is released into soils as a result of weathering and erosion of rocks, and atmospheric precipitation from different sources. The uranium geochemical background in the soils of Europe does not exceed 2 mg/kg, and the recorded values vary from <0.04 to 94 mg/kg (Tab. 22). The low uranium concentrations (0.2–0.5 mg/kg) were recorded in sandy soils of the European Lowlands, and anomalously high values were measured in areas of crystalline massifs of the continent, where the accumulations form uranium ore deposits.

Comparison of statistical parameters of this element in arable field and grazing land soils of Poland indicates its higher concentrations in the latter (Fig. 22). In most of soils, the uranium geochemical background is below 0.9 mg/kg (Plate 22). At several locations in the Polish Lowlands (Noteć River basin, Baltic coast, Masurian Lake District), there are enrichments of uranium (up to 1.9 mg/kg) derived presumably from minerals of soils' parent rocks. The abundance of organic matter creates favorable conditions for its sorption. The possibility of binding of uranium by organic compounds is also one of the factors that create local anomalies (11.2 mg/kg) in peat soils (where the TOC reaches 25%) in the valley of a small stream of Orlanka, a tributary of the Bug River. The anomaly occurs in the Podlasie Depression, where the Ordovician Dictyonema shales are known to contain uranium, molybdenum and vanadium ore mineralization (Miecznik et al., 2011). In the 1960s and 1970s, over 60 deep boreholes were drilled the Podlasie Depression in prospecting and exploration for uranium in the Dictyonema shales. The likely source of uranium in the soils is the remains of excavated material from exploration wells, or of drilling mud. Soils of the uranium anomaly area are also enriched with molybdenum, hafnium, zirconium and selenium.

In the Sudetes, the uranium concentrations at some locations are 1–2 mg/kg. Uranium enrichments were observed in the Bóbr and Nysa Kłodzka river valleys, in soils developed on crystalline rocks showing signs of uranium mineralization, as well as between Lubin and Legnica, where the likely source of uranium contamination is the copper industry. Uranium is an accompanying element (up to 60 mg/kg) in the mined copper-bearing shales.

Tabela 22
Table

Zawartość uranu w glebach (mg/kg)
Uranium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data			2,7	t.	Reimann et al., 2003
Europa – BSS projekt Europe – BSS project	747	<0,1–56	1,4	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	843	0,21–53,2	2	t.	Salminen, ed., 2005
Litwa Lithuania	696	8–153,4	38	t.	Kadūnas et al.,1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<3–94	<3	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,04–73	0,70	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,1–11,2	0,5	a.r.	Obecna praca This study

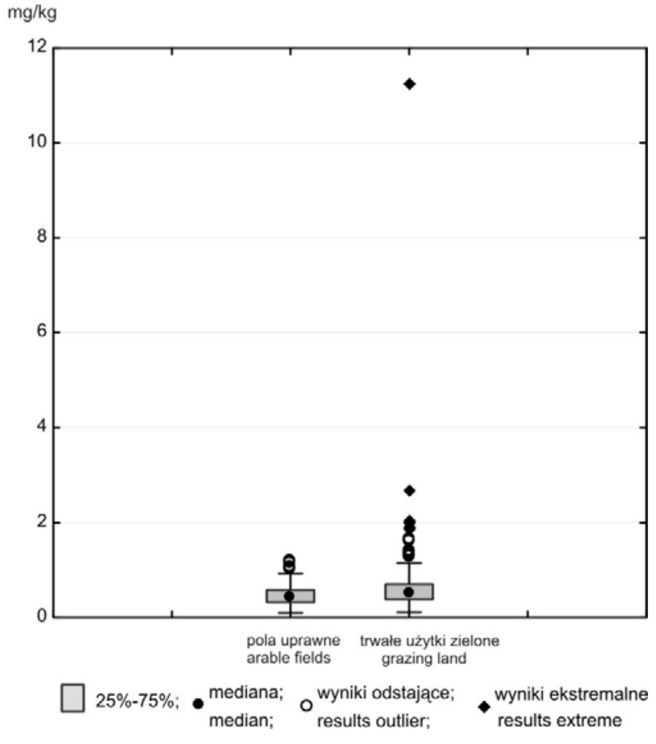

Fig. 22. Porównanie parametrów statystycznych zawartości uranu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of uranium content in arable fields and grazing land soils

W Tungsten

General information

In rocks of the Earth's crust, the tungsten concentration ranges from 0.3 to 2.4 mg/kg, with an average of 1 mg/kg (Kabata-Pendias, Mukherjee, 2007; Dill, 2010). Tungsten is most often associated with other metals (tin, iron, calcium, molybdenum) to form oxides that accumulate predominantly in pegmatitic-pneumatolitic products of granitic magmas. Its primary minerals are wolframite (Fe, Mn) WO_4 and scheelite $CaWO_4$, less important are ferberite $FeWO_4$ and hübnerite $MnWO_4$. These minerals are characterised by high resistance to weathering, and accumulate in placer deposits that form at small distances from primary deposits due to high brittleness. Mobile forms of tungsten can be sorbed by manganese oxides, clay minerals and organic material.

Anthropogenic sources

Tungsten carbide is used as a substitute for industrial diamond in the metal working mining, drilling and petroleum industries. Tungsten is a component of stainless steels, and a catalyst in the petrochemical industry.

Soils

The fluctuations of tungsten concentration in soils from different regions of the world are in the range of 0.4–85.5 mg/kg (Tab. 23). In uncontaminated soils, the tungsten concentration ranges from 0.4 to 5 mg/kg, and in areas of mining and processing of its ores, it can be up to several hundred mg/kg (Kabata-Pendias, Mukherjee, 2007).

The FOREGS project studies employed the XRF method in analysing tungsten concentrations (determination limit 5 mg/kg), and its low detectability did not allow determining the geochemical background value in European soils. It was only possible to indicate a few locations of anomalous tungsten concentration (up to 14 mg/kg). In the territory of Poland, the concentration did not exceed 5 mg/kg in all soil samples analysed by the FOREGS project.

In the GEMAS project, the ICP-MS method was used, which allowed determining the tungsten concentration at <0.1 mg/kg in most of soils of Poland (Plate 23). Higher and more frequent accumulations are observed in grazing land soils compared to arable field soils (Fig. 23). The concentrations of >0.2 mg/kg occur in northern Poland in grazing land soils of the Pisa, Noteć and Obra river valleys. At these locations, glacial sediments are the supposed source of tungsten. Tungsten minerals (especially scheelite) occur in ore veins of granitoids in central and southern Sweden (Drake, 1983; Toverud, 1984). They may have been transported by a glacier and dispersed in Quaternary clays. Tungsten concentrations of >0.2 mg/kg in the valley of the Biała Lądecka River (tributary of the Nysa Kłodzka) were recorded in soils developed on Proterozoic and Cambrian crystalline schists and gneisses (Marks et al., 2006) which can contain wolframite and scheelite, as also can quartz veins in granites from other parts of the Sudetes (Lis, Sylwestrzak, 1986).

Tungsten-enriched soils of the Prosna River valley have developed on Pleistocene glacial tills and kame sands and muds, thus the source of tungsten seems to be of anthropogenic origin. Similar origin is interpreted for local tungsten enrichments (>0.2 mg/kg) in soils near Katowice, where they are probably associated with sewage discharges of the metallurgical industry.

Tabela 23
Table

Zawartość wolframu w glebach (mg/kg)
Tungsten content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		0,4–85,5			Kabata-Pendias, Mukherjee, 2007
Europa – FOREGS projekt Europe – FOREGS project	845	<5–14	<5	t.	Salminen, ed., 2005
Słowacja Slovakia	5189	<1–45	<1	t.	Čurlik, Šefčik, 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	<5–37	<5	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,01–19	0,07	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,1–0,6	<0,1	a.r.	Obecna praca This study

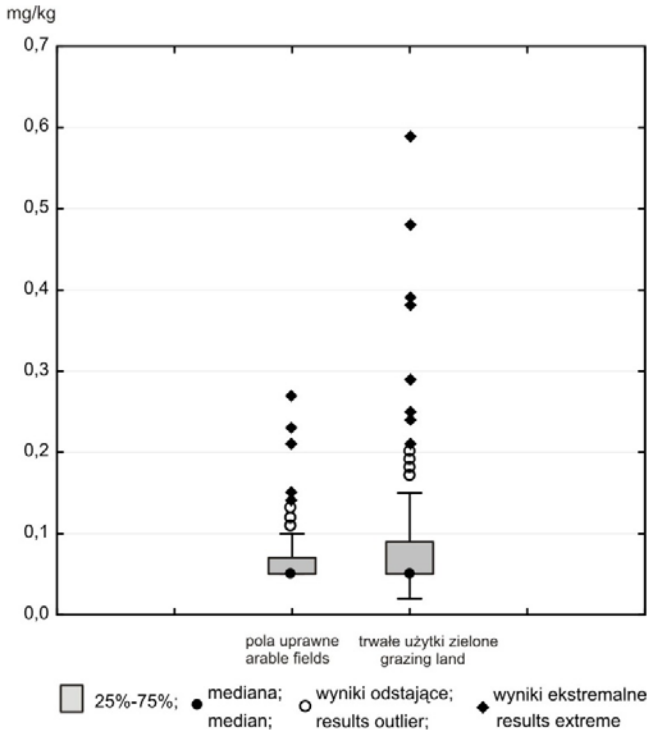

Fig. 23. Porównanie parametrów statystycznych zawartości wolframu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of tungsten content in arable fields and grazing land soils

Y Yttrium

General information

Yttrium is a lithophile element showing chemical properties similar to those of the rare earths elements of the yttrium group. It accumulates in acidic igneous rocks, wherein its concentration is higher (40 mg/kg) compared to ultramafic rocks (2 mg/kg) (Sadeghi et al., 2013). Yttrium forms its own minerals (xenotime, ytterbite, fergusonite) and enters into the structure of biotite, feldspar, pyroxene, garnet and apatite (De Vos, Tarvainen, eds., 2006). Yttrium content in sedimentary rocks is associated with the presence of heavy minerals such as xenotime, zircon and garnets. The greatest amount of yttrium is found in shales and greywackes (approx. 40 mg/kg), smaller in sandstones (approx. 15 mg/kg), and the lowest amount in carbonates (approx. 4 mg/kg). Also loess is among the sediments enriched with yttrium (approx. 25 mg/kg).

Anthropogenic sources

Yttrium is released into the environment from numerous industrial sources. It is used as an alloy additive in metallurgy and as a neutron absorber in nuclear reactors. Together with the lanthanides, it is used in electronics to produce CRT tubes, lasers and microwave devices, as well as in modern automotive engineering (Całus-Moszko, Białecka, 2012).

Soils

According to different authors, the yttrium concentration in soils commonly ranges from 3 to 60 mg/kg, although the maximum values are a few hundred mg/kg (Tab. 24). Yttrium ions that are released during weathering processes are primarily sorbed by kaolinite and illite, which are components of soils (Minařík et al., 1998), and by organic compounds.

According to the FOREGS project, the median of yttrium concentration for the topsoil in Europe is 21 mg/kg; the lowest concentrations were found in soils developed on glacial deposits (<17 mg), and the greatest ones – in soils developed on alkaline crystalline rocks (>30 mg/kg).

An overview study on the content of yttrium in soils of Poland, performed in the early 1990s, showed the concentrations of >4 mg/kg in the Sudetes and the Carpathians and their forelands, as well as in the Lublin Upland, Żuławy region and in the area of ice-dammed lake deposits in northern Poland. Soils of the Polish Lowlands commonly contained 2–4 mg/kg of yttrium (Lis, Pasieczna, 1995). A study on arable fields in the whole country has revealed its connections with iron and aluminum, and the concentrations ranging from <2 to 19 mg/kg indicating geogenic origin (Dudka, 1992).

The spatial distribution of yttrium concentration determined from the GEMAS project data confirms regional differences. In most of analysed soils, the yttrium concentration does not exceed 7.20 mg/kg (Plate 24). Elevated concentrations are found at some locations in soils of southern Poland: in the valleys of the Vistula, Dunajec and Wisłoka rivers, and in Cieszyn Silesia, as well as in northern Poland – in the Żuławy region and in soils developed on ice-dammed lake deposits of the Sępopol region. All these locations show the regularity of higher yttrium concentrations in grazing land soils than in arable field soils (Fig. 24).

Tabela 24
Table

Zawartość itru w glebach (mg/kg)
Yttrium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		7–760			Kabata-Pendias, Mukherjee, 2007
Europa – FOREGS projekt Europe – FOREGS project	845	<3–267	21	t.	De Vos, Tarvainen, eds., 2006
Europa – BSS projekt Europe – BSS project	748	<3–47	14	t.	Reimann et al., 2003
Słowacja Slovakia	5189	3–128	26	t.	Čurlik, Šefčik, 1999
Europa – GEMAS projekt Europe – GEMAS project	4132	3–118	26	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	0,23–77	6,6	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	0,01–10,95	3,05	a.r.	Obecna praca This study

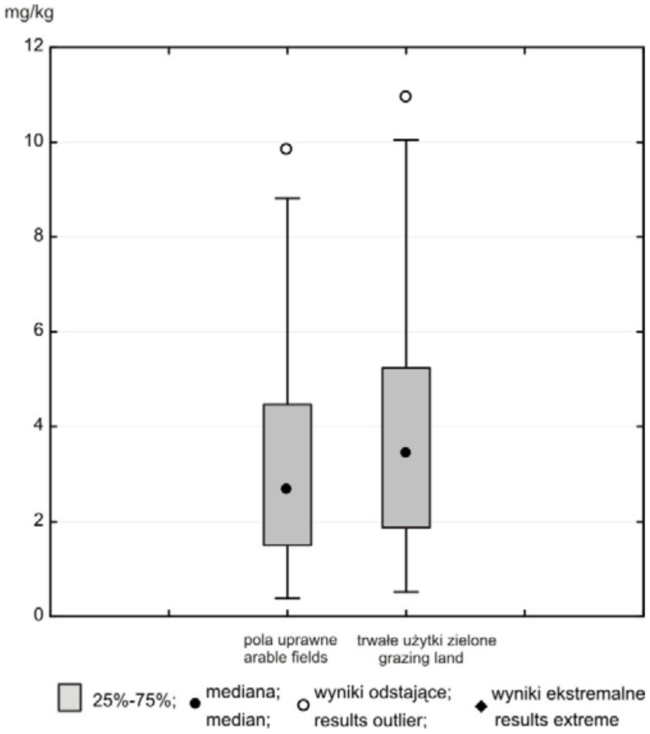

Fig. 24. Porównanie parametrów statystycznych zawartości itru w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of yttrium content in arable fields and grazing land soils

Zr Zirconium

General information

Zirconium easily forms its own minerals occurring as accessory components in igneous rocks, and the most common mineral is zircon $ZrSiO_4$. Part of this element may replace titanium in rutile and ilmenite, and other elements in the crystal lattices of pyroxenes, amphiboles and micas. Zirconium is also dispersed in the minerals of niobium and lanthanides.

Its concentration in granites is approx. 200 mg/kg, in ultramafic rocks – approx. 30 mg/kg, and in limestone and coal – 20 mg/kg. Its hardness and resistance to chemical weathering lead to the accumulation of zirconium minerals in sandy rocks in the form of economic deposits. Zirconium shows very low mobility, even though some amounts are mobilized during the weathering process, and precipitate with ferric and aluminum hydroxides, which leads to its concentration in bauxites (up to several hundred mg/kg). Among sedimentary rocks, also loess is highly enriched with zirconium (400 mg/kg) (Reimann et al. eds., 2014).

Anthropogenic sources

The great majority of zircon is used in the construction of nuclear reactors, in the production of refractories and abrasives, and in the chemical and jewelry industries. Zirconium compounds are used in the industry of packaging and paper products (they are durable, water resistant and non-toxic).

Soils

Accumulation of zirconium in soils depends primarily on its content in the parent rocks. There is also a clear relationship between the zirconium content and their granulometric composition. The smallest contents of this element are found in sandy soils, whereas the greatest concentrations occur in heavy argillaceous soils (Kabata-Pendias, Mukherjee, 2007).

The FOREGS project studies show that the total zirconium concentration in European soils varies within a very wide limits from 5 to 1060 mg/kg (Tab. 25). There is a similar variability in soils of Lithuania. The studies of European soils, performed within the framework of both projects, reveal a distinct difference in the median values between the total zirconium concentration (252 mg/kg) and its part determined after aqua regia digestion (1.7 mg/kg), associated with the resistance of zirconium minerals to acids.

The zirconium concentration in soils of Poland ranges from <0.1 to 8.6 mg/kg, however it does not exceed 2.8 mg/kg in most of the country (Plate 25). The range of zirconium concentration and the median value are higher in grazing land soils (Fig. 25, Tab. 1). Distinct anomalies (>9 mg/kg) occur only in soils developed on ice-dammed lake deposits in the Sępopol region, northern Poland, in the valley of the Orlanka Stream (tributary of the Bug River), and in the Bug River valley in the Lublin region. In these areas, zirconium can originate from the components of soils' parent rocks.

Tabela 25
Table

Zawartość cyrkonu w glebach (mg/kg)
Zirconium content in soils (mg/kg)

	n	Zakres Range	Mediana Median	Rozkład Extraction	Źródło Source
Gleby świata Soils – worldwide data		30–250			Kabata-Pendias, Mukherjee, 2007
Europa – BSS projekt Europe – BSS project	747	1,1–255	66	HF	Reimann et al., 2003
Europa – FOREGS projekt Europe – FOREGS project	845	5–1060	231	t.	Salminen, ed., 2005
Litwa Lithuania	696	5–1020	258	t.	Kadūnas et al.,1999
Europa – GEMAS projekt Europe – GEMAS project	4132	4–963	252	t.	Reimann et al., eds., 2014
Europa – GEMAS projekt Europe – GEMAS project	4132	<0,1–376	1,7	a.r.	Reimann et al., eds., 2014
Polska – GEMAS projekt Poland – GEMAS project	258	<0,1–8,6	0,6	a.r.	Obecna praca This study

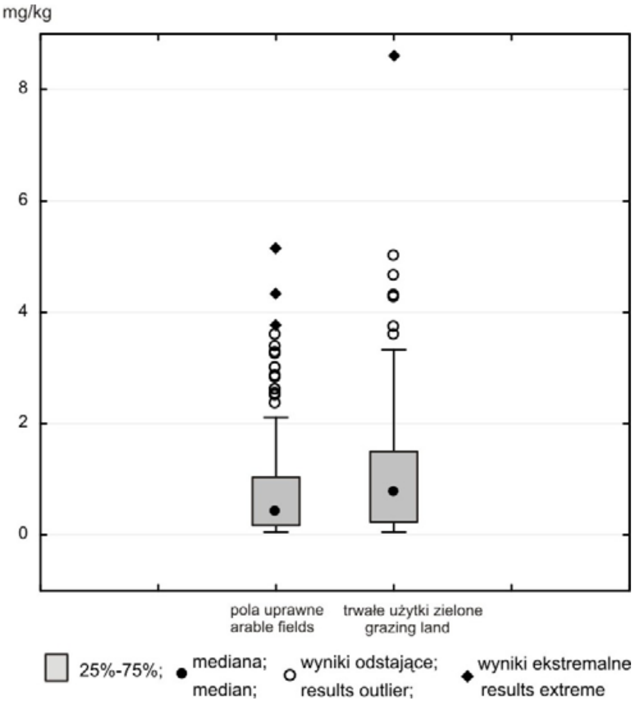

Fig. 25. Porównanie parametrów statystycznych zawartości cyrkonuu w glebach pól uprawnych i trwałych użytków zielonych
Comparison of statistical parameters of zirconium content in arable fields and grazing land soils

CONCLUSIONS

The results of geochemical studies of elements whose concentrations are rarely determined in soils of Poland, presented in a small-scale map (with a density of 1 sample/2500 km^2), made it possible to assess their content and to compare the results with the geochemical background values in European soils. It was often possible to classify the discovered anomalies in terms of their origins (natural or anthropogenic anomalies), and to identify their possible sources.

The content of the analysed elements in arable field and grazing land soils has proven to be dependent primarily on their quantity inherited from the parent rocks exposed on the surface or lying at a small depth. It is worth emphasizing that the chemical composition of agricultural soils of Poland is neither significantly affected by the urbanization, industrial and transport activity, nor by long-term use of fertilizers and pesticides.

Considering individual locations, the elements concentrations were generally higher in grazing land soils than in arable fields due to a greater content of organic matter in the former, which has the ability to binding of many the elements. The TOC contents are significantly higher in grazing land soils (mainly grassland) than in arable field soils.

The spatial distributions of most of the elements indicate their clearly different contents between the northern geochemical province (Polish Lowlands) and the southern province (the Carpathians and the Sudetes). The soils of the northern province, which developed on Quaternary glaciofluvial and fluvial sandy deposits, contain much less elements in comparison with the soils of the Carpathians (developed on flysch deposits) and the Sudetes (developed on igneous and metamorphic rocks, often with abundant signs of mineralization). Soils of the Sudetes reveal anomalies of beryllium, bismuth, cerium, cesium, tin, gallium, indium, lanthanum, niobium, rubidium, scandium and uranium. In the Carpathians, local enrichments with antimony, bismuth, cesium, gallium, indium, molybdenum, rubidium and tellurium are found.

In areas of loess covers (Lublin and Małopolska regions), there are zirconium and hafnium enrichments of soils, which are presumably associated with the presence of both the zircon mineral and admixtures of volcanic components in loess.

The Silesian-Cracow soils are contaminated with thallium, which is a component of zinc and lead sulphide ores, and is spread through ore mining and processing operations.

Local anomalies of several elements in soils of the Polish Lowlands are anthropogenic, but their origin is difficult to clearly define. In some soils developed on alluvial sediments, worth noting is the accumulation of boron, selenium, tin, uranium and tungsten. These anomalous concentrations can be interpreted as originating from the waters and sediments polluted by anthropogenic and lithologic materials derived from the entire rivers basins and accumulated during floods. The favorable environment of these deposits with high sorption capacity (organic muds, as well as clays and peats containing phosphates) determines the concentration of heavy metals and other chemical elements.

REFERENCES

AINSWORTH N., COOKE J.A., JOHNSON M.S., 1990 – Distribution of antimony in contaminated grassland: 1 – Vegetation and soils. *Environ. Pollut.*, **65**: 65–77.

ÁLVAREZ-AYUSO E., OTONES V., MURCIEGO A., GARCÍA-SÁNCHEZ A., SANTA REGINA I., 2013 – Zinc, cadmium and thallium distribution in soils and plants of an area impacted by sphalerite-bearing mine wastes. *Geoderma,* **207–208**: 25–34.

APPLETON J.D., ZHANG QILING., GREEN K.A., ZHANG GUANDI, GE XIAOLI, LIU XINGPING, LI JIA XI, 2006 – Selenium in soil, grain, human hair and drinking water inrelation to esophageal cancerinthe Cixianarea, Hebei Province, People's Republic of China. *Appl. Geochem.*, **21**: 684–700.

ASAMI T., YOSHINO A., KUBOTA M., GOTOH S., 1990 – Background level of indium and gallium in soil with special reference to the pollution of the soils from zinc and lead smelters. *J. Plant Nutritation and Soil Sci.*, **153**, 4: 257–259.

BOHDZIEWICZ L., PAZDRO Z., WRÓBEL B; zaktualizował MOJSKI J.E., 1980 – Mapa geologiczna Polski 1:200 000, ark. Puck. Państw. Inst. Geol. Warszawa.

BOLEWSKI A., 1982 – Mineralogia szczegółowa. Wyd. Geol. Warszawa.

BOJAKOWSKA I., BORUCKI J., 1994 – Molybdenum in stream sediment on the area of occurrence of the Dukla Folds and their margin. *Geol. Quart.*, **38**, 1: 155–168.

BOJAKOWSKA I., BRAŃSKI P., IWASIŃSKA-BUDZYK I., RETKA J., 2010 – Zróżnicowanie zawartości pierwiastków śladowych w iłach poznańskich. *Górnictwo i Geologia*, **5**, 4: 31–40.

BOJAKOWSKA I., LECH D., WOŁKOWICZ S., 2008 – Uran i tor w węglach kamiennych i brunatnych ze złóż polskich. *Gosp. Surow. Miner.*, **24**, 2/2: 53–65.

BOROWSKA K., KOPER J., TYKWIŃSKA T., 2007 – Zawartość selenu w wybranych typach gleb mineralnych regionu Kujaw i Pomorza na tle aktywności oksydoreduktaz. *Ochr. Środ. Zas. Nat.*, **31**: 18–22.

BUGGLE B., GLASER B., ZÖELLER L., HAMBACH U., MARKOVIČ S., GLASER I., GERASIMIENKO N., 2008 – Geochemical characterisation and origin of Southeastern and Easterm European loesses (Serbia, Romania, Ukraine). *Quatern. Sci. Rev.*, **27**: 1058–1075.

CAŁUS-MOSZKO J., BIAŁECKA B., 2012 – Potencjał i zasoby metali ziem rzadkich w świecie oraz w Polsce. *Pr. GIG, Górnictwo i Środowisko*, **4**: 63–74.

CERIUM, 2013. http://www.lenntech.com/periodic/elements/ce.htm#ixzz2iivrDznb

CHOJNICKI J., 2000 – Rare earth elements in alluvial soils of central Vistula valley and Żuławy. *Soil. Sci. Ann.* Poland, **51**: 57–65.

COOK N.J., CIOBANU C.L., SPRY P.G., VOUDOURIS P. & the participants of IGCP-486, 2005 – Understanding gold-(silver) – telluride-(selenide) mineral deposits. *Episodes*, **32**: 249– 263.

CUSTOMS Service of the Republic of Poland. System Isztar – Tariff Information, 2012. http://isztar.mf.gov.pl

CWOJDZIŃSKI S., 2012 – Charakterystyka budowy geologicznej Dolnego Śląska. http://wroclaw.pgi.gov.pl/

ČURLIK J., ŠEFČIK P., 1999 – Geochemical atlas of the Slovak Republik. Soils. Ministry of the Environment of the Slovak Republic.

DE VOS W., TARVAINEN T. (red.), 2006 – Geochemical atlas of Europe. Part 2. Geological Survey of Finland, Espoo.

DIETL C., WABER M., PEICHL L., VIERLE O., 1996 – Monitoring of airborne metals in grass and depositions. *Chemosphere,* **33**, 11: 2101–2111.

DILL H.G., 2010 – The „chessboard" classification scheme of mineral deposits: Mineralogy and geology from aluminum to zirconium. *Earth-Science Rev.,* **100**, 1/4: 1–420.

DOBRZAŃSKI B., ZAWADZKI S. (red.),1993 – Gleboznawstwo. Państw. Wyd. Roln. i Leśne. Poznań.

DRAKE K.M., 1983 – Geochemistry of tin, tungsten and molybdenum in Swedish proterozoic granitoids: Their potential use in regional mineral exploration. *J. Geoch. Explor*. **19**, 1/3: 445.

DUDKA S., 1992 – The concentrations of some scandium subgroup trace metals in soils of Poland. *Geoderma*, **52**, 3/4: 279–289.

DZIEKOŃSKI T., 1972 – Wydobywanie i metalurgia kruszców na Dolnym Śląsku. Wyd. PAN, Warszawa.

ENZMANN R.D., 1972 – Molybdenum: element and geochemistry. *W*: The encyclopedia of geochemistry and environmental sciences. Van Nostrand Reinhold Co, New York.

ENVIRONMENT and Health International, 2006. http://www.ifeh.org/magazine/

ERIKSSON J., 2001 – Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and oil and crops. Swedish EPA Rep. 5159, Stockholm.

EVALUATION of quality control results of aqua regia extraction analysis, 2009 – EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) – NGU Report 2009.049. Geological Survey of Norway, Trondheim. http://www.statistik.tuwien.ac.at/public/filz/papers/2009_049.pdf

FEDORCZUK W.P., MINCER E.F., 1990 – Geołogiczeskij sprawocznik po rtuti, sur'mie, wismutu. Niedra, Moskwa.

FIELD MANUAL, 2008 – EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) – NGU Report 2008.038. Geological Survey of Norway, Trondheim. http://www.ngu.no/upload/Publikasjoner/Rapporter/2008/2008_038.pdf

GUCWA I., WIESER T., 1980 – Geochemia i mineralogia skał osadowych fliszu karpackiego zasobnych w materię organiczną. *Pr. Miner. Kom. Nauk. Miner. PAN*, *Kraków*, **69**: 1–43.

HAMMEL W., DEBUS R., STEUBING L., 2000 – Mobility of antimony in soil and its availability to plants. *Chemosphere,* **41**: 1791–1798.

HILLER E., LALINSKÁ B., CHOVAN M., JURKOVIČ L., KLIMKO T., JANKULÁR M., HOVORIČ R., ŠOTTNÍK P., FLAKOVÁ R., ŽENIŠOVÁ Z., 2012 – Arsenic and antimony contamination of waters, stream sediments and soils in the Western Carpathians, Slovakia. *Appl. Geochem*., **37**: 598–614.

JAKUBOWSKA M., PASIECZNA A., ZEMBRZUSKI W., ŚWIT Z., LUKASZEWSKI Z., 2007– Thallium in fractions of soil formed on floodplain terraces. *Chemosphere,* **66**: 611–618.

JASKÓLSKI S., 1960 – Rudy cyny i kobaltu. *Biul. Inst. Geol.*, **178**: 323–334.

KABATA-PENDIAS A., MUKHERJEE A., 2007 – Trace elements from soil to human. Springer-Verlag Berlin Heidelberg.

KABATA-PENDIAS A., PENDIAS H., 1999 – Biogeochemia pierwiastków śladowych. Wyd. PWN, Warszawa.

KABATA-PENDIAS A., SZTEKE B., 2012 – Pierwiastki śladowe w geo- i biosferze. Wyd. IUNG, Puławy.

KADŪNAS V., BUDAVIČIUS R., GREGORAUSKIENE V., KATINAS V., KLIAUGIENE E., RADZEVIČIUS A., TARAŠKEVIČIUS R., 1999 – Geochemical atlas of Lithuania. Geological Survey of Lithuania. Geol. Inst. Vilnius.

KARAYIGIT A.I., SPEARS D.A., BOOTH C.A., 2000 – Antimony and arsenic anomalies in the coal seams from the Gokler coalfield, Gediz, Turkey. *Intern. J. Coal Geol.,* **44**: 1–17.

KAZANTZIS G., 2000 – Thallium in the environment and health effects. *Environ. Geochem. Health*, **22**: 275–280.

KŁOS A., 2009 – Zastosowanie współczynnika wzbogacenia (EF) do interpretacji wyników badań biomonitoringowych. *Chemia, Dydaktyka, Ekologia, Metrologia*, **14**, 1/2: 49–55.

KOLJONEN T. (red.), 1992 – The geochemical atlas of Finland. Part. 2: Till. Geol. Survey of Finland. Espoo.

KONDRACKI J., 2000 – Geografia fizyczna Polski. Wyd. PWN, Warszawa.

KWECKO P., 2012 – Lantan i cer w glebach Polski. *Prz. Geol*., **60**, 9: 490–495.

LEONARD N.M., WIELAND L.C., MOHAN R.S., 2002 – Applications of bismuth (III) compounds in organic synthesis. *Tetrahedron*, **58**, 42: 8373–8397.

LIS J., PASIECZNA A., 1995 – Atlas geochemiczny Polski. Państw. Inst. Geol. Warszawa.

LIS J., PASIECZNA A., KARBOWSKA B., ZEMBRZUSKI W., LUKASZEWSKI Z., 2003 – Thallium in soils and stream sediments of a Zn–Pb mining and smelting area. *Environ. Sci. Technol*., **37**: 4569–4572.

LIS J., SYLWESTRZAK H., 1986 – Minerały Dolnego Śląska. Wyd. Geol. Warszawa.

LLORENS J.F., FERNANDEZ J.L., QUEROL X., 2000 – The fate of trace elements in a large coal-fired Power plant. *Environ. Geol.*, **40**: 409–416.

LOSKA K., WIECHUŁA D., KORUS I., 2004 – Antimony concentration in farming soil of southern Poland. *Bull. Environ. Contam. Toxicol.*, **72**: 858–865.

LUETH V.W., 1999 – Bismuth: Element and geochemistry. *W*: Encyclopedia of Geochemistry (C.P. Marsshall, R.W. Fairbridge red.): 43–44. Kluwer Academic Publ. Dordrecht, Germany.

MADZIARZ M., SZTUK H., 2006 – Eksploatacja rud cyny w Górach Izerskich: historia czy perspektywa dla regionu. *Pr. Nauk. Inst. Górn. PWroc.*, **117**, 32.

MAŁECKA K., 2007 – Geochemiczna zmienność pierwiastków ziem rzadkich i metali ciężkich w osadach profundalu i litoralu wybranych jezior Polski. *Biul. Państw. Inst. Geol.*, **450**: 63–73.

MARKS L., BER A., GOGOŁEK W., PIOTROWSKA K., 2006 – Mapa geologiczna Polski 1:500 000. Państw. Inst. Geol. Warszawa.

MAYER W., MOCHNACKA K., JANCZYSZYN J., 1997 – REE and trace elements in the schists of Stara Kamienica Belt, Gierczyn area, SW Poland. *Miner. Pol.*, **28**, 1: 69–86.

MIECZNIK J.B., STRZELECKI R., WOŁKOWICZ S., 2011 – Uran w Polsce – historia poszukiwań i perspektywy odkrycia złóż. *Prz. Geol.*, **59**, 10: 668–697.

MIGASZEWSKI Z., GAŁUSZKA A., 2003 – Zarys geochemii środowiska. Wyd. Akad. Świętokrzyskiej w Kielcach.

MINAŘÍK L., ŽIGOVÁ A., BENDL J., SKŘIVAN P., ŠT'ASTNÝ M., 1998 – The behaviour of rare-earth elements and Y during the rock weathering and soil formation in the Říčany granite massif, Central Bohemia. *Sci. Tot. Environ*., **215**: 101–111.

NIEDZIELSKI P., SIEPAK M., SIEPAK J., 2000 – Występowanie i zawartości arsenu, antymonu i selenu w wodach i innych elementach środowiska naturalnego. *Rocz. Ochr. Środ.*, **2**: 317–340.

PARAFINIUK J., DOMAŃSKA J., 2002 – Bismuth minerals from Rędziny (Rudawy Janowickie, SW Poland). *Miner. Pol.*, **33**, 2: 3–14.

PASIECZNA A., 2011 – Naturalne i antropogeniczne czynniki zanieczyszczenia środowiska. http://www.pgi.gov.pl/pl/geochemia-kopalnia-lewe/3678-naturalne-i-antropogeniczne-czynniki-zanieczyszczenia-rodowiska-.html

PASIECZNA A., KWECKO P., 2010 – Projekt GEMAS. Zdjęcie geochemiczne gleb użytkowanych rolniczo i łąk w Europie. *Prz. Geol.*, **58**, 5: 397–400.

PATORCZYK-PYTLIK B., KULCZYCKI G., 2009 – Content of selenium in arable soils near Wrocław. *J. Elementol*., **14**, 4: 755–762.

PAUL Z., 1991 – Szczegółowa mapa geologiczna Polski 1:50 000, ark. Grybów. Państw. Inst. Geol. Warszawa.

PAUL Z., 1993 – Objaśnienia do Szczegółowej mapy geologicznej Polski 1:50 000, ark. Grybów. Państw. Inst. Geol. Warszawa.

PAULO A., 1970 – Minerały niklu i bizmutu w żyłach kruszcowych okolicy Chełmca (Góry Kaczawskie, Dolny Śląsk). *Pr. Miner. PAN Oddz. w Krakowie*, **24**: 61–82.

PAULO A., LIS J., PASIECZNA A., 2002 – Tal pod koniec XX wieku. *Prz. Geol.*, **50**, 5: 403–407.

PAULO A., STRZELSKA-SMAKOWSKA B., 1997 – Cyna w ostatniej dekadzie XX wieku. *Prz. Geol.*, **42**, 9: 844–855.

PAULO A., STRZELSKA-SMAKOWSKA B., 2000 – Antymon pod koniec XX wieku. *Prz. Geol.*, **48,** 2 112–117.

PAULO A., STRZELSKA-SMAKOWSKA B., 2001 – Bizmut pod koniec XX wieku. *Prz. Geol.*, **49,** 1: 28–32.

PERKINS W.T., 2011 – Extreme selenium and tellurium contamination in soils –An eighty year-old industrial legacy surrounding a Ni refinery in the Swansea Valley. *Sci. Tot. Environ.*, **412–413**: 162–169.

PLOUFFE A., RASMUSSEN P.E., HALL G.E.M., PELCHAT P., 2004 – Mercury and antimony in soils and non-vascular plants near two past-producing mercury mines, British Columbia, Canada. *Geochem. Explor. Environ. Anal.*, **4**: 353–364.

PODBIERA-MATYSIK K., GORAZDA K., WZOREK Z., 2012 – Kierunki zastosowania i pozyskiwania metali ziem rzadkich. *Czas. Techn. Chemia*, **16**, 1-Ch: 147–155.

POLAŃSKI A., 1974 – Geochemia i surowce mineralne. Wyd. Geol. Warszawa.

POLAŃSKI A., 1979 – Izotopy w geologii. Wyd. Geol. Warszawa.

POLAŃSKI A., SMULIKOWSKI K., 1969 – Geochemia. Wyd. Geol. Warszawa.

POŁEDNIOK J., 2008 – Speciation of scandium and gallium in soils. *Chemosphere*, **73**: 572–579.

RANK G., KARDEL K., PÄLCHEN W., WEIDENSDÖRFER H., 1999 – Bodenatlas des Freistaates Sachsen. Sächsiches Landesamt für Umweltund Geologie, Dresden.

REIMANN C., ÄYRÄS S., CHEKUSIN V., BOGATYREV I., BOYD R., CARITAT P., DUTTER R., FINNE T.E., HALLERAKER J.H., JÆGER Ø., KASHULINA G., LEHTO O., NISKAVAARA H., PAVLOV V., RÄISÄNEN M.L., STRAND T., VOLDEN T., 1998 – Environmental geochemical atlas of the Central Barents Region. Geol. Survey of Norway, Trondheim.

REIMANN C., BIRKE M., DEMETRIADES A., FILZMOSER P., O'CONNOR P. (red.), 2014 – Chemistry of Eourope's agricultural soils. Part A, Part B. Geologisches Jahrbuch, Sonderhefte, Reihe B, Band B 102–103.Schweizerbart'sche Verlagsbuchhandlung, Hannover.

REIMANN C., MATSCHULLAT J., BIRKE M., SALMINEN R., 2010 – Antimony in the environment: Lessons from geochemical mapping. *Appl. Geochem.*, **25**: 175–198.

REIMANN C., SIEWERS U., TARVAINEN T., BITYUKOVA L., ERIKSSON J., GILUCIS A., GREGORAUSKIENE V., LUKASHEV V., MATINIAN N.N. PASIECZNA A., 2003 – Agricultural soils in Northern Europe: A geochemical atlas. Geologisches Jahrbuch, Sonderhefte, Reihe D, Heft SD 5, Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

ŘÍDKOŠIL T., SKÁLA R., JOHAN Z., ŠREIN V., 2001 – Telluronevskite, Bi_3TeSe_2, a new mineral. *Europ. J. Miner.*, **13**, 1: 177–185.

SADEGHI M., PETROSINO P., LADENBERGER A., ALBANESE S., ANDERSSON M., MORRIS G., LIMA A., DE VIVO B., and the GEMAS Project Team, 2013 – Ce, La and Y concentrations in agricultural and grazing-land soils of Europe. *J. Geochem. Explor.*, **133**: 202–213.

SALMINEN R. (red.), 2005 – Geochemical atlas of Europe. Part 1. Geol. Survey of Finland, Espoo.

SAWICKI L. (red.), 1965 – Mapa geologiczna regionu dolnośląskiego w skali 1:200 000. Wyd. Geol. Warszawa.

SENESI G.S., BALDASSARRE G., SENESI N., RADINA B., 1999 – Trace elements inputs into soils by anthropogenic activites and implication for human health. *Chemosphere*, **39**: 343–377.

SHILLER A.M., FRILOT D.M., 1996 – The geochemistry of gallium relative to aluminum in Californian streams. *Geochem. Cocmoch. Acta,* **60**, 8: 1323–1328.

SKIBNIEWSKA E.M., KOŚLA T., 2007 – The evaluation of rubidium content in the soils of Poland. *Ochr. Środ. Zas. Nat.*, **31**: 13–17.

SKOMPSKI S., 2000 – Objaśnienia do Szczegółowej mapy geologicznej Polski 1:50 000, ark. Puck. Państw. Inst. Geol. Warszawa.

TAKEDA A., KIMURA K., YAMASAKI S., 2004 – Analysis of 57 elements in Japanese soils, with special reference to soil group and agricultural use. *Geoderma*, **119**, 3/4: 291–307.

TOMASZEWSKA B., 2010 – Bor w wodach podziemnych i odciekach składowiskowych. *Techn. Poszuk. Geol.*, **1–2**: 161–170.

TOMZA-MARCINIAK A., BĄKOWSKA M., PILARCZYK B., SEMENIUK M., HENZEL D., UDAŁA J., BALICKA-RAMISZ A., TYLKOWSKA A., 2010 – Stężenie selenu w glebie i wybranych narządach saren (*Capreolus capreolus*) z terenu województwa wielkopolskiego. *Acta Sci. Pol., Zootechnica* **9**, 4: 251–260.

TOVERUD Ö., 1984 – Dispersal of tungsten in glacial drift and humus in Bergslagen, southern central Sweden. *J. Geochem. Explor*., **21**, 1/3: 261–272.

VANĚK A., CHRASTNÝ V., MIHALJEVIČ M., DRAHOTA P., GRYGAR T., KOMÁREK M., 2009 – Lithogenic thallium behavior in soils with different land use. *J. Geochem. Explor*., **102**, 1: 7–12.

VANĚK A., CHRASTNÝ V., KOMÁREK M., PENÍŽEK V., TEPER L., CABALA J., DRÁBEK O., 2013 – Geochemical position of thallium in soils from a smelter-impacted area. *J. Geochem. Explor*., **124**: 176–182.

VESELÝ J., NORTON S.A., SKŘIVAN P., MAJER V., KRÁM P., NAVRÁTIL T., KASTE J.M,. 2002 – Environmental chemistry of beryllium. *Rev. Miner. Geochem.*, **50**: 291–317.

WATANABE N., INOUE S., ITO H., 1999 – Antimony in municipal waste. *Chemosphere*, **39**, 10: 1689–1698.

WEDEPOHL K.H., 1995 – The composition of the continental crust. *Geoch. Cosmoch. Acta*., **59**, 7: 1217–1232.

WIERZBICKA M., SZAREK-ŁUKASZEWSKA G., GRODZIŃSKA K., 2004 – Highly toxic thallium in plants from the vicinity of Olkusz (Poland). *Ecotoxicol. Environ. Safety*, **59**, 1: 84–88.

WILLIAMS-JONES A., MIGDISOV A.A., ARCHIBALD S.M., XIAO Z., 2002 – Vapor-transport of ore metals. Water-rock interactions, ore deposits, and environmental geochemistry. The Geochemical Society, Special Publication No. 7: 279–306. http://www.eps.mcgill.ca/~artas/publish/Crerar.pdf

WYDOBYCIE URANU W PRL. http://www.atom.edu.pl/index.php/ej-w-polsce/wczoraj/wydobycie-uranu-zaklady-r-1.html

YANG N., SUN H., 2007 – Chemistry of bismuth. *Coord. Chem. Rev*., **251**, 17/20: 2354–2366.