INTRODUCTION

The Polish Geological Institute – National Research Institute has conducted geochemical studies of urban and industrial areas for 25 years. Their goal is to assess the degree of contamination of soils, sediments of inland water bodies, and surface waters in areas of urban agglomerations of Poland.

The first study made within the whole research programme, published in the form of maps, was the *Geochemical Atlas of Warsaw and Environs, scale 1:100,000* (Lis, 1992). That atlas provided results of analysis of topsoil and sediments examined in the years 198921990. The range of determinations comprised a much smaller spectrum of elements and indicators as compared to the present-day analytical potential. Density of sampling was half the density used within the present study. Moreover, the *Atlas* from 1992 is out of print now. Simultaneously, the demand for environmental data has increased over the last years. Such information is useful in assessing local land use plans, making decisions concerning environmental constraints, giving water-legal permits, assessing groundwater hazards, and discharging duties imposed upon district governors by the Environmental Protection Law, i.e. conducting regular soil quality tests within the framework of state monitoring system.

On account of the rapid pace of changes in the landscape of the city in the past 20 years, it has been necessary to update the geochemical maps of surface environments in Warsaw. In 2013, the Ministry of the Environment ordered to undertake a research project to produce a new *Geochemical Atlas of Warsaw and Environs*. The project was financed by the National Fund for Environmental Protection and Water Management.

The study area (about 1200 km²) covers the territory of Warsaw and its environs, including Łomianki, Ząbki, Marki, Zielonka, Kobyłka, Wołomin, Sulejówek, Józefów, Otwock and Piastów, as well as parts of Konstancin-Jeziorna, Piaseczno and Pruszków. The aim of the project is to present, in the cartographic form, the current degree of contamination of soil from two depth intervals, as well as of river, stream and lake sediments, and surface waters. Samples of soils, sediments and surface waters from the city were collected based on a regular grid of 500×500 m, in order to produce maps at the scale of 1:50,000 for areas within the limits of Warsaw. It is worth noting that there is no other agglomeration in Europe covered by such a detailed geochemical study.

It is important to undertake examinations of sediments and surface waters which are very sensitive indicators of pollution sources and are the first sign that warns people of environmental hazards. They may give rise to take rapid action to eliminate degradation. Of particular importance are studies of small stagnant water bodies and small watercourses, which are most vulnerable to pollution and are not covered by the water monitoring system conducted by the Chief Inspectorate of Environmental Protection.

The new *Geochemical Atlas of Warsaw and Environs* is published as a printed version and will be available on-line on the websites of PGI-NRI (www.mapgeochem.pgi.gov.pl) and the Ministry of the Environment.

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CHARACTERISTICS OF THE MAP AREA

Amongst large European capitals, Warsaw is a unique city in terms of its natural environment. It lies on the Vistula River, one of the largest rivers of Europe. The river's landscape has been

transformed insignificantly by human impact. In the immediate proximity to the city there are large protected areas. These include: Kampinos National Park, Masovian Landscape Park (lying partially within the boundaries of Warsaw) and Chojnów Landscape Park. By the end of 2013, 23.6% of the area of Warsaw constituted a legally protected area of outstanding natural beauty. The greatest contribution (64.7%) to the area is made by protected landscape areas (Panorama ..., 2014) included in the Warsaw Protected Landscape Area (Warszawski Obszar Chronionego Krajobrazu – WOChK), located within 50 municipalities of the Masovian Voivodeship and within most of the districts of Warsaw. The Warsaw Protected Landscape Area includes areas protected for their distinguishing landscape features characterised by diverse ecosystems, which also serve as the places of rest and recreation for the residents of Warsaw and nearby towns. In the area of Warsaw and its surroundings there are also nature reserves, ecological sites, landscape-nature protected complexes and natural monuments.

Part of the map sheet comprises areas included in the European ecological network of Natura 2000, e.g. the special protection area for birds – Middle Vistula River Valley, covering an area of 2350.6 ha within the limits of Warsaw (Europejska Sieć..., 2015). Special areas of conservation of natural habitats include: Białe Błota (in the municipality of Wołomin), Bielany Forest, Jan III Sobieski Forest, Natolin Forest, Czarna Struga Riparian Forests, Rembertów military area, Kampinos Forest, Strzebla Błota (in Zielonka).

Geographical and administrative setting. Warsaw is the capital of Poland and the Masovian Voivodeship, and the largest city in the country in terms of both area (517.2 km²) and population (1,735,400 residents –as at 31.12.2014; Dane o Warszawie..., 2014). Warsaw is divided into 18 districts (quaters).

Warsaw is located in the middle course of the Vistula River that divides the city into the left-bank side and right-bank side. The natural water system in the area covered by the *Atlas*, wholly included in the Vistula River drainage basin, is represented by natural watercourses and reservoirs, as well as water facilities (canals). The natural watercourses drain mostly less urbanized areas – the suburbs of Warsaw and their surroundings. The most important watercourses include: Utrata, Raszynka, Łasica, Czarna, Długa, Świder, Jeziorka, Wilanówka and Potok Służewiecki. The kettle lakes and oxbow lakes are of natural origin, mainly glacial. Artificial reservoirs are represented predominantly by postmining depressions in areas of extraction of ceramic clays for the construction industry (so-called clay pits), water storage and fire protection reservoirs, ponds in parks, fortification moats, and port basins. Beyond the city limits there are also fishing ponds.

Relief and geomorphology. According to the physico-geographical regionalization of Poland, the whole map sheet area lies within the Central Masovian Lowland of the Middle-Polish Lowlands (Kondracki, 2009). The major morphologic units present in the territory of Warsaw and its environs include moraine uplands and the Vistula River valley.

Relief of the upland surfaces originated during the Middle Polish Glaciations. Most of the Warsaw left-bank side is located in the Warsaw Plain that passes westward into the Łowicz-Błonie Plain, and is bounded to the east by the steep escarpment of the Vistula valley, 10–30 m in height (Krzywicki, 2013). The Wołomin and Garwolin plains cover the eastern and south-eastern parts of the map sheet area.

The eastern part of Warsaw is located on alluvial terraces of the Vistula (op.cit.).

Four over-flood fill terraces and two flood terraces have developed in the Vistula valley (Morawski, Nowacka, 2007; Morawski, 2008). The oldest and uppermost terrace in the map sheet area within the Vistula valley is the Warsaw-Błonie cut-fill terrace (northern part of the Warsaw Plain).

A characteristic element of the flood terrace relief are sand dunes and covers of aeolian sands. Landscape of the flood terraces reveals preserved oxbow lake depressions; some of them still filled with water. The largest ones include the lakes of Wilanowskie, Czerniakowskie and Kamionkowskie (Sarnacka, 1992).

The natural highest elevation point on the left-bank side of the map sheet is located in the district of Wola, in the area of the bus depot "Redutowa" (115.7 m a.s.l.). On the right-bank side such a point is in Pogorzel, east of Otwock (125.7 m a.s.l.).

There are several anthropogenic mounds in the topography of the city. The highest one – Górka Szczęśliwicka hill (152 m) – was formed from rubble and debris stored here in the 1950s, and later also from garbage and soils brought from construction sites. The Warsaw Uprising Mound in Siekierki was also formed from garbage and rubble of destroyed buildings of Warsaw. The Kazurka Górka and Kopa Cwila hills in Ursynów have been built of soil, till and sand from excavations for the construction of buildings, roads and the metro tunnels (Krzywicki, 2013).

Relief transformation in Warsaw is also a result of the backfill of topographic lows, ponds, clay pits and oxbow lakes with soils and debris.

Built-up areas and land use. The land use structure in the Capital City of Warsaw is as follows: 55.6% – built-up and urbanized areas, 22.6% – agricultural land, 17.0% – woodlands, wooded and shrubbed areas, 4.8% – land under water and others (Przegląd..., 2015). Field observations during sampling show that the areas surrounding the city are represented by built-up zones and wasteland (approx. 45%), arable land (approx. 18%) and forests (approx. 35%) (Pl. 3).

Economy. The Capital City of Warsaw is an important economic, political, scientific and cultural centre. It is the second, after the Upper Silesian Industrial District, largest industrial centre of Poland, despite the fact that many old large industrial plants have been closed down as a result of political system changes after 1989. The main industrial branches currently operating in Warsaw include: electrical engineering, chemical, printing, food, metallurgical and energy industries.

The localities around Warsaw are the areas where small factories and trade and service companies operate. Single larger industrial plants, representing the glass, chemical, fuel, machinery, metal,

electrical, food, wood and energy industries are distributed in Wołomin, Kobyłka, Marki, Piastów, Pruszków and Ożarów Mazowiecki.

Warsaw is a major international and domestic transport hub, including road, railway and air transportation. By the end of 2014, 1299.9 thousand motor vehicles were registered in Warsaw, of which 81.9% were passenger cars (Przegląd..., 2015).

GEOLOGY AND MINERAL DEPOSITS

The map sheet area covers the central part of the Masovian Depression that developed within Mesozoic deposits and is filled with Cretaceous, Palaeogene, Neogene and Quaternary formations.

On the geological map (<u>Pl. 1</u>), lithological distinctions for the deposits exposed at the surface are numbered in a sequence from the youngest to the oldest (1-44).

Cretaceous. The oldest deposits found in the map sheet area are Cretaceous marine marls, limestones and sandstones (Morawski, Nowacka, 2007; Morawski, 2008). In the central part of the depression their top surface occurs at a depth of 260–290 m (Frankowski *et al.*, 2000).

Palaeogene.<u>Oligocene</u> deposits form an almost continuous layer above Cretaceous rocks, lining the bottom of the Masovian Depression. These are marine clastics with glauconite, represented largely by quartz sands, muds and clays. Their thickness varies from 50 to 60 m (Sarnacka, 1992).

Neogene. The sub-Quaternary basement is represented throughout the area by Neogene deposits (44). These are glaciotectonically strongly deformed <u>Miocene</u> clays, the so-called variegated clays, outcropping or underlying a thin cover of Quaternary deposits in the elevations of the so-called Warsaw folds – near Lipków, Łomianki and Otwock (Morawski 1979, 1980, 2008; Morawski, Nowacka, 2007). They also crop out at some places in the Warsaw Escarpment, e.g. in Młociny (Krzywicki, 2013).

Quaternary. Nearly the entire study area is covered by Quaternary deposits. They are only lacking in areas of glaciotectonically elevated outcrops of the Neogene clays. The greatest thicknesses (up to 225 m) are recorded in deep erosional incisions, whereas the smallest ones (20–60 m) are observed in zones of simple tectonic setting (Frankowski *et al.*, 2000; Krzywicki, 2013).

<u>Pleistocene</u> deposits of the area (usually glacial tills) incorporate relatively frequent detached rocks of Neogene and Palaeogene age. These are usually sands and muds with lignite, and the Neogene variegated clays (43) (Morawski, 2011; Morawski, Pielach, 2011). Detached Neogene deposits are exposed near Sulejówek and Zabraniec (SE of Wołomin).

Pleistocene deposits of the Warsaw area are represented by the following complexes: Preglacial, South Polish, Middle Polish and North Polish (*op.cit.*).

The Preglacial fluvial and lacustrine deposits, up to 29 m thick (known from boreholes only), occur predominantly in the upland area of the left-bank side of Warsaw at depths of 27–67 m (Morawski, 1979, 1980; Krzywicki, 2013).

Among deposits representing the South Polish Complex, the only ones exposed at the surface are tills of the S a n i a n 2 G l a c i a t i o n (42), occurring as small patches to the NE of Otwock. Their presence at the surface is associated with an uplift of Neogene deposits in this area, in the so-called Wólka Mlądzka Elevation (Baraniecka, 1975, 1976).

The Middle Polish Complex is represented by deposits of the Krznanian and Odranian glaciations. During the K r z n a n i a n G l a c i a t i o n, glaciolacustrine deposits were accumulated in valleys and topographic lows (41). Vast upland areas extending on both sides of the Vistula River were the zones of glaciofluvial accumulation of sands and gravels (40), several metres in thickness (Sarnacka, 1992). Glaciolacustrine sands and muds (41) of this glaciation are exposed at the surface of the denuded escarpment of the Warsaw-Błonie terrace in the Wólka Węglowa–Laski region, whereas glaciofluvial deposits (40) appear at the surface to the NE of Otwock near Wólka Mlądzka and Żanęcin.

Deposits of the Lower, Middle and Upper stadials of the O d r a n i a n G l a c i a t i o n are present at the surface of the uplands on both sides of the Vistula valley (Morawski, 2011). Glaciolacustrine clays (39) of the Lower Stadial occur in the Warsaw Upland (districts of Śródmieście and Mokotów) upon the eroded surface of the Warsaw-Błonie terrace, and in the Vistula valley. These are brown and grey varved clays of the "Lower Pilica Lake", exceeding 20 m in thickness. These deposits are exposed at the south-western edge of the map sheet area near Kajetany. Dark grey concise sandy tills of the Lower Stadial (38), frequently containing detached Neogene deposits, are found almost throughout the whole area. On the western side of the Vistula valley, they form a continuous layer with a thickness from a few to several metres. They are exposed in the Warsaw Escarpment in Ursynów and from Służewiec to the Citadel, in Żoliborz, Bielany and Włochy, as well as in the Stare Babice and Raszyn areas. On the eastern side of the Vistula, outcrops of glacial tills (38) were reported from the Świder region.

The oldest deposits assigned to the Middle Stadial of the Odranian Glaciation are represented by the lowermost series of the Warsaw Ice-Dammed Lake. These are glaciolacustrine brown clays and muds (37), exceeding a thickness of 11 m (Sarnacka, 1980a, b). The deposits are exposed in the slopes of the Vistula and Jeziorka valleys, in the districts of Bielany, Żoliborz, Bemowo and Włochy, as well as near Sulejówek (in the Długa River valley).

In the Warsaw Upland, glaciofluvial sands and gravels (36) are fairly common deposits. They were accumulated during the ice-sheet advance of the Middle Stadial (Morawski, 2011; Morawski, Pielach, 2011), and overlie glaciolacustrine deposits or glacial tills of the Lower Stadial. In some places they consist of two or three levels with a thickness from a few to several metres. These are fine- and medium-grained sands with admixture of gravel. They occur at the surface in the districts of

Śródmieście, Żoliborz, Wola, Bemowo, Ochota, Włochy and Mokotów, and outside of Warsaw in the Stare Babice area, between Piastów and Pruszków, as well as in the Otwock region (Baraniecka, 1975, 1976).

The glaciofluvial and glaciolacustrine deposits are covered by glacial tills laid down by the ice sheet of the Middle Stadial: brown sandy tills, weathered and decalcified at the top (35). These deposits occur in the uplands but have been removed by erosion in the Vistula valley. In the Warsaw Upland area the tills are preserved only in the form of thin patches, mainly in the districts of Śródmieście, Żoliborz, Wola, Ochota and Włochy, as well as in the areas of Iwiczna, Mysiadło, Janki and Pruszków. On the eastern side of the Vistula valley, small patches of the tills are exposed south of Sulejówek.

Small glacial depositional landforms of the Middle Stadial of the Odranian Glaciation are preserved mainly in the upland area on the eastern side of the Vistula valley. Patchy covers of sands and gravels with boulders (34) occur near Sulejówek and in the Duczki area (NE of Wołomin). Gravels and sands of end moraines compose depositional landforms found in the Sulejówek and Konstancin-Jeziorna regions (33). Small landforms represented by gravels and sands of dead-ice blocks are observed east of the village of Majdan (32). Denuded surface of the Warsaw Upland and Warsaw-Błonie terrace (near Stare Babice, between the villages of Klaudyn and Macierzysz) is covered by ridges (31) trending NNE–SSW and attaining a relative height of 2–7 m, interpreted as eskers or crevasse-fill landforms (Morawski, 1979, 1980). Fine-grained sands and sandy muds of kames (30) form small but locally relatively extensive landforms in the Pruszków region, south of Raszyn, near Iwiczna, and in Ursynów.

During the Middle Stadial ice-sheet retreat, glaciofluvial sands, gravels and muds (29) were accumulated. On the eastern side of the Vistula River valley these deposits (a few metres thick) overlie glacial tills of the Middle Stadial and cover large areas in the Aleksandrów and Stara Miłosna regions. In the Warsaw Upland, similar deposits occur as isolated patches in the districts of Wola, Śródmieście and Żoliborz. Larger areas of these deposits are found in Włochy, Ursynów and, outside of Warsaw, southwest of Raszyn and between Wólka Węglowa and Stare Babice.

During the interstadial period, strong fluvial erosion took place in Masovia. Deposits of that age – fluvial sands, gravels and muds with peats and peaty muds (28) – occur at the surface in Raszyn (7.8 m thick) in the Raszynka River valley (Morawski, 2008) and in the vicinity of Pruszków in the Utrata River valley. Well-sorted, river-washed variously grained sands with gravel, locally with interbeds of peats and muds (27), are exposed in the Jeziorka River valley near Konstancin-Jeziorna and in the Jeziorka drain valley. Minor outcrops of these deposits occur also at the escarpment edge in the area of Konstancin-Jeziorna and Natolin.

During the ice-sheet advance of the Upper Stadial, glaciolacustrine clays and sands of the Warsaw Ice-Dammed Lake were accumulated (26). These are varved clays, a few metres thick, with glaciolacustrine sands at the top, exposed in the Jeziorka drain valley.

Heavily washed brown tills (2–6 m thick) of the Upper Stadial of the Odranian Glaciation (25) are found in the Czarna River valley (NW of Wołomin). Closer to the Vistula valley this series has been removed by erosion (Morawski, 2011; Morawski, Pielach, 2011). The Upper Stadial ice sheet also deposited sands and gravels with boulders (24) encountered as small patches in the north-eastern part of the map sheet (near Nowe Grabie and Stare Grabie). Small glacial depositional landforms represented by eskers (23) and end moraine ridges (22) are preserved in the same area.

During the Upper Stadial ice-sheet retreat, glaciofluvial sands and muds were deposited (21). Covers of fine- to medium-grained sands with intercalations of coarse-grained sands and gravels, usually attaining a thickness of 2 m, occur to the NE of Wołomin. They comprise the south-western part of a large outwash plain. In the Wołomin region, there are also local occurrences of glaciolacustrine deposits – clays, muds and sands (20).

The North Polish Complex is represented by Eemian Interglacial and Vistulian Glaciation deposits.

During the Eemian Interglacial, after the ice sheet retreat, the Vistula River incised into the upland area to a depth of 40 m to form a wide valley, 11 km in width, similar in shape to the present-day. A complex of fluvial sediments was formed within the valley, which comprises three sedimentary cycles with a total thickness of up to 40 m. It consists mostly of gravels with admixture of pebbles and coarse-grained sands (19) occurring over relatively large areas in the eastern part of the map sheet. Lacustrine deposits – peats, gyttjas, lake chalk, bituminous shale and lake clays (18) – were also deposited at that time. They fill fossil lake basins in a tunnel valley crossing Warsaw and running from Żoliborz through Wola and Szczęśliwice to Okęcie. In the district of Wola the valley splits toward the west to form another parallel valley running along the line Wola–Włochy–Opacz (Morawski, 1979, 1980). The thickness of the organic deposits in the Moczydło area is 11 m, and in the district of Włochy – 6.5 m. On the surface these deposits are exposed in Okęcie.

During the V i s t u l i a n G l a c i a t i o n the ice sheet did not cover the area of Warsaw and its surroundings. In the ice-marginal zone, erosional and denudational processes operated throughout upland areas. The Żoliborz tunnel valley was being filled with glaciofluvial deposits, while the accumulation of glaciolacustrine sediments occurred in the rejuvenated Warsaw Ice-Dammed Lake. The northern part of the map sheet was an area of limited glaciofluvial and fluvial deposition. Later in time, fluvial erosion and accumulation of fluvial terraces took place in the Vistula River valley. At the end of the glaciation, aeolian sediments were deposited.

Lacustrine and local fluvial sands and muds (17) comprise the uppermost part of the deposits filling the Żoliborz-Szczęśliwice tunnel valley and its branch. These deposits are a few metres thick and locally contain patches of alluvial muds and peats.

Glaciofluvial sands and gravels (16) deposited by melt waters flowing from the ice front from the north and northwest occupy large areas between Tarchomin and Legionowo.

The Vistulian ice-sheet hampered the outflow of river waters toward the north, resulting in the formation of a vast ice-dammed lake (Warsaw Ice-Dammed Lake) where younger deposits were

accumulated (Morawski, 2011; Morawski, Pielach, 2011). These are represented by chocolate-brown varved clays with intercalations of clayey muds and silty sands (15), occurring in the Wołomin Plain where they form a continuous layer attaining a thickness of several metres. Small patches of these deposits are exposed locally in Radość, Targówek near the Kawęczyn power plant, and in the areas of Kobyłka and Marki.

Erosion associated with the migration of the Vistula River channel resulted in the formation of the Warsaw-Błonie cut-fill terrace where fluvial sands and gravels are exposed between Marymont and Młociny (14).

A stepwise retreat of the ice-sheet and, consequently, the unblocking of the Vistula River valley gave rise to repeated cycles of fluvial erosion and accumulation, which resulted in the formation of upper over-flood terraces of the Vistula. Fluvial sands and gravels composing the upper over-flood terraces (Otwock and Falenica/Kampinos terraces) occur in a wide belt on the right bank of the Vistula River (13). The lower over-flood terraces (upper Praga and lower Praga terraces) are made up of sands and gravels and local patches of muds on the surface (12 and 11). These deposits have a thickness of 6–10 m and lie at an elevation of 75–80 m a.s.l. *(op. cit.)*. They are exposed on both sides of the Vistula River, however over a much larger area on its eastern side.

Alluvial fan deposits (sands with gravel), a few metres in thickness (10), are observed only in Łazy (S of Magdalenka).

<u>Pleistocene and Holocene</u>. Distinguishing between deposits that accumulated at the end of the Odranian Glaciation and those deposited during the Vistulian Glaciation is often impossible. It refers especially to deposits accumulated on upland areas as a result of denudational, weathering, slope and aeolian processes.

Residual deposits occur over small areas of the uplands, especially on slopes. These are covers of loamy sands with gravels and loamy lenses (9), up to 2 m in thickness. On the surface, they occur along the northern and north-western boundary of the Warsaw-Błonie terrace (Łomianki region, from Izabelin to Młociny) and in the Wólka Mlądzka elevation.

Eluvial deposits consist of two series of different origins (8). Sands with gravels and boulders occur on valley slopes and in closed drainage depressions in the vicinity of Wołomin, Sulejówek and Aleksandrów. Another lithologic type is represented by weathering mantles composed of deposits resembling loess in terms of structure and mechanical composition. They cover the Warsaw-Błonie terrace, ranging in thickness from several tens of centimetres to 2 m in the area situated west of Włochy and Bemowo.

The aeolian deposits are represented by light yellow and yellow-beige fine-grained sands (6 and 7) forming covers attaining a thickness of 3 m, and dunes. They occur on the Vistula over-flood terraces, mainly the Otwock and Kampinos terraces, from which they spread onto the Warsaw-Błonie terrace. The dunes commonly form longitudinal or NW–SE-trending ridges as well as parabolic landforms and others. The relative height of the dunes ranges from several to 20 m.

In the <u>Holocene</u>, flood terraces developed and the present-day Vistula riverbed was shaped as a result of three successive cycles of erosion and accumulation. The flood terraces are composed of variously grained sands with admixture of gravel (4) and have a thickness of a few metres. They occupy large areas on both sides of the river.

During floods, alluvial muds were deposited on lower over-flood terraces and flood terraces. Their lithology varies from light silty-sandy sediments to heavy clayey ones (3). Massive areas of mud covers occur on both sides of the river, mainly on flood terraces in the southern part of the Vistula valley. The thickness of the muds on the over-flood terraces is 0.5–1.5 m, and on the flood terraces it is usually around 2 m, locally attaining 5 m in the area of Gocław (Sarnacka, 1980a, b).

The oxbow lakes and closed drainage depressions were filled in the Holocene with alluvial and organogenic deposits. Sands and lacustrine muds (5) were deposited in shallow water bodies on the upland area. They occur in the village of Rżyska north of Wołomin and near Dziekanów Leśny. Peaty muds and humic sands (2) were accumulated in closed drainage depressions and in valley bottoms located on over-flood and flood terraces of the Vistula River, as well as on the uplands. These deposits occupy large areas in the valley on both sides of the Vistula River, as well as in the valleys of the Raszynka, Utrata, Jeziorka, Łasica, Czarna and Długa rivers.

A common feature of the study area is peat (1). In the Vistula River valley it fills oxbow depressions on flood terraces (e.g. at the foot of the upland edge in Wilanów), and shallow blowouts on over-flood terraces. Peats are also found on upland areas in the valleys of the Raszynka, Utrata, Łasica, Długa and Mienia rivers and in closed drainage depressions. The largest peat areas are located at the foot of the Falenica terrace near Ząbki and in the north-eastern margin of Białołęka as well as a little further north. The thickness of the peats varies usually from several tens of centimetres to approximately 2 m.

Centuries-long human activity has led to numerous transformations of the original morphology of the terrain and the emergence of anthropogenic made grounds. They cover a significant area of Warsaw mainly in the district of Śródmieście, and partly in Mokotów, Wola, Ochota, Włochy, Żoliborz and, to a lesser extent, in Praga. At a depth of 2 m, the area of made grounds is almost exclusively limited to the district of Śródmieście (Frankowski *et al.*, 2000). The oldest made grounds, even hundreds of years old, can be found in the Old and New Town. They consist of garbage dumped on the Vistula Escarpment and beyond it. The Gnojna Góra hill, adjoining the walls of the Old Town near Jezuicka Street, is a very old damping site of waste disposed of on the embankment by the residents over several centuries. A thick layer of made grounds (3–10 m) occurs on the Vistula terraces between the New Town and Łazienkowska Thoroughfare, as well as near the Traugutt Park (1–6 m; Krzywicki, 2013). Among the old man-made embankments are the brick and earth fortifications of the nineteenth-century Warsaw Fortress. Younger embankments consist mainly of post-war debris and attain a thickness of up to 8 or even 10 m (Frankowski *et al.*, 2000). The thickest debris cover was found in Muranów. After World War II, the rubble from destroyed buildings was stored on the

Warsaw Escarpment in Mokotów and Żoliborz. It was also dumped at the slope of the New Town and the Citadel as well as in the swampy terrain of Marymont. Part of the waste was taken away and disposed of on the Wisłostrada Thoroughfare embankment in the area of Bielany (Krzywicki, 2013). Embankments composed of rubble and soil are also under the Warsaw's stadiums (National Stadium, Warszawianka Stadium) and under the communication routes.

Mineral deposits. In total, 39 mineral deposits have been registered across the area of the map sheet (Szuflicki *et al.*, ed., 2014). All of them are located outside of Warsaw, since it is impossible to carry out any exploration and extraction operations for mineral resources in the heavily urbanized area of the city. Apart from one mineral water deposit in Konstancin-Jeziorna, the remaining deposits are represented by construction raw materials (ceramic clays, quartz sands, natural aggregates) or glassmaking raw materials. 23 mineral deposits have the status of abandoned deposit, and one was deleted from the register. Four deposits are developed, including: one ceramic clay deposit of Kobyłka Kolonia Chór 5, and natural aggregate deposits of Sokołów-Żwirownia 1, Janki-Sokołów VII and Janki-Sokołów I (extracted periodically). Ten undeveloped mineral deposits are documented in detail in category $A+B+C_1$.

HUMAN IMPACT

Air contamination. The air quality is affected by dust and gas emissions from industrial activities (point emissions), household sector (surface emissions) and communication sources (linear emissions). The amount of particulate matter introduced into the air in Warsaw in 2013 amounted to 849 Mg, and of gaseous pollutants (excluding carbon dioxide) - 26,704 Mg (Dane powiatowe..., 2014). Almost 100% of particulate matter and nearly 50% of gaseous pollutants (excluding carbon dioxide) have been captured by the facilities for pollution reduction.

The main point sources of air pollution are power and industrial plants. The most important ones in the study area are heat and power plants (Siekierki, Żerań, Pruszków, Kawęczyn, Wola and Regaty), and the major technological emitters are the ArcelorMittal steelworks, Zakład Unieszkodliwiania Stałych Odpadów Komunalnych (ZUSOK – Municipal Solid Waste Treatment Plant) and the companies of Danone and Polfa Tarchomin.

Local domestic boilers and furnaces are significant sources of surface emission, introducing mainly sulphur dioxide, nitrogen oxides, particulate matter, soot, carbon monoxide and aromatic hydrocarbons into the atmosphere (so-called low emission).

Linear emissions, originating from communication sources, account for more than half of the total amount of atmospheric emissions. They come from the combustion of fuels in vehicle engines, and sources related to road traffic (wearing of road surfaces, tires and brake linings), and dust entrained from roads.

The results of atmospheric air tests carried out within the framework of state environmental monitoring in 2014 have shown that the permissible concentration limits for pollutants such as benzene, lead, arsenic, cadmium, nickel, sulphur dioxide and carbon monoxide are not exceeded. Permissible limit values were exceeded as regards the concentrations of PM10, PM2.5, nitrogen dioxide and benzo(a)pyrene (Roczna ocena..., 2015). Poor air quality conditions in Warsaw are caused mainly by surface emissions associated with heating of homes from the municipal and household sector, and linear emissions related to road traffic and fuel combustion. Effect of the point emission, e.g. from a power plant, is just a few percent of the overall balance of contaminants *(op.cit.)*.

Sewage. Watercourses and water reservoirs in the study area are contaminated mostly by industrial and municipal sewage and wastewater and by runoff from urbanized and rural areas. The quality of waters and sediments of the Vistula River is also affected by pollution coming from areas in the southern part of its drainage basin.

In the years 2010–2013, the amount of untreated sewage discharged into the environment in the Masovian Voivodeship decreased more than seven times, which is associated primarily with the completion of the extension and modernization of the Czajka Sewage Treatment Plant in Warsaw (Stan..., 2014). Currently, all waste from the Warsaw agglomeration is purified before discharging into the river.

The Czajka Sewage Treatment Plant of the MPWiK (Municipal Water and Sewerage Company) in Warsaw is the largest plant of its kind in the study area. It collects sewage from the right-bank and most of the left-bank districts of Warsaw as well as from Legionowo, Zielonka, Jabłonna, Marki and Ząbki. The plant facilities, located in Białołęka, include also the Wastewater Sludge Thermal Utilization Station. In the district of Wilanów, there is the smaller Południe Plant collecting sewage from the left-bank side of Warsaw. Both of them are mechanical-biological treatment plants with increased removal of biogenic compounds from wastewater. Other plants belonging to Warsaw's MPWiK are located outside the map sheet area in Pruszków and Wieliszewo (municipality of Legionowo).

Urban and municipal biological sewage treatment plants discharge sewage to the Vistula, Długa, Mienia, Raszynka and Utrata rivers and to the Jagodzianka, Struga and Perełka streams.

Several local sewage treatment plants (operating in factories, housing estates and households) discharging treated sewage into water bodies are located in both Warsaw and the neighbouring municipalities.

In the map sheet area, there are several control and measurement points at which surface water monitoring is conducted within the National Environmental Monitoring. Assessment of the surface water status is carried out for surface water bodies (SWB, in Polish JCWP) on the basis of the assessment of the ecological status/potential and chemical status (Rozporządzenie..., 2011). Monitoring of river waters, carried out in 2010–2013 by the Regional Inspectorate of Environmental Protection in Warsaw, shows that the quality of waters in Warsaw and surrounding areas is poor,

which was due primarily to their poor ecological status/potential. Poor water condition was found in the Vistula River (from the Jeziorka to Młociński Canal), Wawerski Canal and Jagodzianka stream (from the tributary from Regut to the stream mouth). The crucial factors determining the results of ecological status/potential of the waters were biological and physico-chemical indicators: total Kjeldahl nitrogen, phosphates, total phosphorus, COD and pH. Chemical status of the vast majority of the examined SWB was worse than good, mostly due to the exceeded allowable average annual concentrations of PAH compounds (the sum of benzo(ghi)perylene and indeno(1,2,3-cd)pyrene). Good chemical status was found only for the Jagodzianka SWB along the stream section from the tributary from Regut to the stream mouth (Monitoring..., 2015).

Surface water monitoring is supported by the monitoring of bottom sediments of rivers, canals and lakes. In the study area, bottom sediments of the Vistula River and Żerański Canal were examined. The results of studies conducted in 2014 show that the Vistula River sediments in Warsaw are not contaminated by metals and organic compounds (PAHs, PCBs and organochlorine pesticides) (Raport..., 2014). In contrast, the Żerański Canal sediments in Warsaw are contaminated with silver, cadmium, copper, lead and zinc as well as PAH and DDT compounds.

Soil contamination. Soils in urban and industrial areas undergo various forms of degradation. Their resistance to changes depends on their composition and physical and chemical properties such as pH, redox and sorption capabilities. The lowest resistance to degradation is characteristic of light soils occurring on the Vistula terraces composed of fluvial sands, and in the areas covered by aeolian sands. The most degradation-resistant soils are those developed from tills, clays and alluvial muds.

Soil contamination in urban areas is caused not only by industry and road traffic, but also by agricultural and horticultural activities. Harmful elements and compounds are introduced into the soil as a result of precipitation of dust and gases, and from acid rains, fertilizers, pesticides, sewage and leachate from warehouses and storage sites.

The largest sources of soil contamination in Warsaw and surrounding areas are:

- power plants: thermal power stations (Siekierki, Żerań, Pruszków, Kawęczyn, Wola and Regaty), Energetyka Ursus Thermal Power Station, Veolia Energia Warsaw, Międzylesie Thermal Power Station, Thermal Power Station in Wołomin, Energopep Company for Thermal Power Station in Konstancin-Jeziorna;
- large industrial objects such as: ArcelorMittal Poland Steelworks, ZUSOK solid waste treatment plant, Danone, Polfa Tarchomin, Lotte Wedel, Procter and Gamble DS Polska, EADS PZL Warsaw-Okęcie aviation manufacturer, PIT-Radwar, Warszawskie Zakłady Przemysłu Nieorganicznego Stochem chemical plant, Termisil Wołomin Glassworks, DJCHEM Chemicals Poland in Wołomin, Huta Szkła Gospodarczego glassworks in Wiązowna, Piastowskie Zakłady Przemysłu Gumowego Stomil rubber company, Przedsiębiorstwo Produkcyjno-Handlowe (Trade and Production Company) POLAMP-WARSAW in Ożarów Mazowiecki;
- the airfields of Okęcie and Bemowo;

- warehouses, liquid fuel stations and storage sites;
- old transformer stations and vehicle dismantling facilities;
- hospitals and waste disposal points;
- polygons and military bases;
- sites of wastewater discharge into surface waters;
- surface rail infrastructure (railway tracks, sidings, repair workshops);
- tram tracks and road corridors;
- pipelines and linear installations of various types.

In the study area, especially in Warsaw, the quality of soils has been highly affected by historical industrial and craft activities which, in the late 19th to early 20th century, were concentrated mainly in the following areas: Powiśle, the so-called Western District (between the streets of Towarowa, Okopowa and the N-S Thoroughfare), Wola, Nowa Praga, Szmulkowizna and Kamionek. After World War II, in the 1950s, two new industrial areas appeared on the map of Warsaw: Żerań and Służewiec. A few tens of large companies representing various industrial sectors, mainly the electronics, electrical engineering, precision and machine industries, had operated until the late 1980s in the so-called Industrial Służewiec district (Rutkowska-Gurak, 2000).

Many industrial plants that operated during the period of People's Republic of Poland (many of them continued pre-war production) did not survive the process of political and economic transformation after 1989. However, their long-term business, usually combined with a lack of care for the environment, had caused contamination of surface environments. The most prominent, currently defunct companies in the study area include: Zakłady Mechaniczne Ursus Factory, Fabryka Samochodów Osobowych (automobile factory) in Żerań, Warszawskie Zakłady Fotochemiczne Foton (photochemical plant), Zakłady Wytwórcze Lamp (electric lamp company) Róża Luksemburg, Zakłady Radiowe (electronics company) Marcin Kasprzak, Zakłady Mechaniczne PZL-Wola (engine factory), Naukowo-Produkcyjne Centrum Półprzewodników CEMI (semiconductor factory), Zakłady Ceramiki Radiowej CERAD (electronic company), Pollena-Uroda (cosmetic company), Thomson Technicolor Polska, and Fabryka Kabli Ożarów (cable factory). The largest currently operating industrial companies of Warsaw are concentrated mainly in the districts of Praga Północ, Praga Południe, Targówek and Białołęka.

Geochemical studies of soils in Warsaw show they are contaminated by metals, and the identified anomalies of copper, cadmium, lead and zinc, as well as some arsenic anomalies are found to be anthropogenic (Lis, 1992). The soils that are most contaminated by these elements have been found in the districts of Śródmieście and part of Praga. The contamination is considered to be due to the past and present activities of industrial plants (non-ferrous metals processing plants, ceramic factories, chemical companies, electroplating and dyeing manufacturers, and thermal power plants) and heavy road traffic. Research conducted by a team of specialists under the leadership of Czarnowska and in the period of 1973–2000 showed contamination of the topsoil layer by metals in the street and residential lawns and garden plots located near roads (Nowakowski, 2004).

Waste landfills. In the study area there is an active municipal landfill at Lipiny Stare in the municipality of Wołomin. Closed, already reclaimed municipal waste landfills are located on the outskirts of Józefów and Marki. On the border between Warsaw and Stare Babice is the Radiowo landfill where municipal wastes have been stored till 1991. Today, it is a technological object receiving the so-called ballast waste from a composting plant, and, since 2012, also mechanically and biologically processed municipal wastes (especially those containing large amounts of organic matter). Installations for mechanical-biological processing are located in Warsaw in the streets of Gwarków, Wólczyńska and Zawodzie.

In Warsaw and its surroundings there are a few active and closed landfills of industrial waste.

An active landfill of combustion waste of the Siekierki thermal power plant operates in the Zawada housing estate in Warsaw, Wilanów district. A landfill of combustion waste of the Żerań thermal power plant is located in the district of Warsaw-Białołęka. It is currently inactive and under the process of land reclamation (Plan..., 2008).

In the district of Warsaw-Bielany is located a landfill of smelting waste of the ArcelorMittal Steelworks. Currently, the waste is no longer disposed of in the landfill, and the stored materials are subject to recovery processes.

In Konstancin-Jeziorna, in the former Warszawskie Zakłady Papiernicze paper company, there is a closed landfill of industrial waste of the Metsa Tissue Company.

Two landfills of industrial waste of the Fabryka Okładzin Ściernych (brake linings factory) are located in Marki – one of them was closed down in 1999, and the other is new. Asbestos and nitro paints waste, ashes, plastics and cleaning materials have been stored in these landfills (Monitoring..., 2006).

In recent years there has been an increase in the number of illegal dumping in Warsaw. In 2013, all illegal landfills (12) were distributed in the Warsaw district of Targówek and they occupied an area of 30,835 m² (Stan..., 2014).

In the study area, like in the whole region, all hazardous waste landfills that pose a dangerous source of pollution, especially for groundwater, have been eliminated (Stan..., 2014).

SCOPE AND METHOD OF RESEARCH

The research was carried out in the period of 2013–2015 and included a study of published and archived materials, planning of soil sampling sites on topographic maps at a scale of 1:10,000, sampling and measuring of coordinates at their location, chemical analysis of samples, development of field and laboratory databases, development of vector topographic base map, statistical calculations,

compilation of a geological map and construction of the geochemical maps, as well as interpretation of the results. The sequence of works is illustrated in the attached diagram ($\underline{Fig. 1}$).

FIELD WORKS

Within the administrative boundaries of Warsaw, soil samples were collected on a regular grid basis of 500x500 m (4 samples/km²), and outside of Warsaw – 1,000x1,000 m (1 sample/km²). The total number of soil samples was 2764. At each sampling site, the samples were collected from depths of 0.0–0.3 and 0.8–1.0 m (or from a shallower depth if there was an anthropogenic layer difficult to be drilled through) and intended for the determination of grain-size composition, pH and inorganic components content. Soil samples (weighing approx. 500 g) were taken using a hand auger, 60 mm in diameter, placed in cloth bags marked with numbers, and then dried.

In addition, at every fourth sampling point, samples from the soil surface layer were taken to determine the content of organic compounds. The samples were placed in 250-ml jars made of dark glass.

Sediment and surface water samples were collected from rivers, streams, drainage ditches, canals, lakes, ponds, and moats of fortifications. The distance between sampling sites on watercourses was approximately 500 m within the boundaries of Warsaw, and approximately 1,000 m outside the administrative boundaries of the city.

Sediment samples that weigh approximately 500 g (and as fine-grained as possible) were collected from the edges of water bodies using a dipper, and placed in 500-ml plastic containers labelled with numbers. An additional sediment sample was taken at every fourth sampling point to analyse the content of organic compounds. The samples were placed in 250-ml brown glass jars.

Surface water samples were collected from the same sites as sediment samples. Electrolytic conductivity (EC) and pH of water were measured in the field. EC measurements were made using an electrolytic conductivity meter with automatic temperature compensation, assuming the reference temperature of 25°C. Water samples that were taken to determine cations were filtered in the field using the 0.45-µm Milipore filters, and then acidified with nitric acid after pouring into 30-ml bottles. Water samples that were taken to determine anions were transported to the laboratory in 250-ml bottles placed in refrigerated containers. An additional sediment sample was taken at every fourth sampling point to determine the chemical oxygen demand (COD) and the contents of ammonium ions, dissolved organic carbon and total suspended solid. The samples were placed in 15-ml bottles labelled with numbers.

All sampling sites were marked on 1:10,000 topographic maps, also putting an appropriate number.

Position of the sampling sites was determined by GPS (*Global Positioning System*) using a device equipped with an external antenna and a computer enabling the measurements of coordinates and the recording of additional information (pH and EC of water, information about the land development and

land use and the lithology of samples). Coordinate data are recorded with an accuracy of $\pm 2-10$ m. Before going to the field, data on the coordinates of sampling sites were input into the GPS device memory. Successive sampling sites were searched in the field using satellite navigation. For better safety all the field data are recorded also on specially prepared sheets (Fig. 2).

LABORATORY WORKS

Sample preparation. Soil samples were transported to the laboratory, dried at room temperature and sieved through a 2-mm-mesh nylon sieve. After sieving and quartering, each soil sample (from both depth levels) was divided into three portions: one for chemical analysis, the other one for grain-size analysis, and the third – for archival purpose. Soil samples for chemical analyses were ground to the grain-size fraction <0.06 mm in agate ball mills.

Sediment samples were dried at room temperature and sieved through a nylon sieve with a mesh of 0.2 mm. After quartering, the <0.2 mm fraction was divided into two sub-samples: one for chemical analysis and the other to be archived (Fig. 1).

Soil and sediment samples intended for analysis of organic compounds were air-dried and handpounded.

The samples are archived at the Polish Geological Institute – National Research Institute in Warsaw.

Chemical analyses were carried out by the Chemical Laboratory of PGI-NRI in Warsaw.

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

Determinations of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in soils and sediments were performed by atomic emission spectrometry with inductively coupled plasma (ICP-OES). Analysis of mercury in soil and sediment samples was carried out by atomic absorption spectrometry coupled with cold vapour (CV-AAS) and the FIAS-100 flow system. Soil's pH was determined in aqueous extracts using the potentiometric method. The content of organic carbon was measured by the coulometric method and the high-temperature combustion method (Elemental Analysis) with thermal conductivity detection (EA-TCD).

Analysis of PAHs in solid samples was performed using gas chromatography with mass spectrometry (GC-MS) after extractive separation with dichloromethane. Determinations of PCBs and organochlorine pesticides in soils and sediments were made using gas chromatography with electron capture detection (GC-ECD) after extractive separation with dichloromethane. Analysis of the content of mineral oils in solid samples was carried out using infrared spectroscopy (FTIR) after extractive separation with tetrachloroethene.

In water samples, determinations of B, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, P, SiO₂, Sr and Zn were carried out using the ICP-OES method, determinations of Ag, Al, As, Cd, Co, Cu, Li, Mo, Ni, Pb, Sb,

Tl, U and V – by the ICP-MS method, and determinations of Br, Cl, F, NO₂, NO₃ and SO₄ – using the ion chromatography method. Analysis of the contents of HCO₃, NH₄, DOC, suspended solids and COD values were performed by the spectrophotometric method.

Summary of the analytical methods and limits of detection for elements and organic compounds is presented in Tables 1 and 2.

Control procedures for the chemical determinations are summarized in Table 3.

As regards solid samples, the accuracy of determinations of cations is $\pm 10-15\%$ (based on the analysis of duplicate samples). For water samples, the accuracy is $\pm 10-20\%$ (depending on the element content).

Grain-size analysis of soils was carried out at the Chemical Laboratory of PGI-NRI in Warsaw, combining the sieve analysis and laser particle size measurements. The grain-size analysis was performed using unconventional methods (such as those in accordance with relevant standards in soil science). Their results cannot therefore be used for the classification of soils according to the soil science criteria. However, they are very helpful when interpreting the results of geochemical studies.

Samples were sieved through a set of sieves with a mesh of 2 mm, 1 mm and 0.5 mm. Some clayey soil samples were crushed before sieving in a porcelain mortar. The obtained fractions (2–1 mm, 1.0– 0.5 mm and <0.5 mm) were weighed. Grain-size measurements for the fraction of <0.5 mm were carried out using a laser particle sizer.

The results of grain-size analysis (recalculated to percentages) are shown on the maps with respect to the grain-size classes: 1.0-0.1 mm - sand fraction, 0.1-0.02 mm - silt fraction, <0.02 mm - clay fraction (Pls. 4–9).

DATABASES AND GEOCHEMICAL MAPS CONSTRUCTION

Topographic base map. The topographic base map for the production of geochemical maps, scale 1:100,000, was compiled from the most up-to-date 1:50,000 maps with the *1992* coordinate system, including the following map sheets: N-34-126-D, N-34-127-C, N-34-127-D, N-34-138-B, N-34-138-D, N-34-139-A, N-34-139-B, N-34-139-C and N-34-139-D (VMap L2 vector data). The topographic base map consists of the following vector information layers:

- terrain relief,
- hydrography (subdivided into rivers, streams, ditches and stagnant water bodies),
- road network (subdivided into classes),
- railway network,
- land development,
- forests,

• industrial areas (industrial objects and dumps).

Geological map. To illustrate the geology of the study area, a geological map was developed using relevant parts of vector images of the Geological Map of Poland, 1:200,000, Warsaw Zachód sheet (Morawski, Nowacka, 2007) and Warsaw Wschód sheet (Morawski, Pielach, 2011). The resulting digital image of the geological map was combined with the topographic base map at the scale of 1:100,000 (<u>Pl. 1</u>).

Databases. Separate databases were developed for:

- soils from a depth of 0.0–0.3 m (topsoil),
- soils from a depth of 0.8–1.0 m (subsoil),
- sediments,
- surface waters.

Databases for soils include: numbering of samples, coordinates at sampling sites, record of field observations (land development, land use, soil type, sampling site location – district, municipality, locality), date and name of the person who collected the sample, and results of chemical analyses.

Databases for sediments of inland water bodies and surface waters include: numbering of samples, coordinates at sampling sites, record of field observations (land development, land use, water body type, sediment type, sampling site location – district, municipality, locality), date and name of the person who collected the sample, and results of chemical analyses.

Statistical calculations. The data stored in databases were used to separate subsets for statistical calculations according to different environmental criteria, for example the contents of elements in soils of industrial areas, forest soils and urban soils, and in sediments and waters of individual drainage basins, as well as for the development of geochemical maps. The calculation of statistical parameters was made for both entire datasets and subsets created for soils, sediments and surface waters. The statistical calculations were made assuming a content equal to half the detection limit for the analytical method if the content of elements was below the detection limit for this method. The arithmetic mean, geometric mean, median and minimum and maximum values were subsequently calculated. These data are presented for individual elements and indicators in Tables 4–11 and in the geochemical maps. Other statistical parameters, such as variance and standard deviation, do not satisfactorily characterise the populations because we deal with undetermined natural distributions.

Maps construction. The following maps were constructed (<u>Pls. 2–80</u>):

- land development,
- land use,
- contents of sand, silt and clay fractions in soils from a depth of 0.0–0.3 m and in soils from a depth of 0.8–1.0 m,
- organic carbon content in soils from a depth of 0.0–0.3 m,
- pH of soils from depths of 0.0–0.3 m and 0.8–1.0 m,

- contents of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn in soils from depths of 0.0–0.3 m and 0.8–1.0 m and in sediments,
- contents of dieldrin, endosulfan I, total DDT and derivatives, total HCHs, total PCBs, total PAHs, and mineral oils in soils from a depth of 0.0–0.3 m and in sediments,
- pH, EC, COD and contents of Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, DOC, F, Fe, HCO₃, K, Li, Mg, Mn, Mo, Na, NH₄, Ni, NO₂, NO₃, P, Pb, SO₄, Sb, SiO₂, Sr, Ti, Tl, U, V and Zn in surface waters,
- classification of soils from a depth of 0.0–0.3 m, showing proper mode of their use (including subdivision into soil use groups based on Rozporządzenie..., 2002).

Land development, land use and the classification of soils from a depth of 0.0-0.3 m, showing proper mode of their use, is presented as dot maps (Pls. <u>2</u>, <u>3</u> and <u>80</u>).

To depict the distribution of grain-size classes (Pls. 4–9) and the contents of elements in soils, an isoline (areal) mapping method was chosen because of its clarity and legibility. The geochemical contour maps were produced with the Surfer software, using the method of *Inverse Distance to a Power*. Element content classes were selected according to the percentile ranges: 25, 50, 75, 90, 95 and 97.

The pH of soils (Pls. <u>10</u> and <u>11</u>) is shown using the scale adopted from soil science (with the subdivision into acidic, neutral and alkaline soils). The pH of water (<u>Pl. 10</u>) is shown using the scale adopted from hydrogeology (with the subdivision into the acidic, weakly acidic, neutral, weakly alkaline and alkaline waters).

The geochemical maps of sediments of water reservoirs and surface waters were constructed as dot maps, attributing the circle diameters to the individual element content classes established in accordance with the division into percentile ranges (25, 50, 75, 90, 95, 97).

While constructing the surface soil classification map (Pl. 80) indicating the proper mode of their use, the results of geochemical studies were referred to the values of permissible concentrations of metals, specified in Rozporządzenie Ministra Środowiska (2002) which says: "soil or land is considered to be contaminated when the concentration of at least one substance exceeds the permissible limit value".

Based on the contents of each of the investigated metals and organic compounds (Rozporządzenie..., 2002), each of the tested soil samples was classified into group A, B or C. In the case of identical limits of permissible values for groups A and B (specified for arsenic, barium and cobalt in Rozporządzenie..., 2002), it was assumed that the soils would be categorised into group A, which is more favourable to the user and allows for multi-purpose land use.

For the purpose of publication the geochemical maps were constructed by combining maps in pairs on the same Plate: the geochemical map of soils from a depth of 0.0-0.3 m with the geochemical map of sediments, and the geochemical map of soils from a depth of 0.8-1.0 m with the geochemical map

of surface waters. Such presentation allows a direct comparison of geochemical images of different environments.

In the comments to the geochemical maps, limit values of water quality indicators relating to surface water bodies, specified in Rozporządzenie...(2014), were used to assess the degree of contamination of surface waters.

RESEARCH RESULTS

ELEMENTS IN SOILS, SEDIMENTS AND SURFACE WATERS GRAIN-SIZE COMPOSITION

Soils: Pls. 4-9

Grain composition of the soil determines largely its resistance to degradation and has a significant effect on the content of chemical elements. Soils with a high proportion of the clay (<0.02 mm) and silt (0.1–0.02 mm) fractions are usually characterised by an increased content of elements and their lower mobility under hypergenic conditions. The standards and guidelines defining the permissible concentrations of metals in soils usually involve the grain-size composition, allowing greater concentration limits for soils with a high proportion of clay fraction, and lower concentration limits for soils with a high proportion of sand fraction (Kabat-Pendias *et al.*, 1995).

For the study of soils from both depth ranges, the following grain-size groups have been defined: 1.0-0.1 mm, 0.1-0.02 mm and <0.02 mm, in accordance with the standard BN-78/9180-11 recommended by the Polish Society of Soil Science (Prusinkiewicz *et al.*, 1994). The study results show that the grain-size composition of soils is associated primarily with the lithology of the bedrock, and this relationship is more clearly visible in soils from a depth of 0.8–1.0 m. In the topsoil the original grain-size composition has been obliterated over large areas as a result of earthworks, construction works, and even gardening activities (especially in the city area during the post-war period).

Soils rich in the sand fractions are distributed mainly on the over-flood terraces on the eastern side of the Vistula River. On the western side, the soils containing >75% of sand fraction were found in the Kampinos National Park, in the northern part of Warsaw (districts of Bielany, Żoliborz and Bemowo) and in the Sękocin Forests. These soils have developed on fluvial sands and gravels of the over-flood terraces and the Warsaw-Błonie terrace (Bielany), or on aeolian and river valley sands.

In both of the soil layers the distribution of silt fraction is similar. About 70% of the soils is characterised by its content <25%. Approximately 10% of the topsoil and approximately 16% of the subsoil contain >50% of silt fraction. The greatest amount of silt fraction is found in alluvial muds of flood and over-flood terraces and in soils developed on glacial tills and eluvial sediments (sands, muds and loams).

The clay fraction accounts for the smallest proportion in the soils. As regards the topsoil layer, as much as 81% of the soils contain <15% of clay fraction, but at a depth of 0.8–1.0 m, approximately 70% of the soils is poor in this fraction. The greatest quantities are found in soils from the left-bank side of Warsaw (Śródmieście, Mokotów, Wola, Ursus, Włochy) and in soils from the western periphery at a depth of 0.8–1.0 m. These soils have developed on glacial tills, kame sands and muds, as well as on weathering-aeolian sediments (sands, silts and loess-like muds). Increased proportions of the finest fraction (>30%) are typically found in the topsoil in the north-western part of the map sheet area, on the flood terraces of the Vistula River (near Jablonna and west of Legionowo). In both of the studied soil layers (but mostly at a depth of 0.8–1.0 m), local enrichment in the clay fraction is observed in the eastern part of the map sheet area. It is associated with the occurrence of tills or eluvial deposits (sands, silts, loams) in the basement.

pН

Soils: Pls. 10-11, tab. 4-5

The soil pH depends on the bedrock lithology (predominantly in the subsoil), soil use, and anthropogenic factors.

As regards the topsoil, acidic reaction (pH <6.3) is observed in forest soils. Farmland soils are commonly neutral or slightly alkaline, and the soils from the most urbanized areas are mainly alkaline (pH >7.4), as in other cities of Poland (Pasieczna, 2003). Alkalization of soils is caused primarily by the fallout of particulate matter emitted from power plants and other industrial plants. Another factor contributing to soil alkalization is a huge proportion of rubble in anthropogenic embankments throughout much of the central area of the city. The largest areas of strongly alkaline soils (pH >8.0) occur in Białołęka (Żerań and Tarchomin) and in Łuk Siekierkowski (in areas close to the major power plants), and in the case of Białołęka also within the range of impact of numerous industrial plants (some already inactive, e.g. FSO automotive company). The highest pH value of 10.3 is recorded in the topsoil at the ArcelorMittal steelworks in Bielany.

The human impact on soil reaction is evidenced by a much lower average soil pH value of the topsoil in undeveloped areas (median 6.5) compared with the areas of urban and industrial development (medians 7.6 and 7.8, respectively).

At a depth of 0.8–1.0 m, acidic soils are found only locally in small patchy areas. Neutral and slightly alkaline soils are prevalent. In comparison with the topsoil, highly alkaline soils occur over much greater areas. In urban areas it is caused by the spread of industrial dust rich in calcium and magnesium compounds and by the migration of these compounds into the soil profile. In the very centre of Warsaw, alkalization can also be partly associated with the occurrence of anthropogenic grounds. In other areas of the map sheet, high pH values result from natural enrichment of the bedrock in calcium. Elevated contents of calcium and magnesium are common, among others, in alluvial muds

found in the Vistula River valley, as well as of weathering-aeolian loess-like covers stretching along a wide belt from the western outskirts of Warsaw toward Ożarów. At a depth of 0.8–1.0 m the most alkaline soils are found in the inactive Warsaw cement works in Żerań.

Waters: <u>Pl. 10</u>, <u>tab. 7</u>

Definitely, most of the waters (79.8%) show a slightly alkaline pH 7.0–9.0. Acidic waters (pH <5) were present in 0.4% of analysed samples, slightly acidic (pH 5–6.5) in 3.6%, neutral (pH 6.5–7.0) in 15.3%, and alkaline (pH >9) in 0.9% of samples (classification by Kleczkowski, Różkowski, 1997). Acidic, slightly acidic and neutral waters (pH <7) occur primarily in the areas of Wilanów, Ursynów, Konstancin-Jeziorna and Raszyn, as well as in forested areas (Kampinos Forest, Rembertów Forests and Otwock Forests).

The lowest pH (4.6) is recorded in the water of a pond/marsh from a forest area of Zagórze (Wiązowna municipality). In contrast, the most alkaline waters are those of the Vistula River (pH 8.1), showing additional seasonal fluctuations (pH >8.5 in July and August and 7.1–7.9 in May, June and October).

Alkaline pH is typical of the waters of some stagnant water bodies (a small pond in Ogród Saski (Saxon Gardens), Stawy Kacze ponds in the Skaryszewski Park, Cietrzewia pond, Szczęśliwickie clay pit ponds), fishing ponds at Raszyn (Falencki and Puchalski ponds), and of the waters of local watercourses and other water bodies in the drainage basins of the Czarna and Długa rivers. The pH value in a pond at Konik Nowy (Halinów municipality) is 9.9.

EC ELECTROLYTIC CONDUCTIVITY

Waters: Pl. 11, tab. 7

The value of electrolytic conductivity of water is used to evaluate the water mineralisation (salinity) and the degree of contamination. The water is considered contaminated if the EC values are above 1 mS/cm (Witczak, Adamczyk, 1994), and the maximum permissible conductivity of drinking water is 2.5 mS/cm (Rozporządzenie..., 2010). The electrolytic conductivity of most of the analysed waters (87%) is ≤ 1.0 mS/cm, meeting the standard for water quality class I. Class II waters (EC ≤ 1.5 mS/cm) account for 9% of all the waters. The highest average electrolytic conductivity is recorded in the drainage basin of the Lasica River (median 0.85 mS/cm).

Increased conductivity is observed in a number of closed water bodies. EC values >1.39 mS/cm were reported from the following reservoirs: Bernardyńska Woda moat (3.06 mS/cm), Jeziorze pond (2.91 mS/cm), Czerniakowski Fort moat, Piłsudski Fort moat, Blizne Fort moat, Staw pod Królikarnią pond, Łacha Potocka oxbow lake, a pond near Dolna Street, and a pond at Paluch. The main source of contaminants in the reservoirs is probably surface runoff. A large amount of organic matter and the weak or totally limited flow-through favour accumulation of many compounds on site.

Anomalous EC values were also observed in the waters of some ditches and channels: a ditch at Paluch near the Chopin Airport (2.33 mS/cm), the ditch flowing from the Wólka Węglowa region and recharging the Lipkowska Woda stream (up to 2.33 mS/cm), the ditch running along Piaseczyńska Street (2.14 mS/cm), Kanał Henrykowski canal (up to 1.99 mS/cm), Kanał Czerniakowski canal (up to 1.51 mS/cm), and Kanał Sielecki canal (1.47 mS/cm).

The water contamination in the Kanał Henrykowski canal is probably caused by industrial waste. The waters of canal contain significant concentrations of arsenic (14 μ g/dm³), barium (303 μ g/dm³), bromine (0.16 mg/dm³), calcium (177.3 mg/dm³), cadmium (0.09 μ g/dm³), chlorine (316 mg/dm³), cobalt (10.26 μ g/dm³), copper (6.38 μ g/dm³), fluorine (0.2 mg/dm³), hydrocarbonates (468 mg/dm³), manganese (5,578 μ g/dm³), molybdenum (5.21 μ g/dm³), sodium (218.1 mg/dm³), ammonium ions (29.2 mg/dm³), nickel (12.11 μ g/dm³), sulphates (278.0 mg/dm³), antimony (1.97 μ g/dm³), silica (17.3 mg/dm³), strontium (1,025 μ g/dm³), uranium (2.52 μ g/dm³), vanadium (3 μ g/dm³) and zinc (378 μ g/dm³).

Anomalous conductivity values (up to 1.83 mS/cm) are observed in the waters of the lower section of the Rudawka River flowing through the Bielański Las forest nature reserve, which show high concentrations of barium (205 μ g/dm³), calcium (228.7 mg/dm³), chlorine (288.0 mg/dm³), lithium (18.6 μ g/dm³), magnesium (32.4 mg/dm³), molybdenum (4.74 μ g/dm³), sulphates (235.0 mg/dm³), silica (17.2 mg/dm³), strontium (445 μ g/dm³), uranium (2.60 μ g/dm³) and hydrocarbonates (393 mg/dm³).

Outside of Warsaw the watercourses and ponds in the Czarna and Raszynka drainage basins are locally conspicuous by high conductivity. The conductivity of 3.93 mS/cm was measured in a pond/marsh at Pólko near the Warsaw–Wyszków road, where the maximum concentrations of chlorine (1,100 mg/dm³) and sodium (714.2 mg/dm³) are recorded, as well as in a ditch in the village of Wypędy, SW of Raszyn (2.79 mS/cm).

The highest degree of salinity (6.91 mS/cm) is recorded in the water of a small overgrown pond in a marsh area near Dobczyn. This water shows a high phosphorus concentration (2.06 mg/dm³) and is probably contaminated with household sewage.

Ag SILVER

Soils: Pls. 12–13, tab. 4–5

In the vast majority of soils the silver concentration does not exceed the limit of detection (1 mg/kg). There were only 26 topsoil samples and 8 subsoil samples with higher silver concentrations. The maximum concentration of this element (23 mg/kg) is recorded in the topsoil in the industrial and warehouse area of Służewiec (near the streets of Wyczółki and Łączyny). The highest silver concentration (20 mg/kg) in the subsoil was found in Targówek in Bukowiecka Street, and in both

depth ranges – in allotment gardens in Janowiecka Street, 9 mg/kg and 2 mg/kg, respectively. The topsoil of this area is also contaminated by mercury (2.07 mg/kg).

Sediments: Pl. 12, tab. 6

In 90% of sediments the silver concentration is less than 1 mg/kg. Clearly elevated concentrations are found in the sediments of the Kanał Bródnowski Górny canal that has been a receiver of wastewater from industrial plants located in Targówek since the mid-19th century. The sediment contamination by this metal (at a maximum of 17 mg/kg) may have been partly caused by the activity of the ELEMIS television equipment company in 1955–2007. In addition to silver the Kanał Bródnowski canal deposits are also characterised by high concentrations of other elements: arsenic (up to 88 mg/kg), barium (up to 504 mg/kg), cadmium (up to 58.9 mg/kg), cobalt (up to 20 mg/kg), chromium (up to 648 mg/kg), copper (up to 230 mg/kg), iron (up to 9.27%), mercury (up to 2.01 mg/kg), magnesium (up to 0.55%), manganese (up to 5,043 mg/kg), nickel (up to 69 mg/kg), phosphorus (up to 0.627%), lead (up to 166 mg/kg), sulphur (up to 2.583%), strontium (up to 199 mg/kg), titanium (up to 276 mg/kg), vanadium (up to 40 mg/kg) and zinc (up to 2,361 mg/kg).

Elevated silver concentrations relative to the geochemical baseline are also observed in the sediments of the Długa River (downriver from Ossów), in the Potok Służewiecki stream (for many years receiving wastewater from the Służewiec Przemysłowy industrial area where the electronics and electrical engineering industries dominated), in the Jeziorka downriver of Konstancin, in the Wilanówka and in other local reservoirs.

The maximum silver concentration (208 mg/kg) is recorded in the sediments of the Vistula River near the Świętokrzyski Bridge.

AI ALUMINIUM

Soils: Pls. 14-15, tab. 4-5

The distributions of aluminium content in both the topsoil and subsoil layers are very similar, as are the median values (0.34% and 0.33%, respectively). A similar average content of this element (median 0.31%) is found in soils of the Poznań agglomeration (Lis, Pasieczna, 2005). The maximum aluminium content (2.13% in the topsoil and 2.19% in the subsoil) was found in soils from the areas of Wilanów and Powsin.

The spatial distribution of aluminium is determined primarily by the chemical composition of bedrock. In general, higher contents of aluminium are characteristic of soils from the left-bank side of Warsaw, located in the upland area where the surface deposits are represented largely by glacial tills. Aluminium-rich deposits are also found in alluvial muds filling the southern part of the Vistula valley. The area of aluminium content >0.46% in the topsoil fairly well coincides with areas of flood terraces. Enrichment in aluminium observed in soils of the area located on the western outskirts of Warsaw

(Bemowo, Ursus) and in the Ożarów region is natural in origin. These soils developed on a weathering cover, resembling loess in places (Morawski, 2011).

Sediments: Pl. 14, tab. 6

The aluminium content in the sediments varies from 0.05 to 3.47%. Its average content (median 0.33%) is similar to that in the sediments of Poznań and surrounding areas (median 0.31%; Lis, Pasieczna, 2005).

High aluminium content (>0.79%) is found in the sediments of watercourses draining flood terraces on both sides of the Vistula River, in its southern section, which is determined by the bedrock lithology: muds rich in clay material. The maximum content of aluminium is recorded in the sediments taken from a canal flowing into the Kanał Habdziński canal in Konstancin-Jeziorna. Its anomalous contents (>0.93%) also occur locally in the sediments of the Vistula (in the vicinity of the Młociński Park), and of the watercourses in the drainage basins of the Czarna, Kanał Wawerski canal, Mienia and Struga Pogorzelska.

Waters: Pl. 15, tab. 7

In the majority of surface waters the aluminium content is low. There were only 28 samples with the exceeded limit value for water quality classes I and II ($400 \ \mu g/dm^3$). The aluminium-richest waters occur in the eastern part of the map sheet area in the Czarna drainage basin, Magenta canal in Rembertów, Struga Pogorzelska, Świder drainage basin, Kanał Wawerski canal and Nowe Ujście canal.

On the western side of the Vistula valley, elevated aluminium levels are found in the Kanał Młociński canal and locally in the tributaries of the Utrata, Raszynka and Łasica rivers.

The maximum aluminium concentration $(4,209.6 \ \mu g/dm^3)$ is recorded in a forested area near Radzymin, in a ditch of the Czarna drainage basin, which is also abundant in cobalt (4.39 $\mu g/dm^3$), iron (22.8 mg/dm³) and lead (3.51 $\mu g/dm^3$).

The Al-rich waters ($>316.2 \mu g/dm^3$) typically show acidic or slightly acidic pH.

As ARSENIC

Soils: Pls. 16-17, tab. 4-5

The arsenic content in the topsoil layer is slightly variable. It does not exceed the limit of detection (3 mg/kg) in 75% of samples tested.

Enrichment in arsenic (>8 mg/kg) in Białołęka and Targówek are of natural origin; they are found in grassland soils of bog iron deposits. Previous geochemical soil studies conducted in this area showed arsenic concentrations exceeding 250 mg/kg (Lis, 1992). Of natural character are also the anomalies in the peaty valley of the Długa River. Concentrations of arsenic exceeding the geochemical

baseline value are observed locally on the Vistula flood terraces, where this element was probably introduced during periods of high water level.

Elevated arsenic concentrations (>7 mg/kg) in soils from a depth of 0.8–1.0 m are typically found on the Vistula flood terraces, and locally in soils of the Targówek (up to 69 mg/kg) and Tarchomin (39 mg/kg) areas.

The presence of arsenic (up to 22 mg/kg) in the area of the ArcelorMittal smelter is undoubtedly anthropogenic.

Sediments: Pl. 16, tab. 6

In the vast majority of examined sediments the arsenic concentration does not exceed 5 mg/kg. Higher values are characteristic of sediments from the Rów z Lewandowa ditch (up to 127 mg/kg), Kanał Bródnowski Górny canal (up to 88 mg/kg) and minor canals in Białołęka. Increased concentrations are related in part to the drainage from the basement enriched in arsenic, and, in the case of the Kanał Bródnowski canal, also to the discharge of industrial wastewater. Arsenic contamination of sediments in the Kanał Henrykowski canal in Tarchomin (up to 106 mg/kg) is also a result of sewage discharge (presumably pharmaceutical waste). Deposits of this channel are characterised by high concentrations of other elements: barium (up to 580 mg/kg), calcium (up to 5.28%), cobalt (up to 14 mg/kg), chromium (up to 480 mg/kg), copper (up to 225 mg/kg), iron (to 9.51%), mercury (up to 1.11 mg/kg), magnesium (up to 0.71%), manganese (up to 6,510 mg/kg), nickel (up to 35 mg/kg), phosphorus (up to 39 mg/kg), zinc (up to 3,237 mg/kg) and strontium (up to 120 mg/kg).

Waters: <u>Pl. 17</u>, <u>tab. 7</u>

There are only 3% of samples where the arsenic concentration exceeds 5 μ g/dm³, and the values over 10 μ g/dm³ are recorded in a few samples. Therefore, all the tested waters meet the standards for water quality classes I and II (<50 μ g/dm³) with respect to this element.

The maximum arsenic concentration (41 μ g/dm³) is recorded in the Raszynka drainage basin in a ditch draining wasteland in the village of Sokołów. The same sample also shows the maximum iron concentration (40.06 mg/dm³), which may indicate natural origin of both elements.

As in the case of sediments, increased arsenic concentrations were found in the Kanał Henrykowski canal (up to 14 mg/dm³), Rów z Lawendowa ditch and other canals in Białołęka, and in the Kanał Zagoździański canal flowing across the district of Wawer. In the area of agricultural land in the north-eastern and south-western parts of the map sheet area, arsenic in water may origin from surface runoff in cropland where arsenic herbicides were used.

B BORON

Waters: Pl. 18, tab. 7

The boron concentration in the surface waters is in the range from <10 to 3,570 μ g/dm³. Only two water samples show exceeded limit values for the water quality classes I/II (2,000 μ g/dm³). The average boron concentration (median 70 μ g/dm³) is similar to that in the surface waters of the Poznań agglomeration (median 60 μ g/l; Lis, Pasieczna, 2005), but higher than the average in Poland (median 40 μ g/dm³; Lis, Pasieczna, 1995).

The elevated boron concentrations in the waters of small watercourses in the western and northeastern parts of the map sheet area are probably the result of the presence of boron compounds in glacial tills and eluvial deposits rich in clays in the bedrock of these areas. The greatest boron concentrations (880–3,570 μ g/dm³) in the waters of the ditch in Piaseczyńska Street, Lower Mokotów, in the pond of the Morskie Oko Park (1,227 μ g/dm³) and in the pond near Dolna Street (882 μ g/dm³) are probably caused by surface runoff of material rich in the clay fraction.

Ba BARIUM

Soils: Pls. 19-20, tab. 4-5

The distributions of barium concentration in soils from both depth intervals are similar. Larger areas of soils rich in this element are observed in the topsoil, indicating its significant dispersion from anthropogenic sources. Barium concentrations >60 mg/kg are recorded primarily in heavily urbanized and industrialized areas of Warsaw, and in Wołomin and Piastów.

The maximum barium concentration in the topsoil layer (1,577 mg/kg) was found at the premises of the Polfa Tarchomin pharmaceutical company, which can be explained by the use of barium compounds in the pharmaceutical industry. Anomalous barium concentrations in the topsoil near the power plants of Siekierki (903 mg/kg) and Kawęczyn (352 mg/kg) as well as near the landfills of furnace waste at Zawady and Żerań are probably due to settling of dust from coal burning. The studies of Różkowska and Ptak (1995a, b) show that the average barium concentration in the Upper Silesian coals is 176 mg/kg, and in their ashes it may reach a value of 1,274 mg/kg. The topsoil is also rich in barium near the Jaworzno power plant (Pasieczna, 2014).

High barium concentrations (250–710 mg/kg) in the topsoil of the Służewiec Przemysłowy industrial area are probably related to a 50-year long activity of the already inactive Zakłady Ceramiki Radiowej ceramics manufacturer. It emitted lead and barium compounds into the atmosphere, released during the ceramic firing process (Rutkowska-Gurak, 2000).

The abundance of barium in soils of the Vistulian flood terraces can be associated with the supply of this element along with the material transported during floods by the river waters from the south.

In the subsoil, the barium concentration anomalies are better pronounced and less extensive, but the trends characteristic of the topsoil layer are also observed.

Sediments: <u>Pl. 19</u>, <u>tab. 6</u>

In 75% of sediment samples the barium concentration does not exceed 95 mg/kg. The maximum value (807 mg/kg) was found in a sediment rich in organic matter from a ditch in a forest area extending east of Wiązowna.

In the sediments of the Rów z Lawendowa ditch the barium concentration up to 637 mg/kg may result from wastewater discharge from the currently developing residential area. These sediments are also enriched in arsenic (up to 127 mg/kg), cobalt (up to 12 mg/kg), iron (up to 17.44%) and manganese (up to 7,029 mg/kg).

The barium contamination of sediments in the Kanał Bródnowski Górny canal (up to 504 mg/kg) is likely caused by coal burning in the Kawęczyn thermal power plant, whereas sediments of the Kanał Henrykowski canal are enriched in this element (250–580 mg/kg) originating from sewage discharged from the Polfa Tarchomin pharmaceutical company.

Anomalous barium concentrations (>244 mg/kg) occur in the regions where soils are enriched in this element, e.g. in the sediments of watercourses draining the Vistula flood terrace. Sediments of the Jeziorka (up to 302 mg/kg of barium) and the Wilanówka (up to 450 mg/kg) can be additionally contaminated by sewage discharges. Until the 1950s, the Wilanówka was the lower course of the Jeziorka River that received municipal and household sewage from Konstancin and Jeziorna, as well as by industrial sewage from a paper manufacturer that operated near the river for almost 250 years. Chemical analysis of sediments from biological ponds in the premises of sewage treatment plant (which collected also municipal sewage) at the former paper manufacturer showed the barium concentrations of up to 609 mg/kg (Kostrz-Sikora *et al.*, 2015).

Waters: <u>Pl. 20</u>, <u>tab. 7</u>

The surface waters show variable barium concentrations (7–453 μ g/dm³), and the average concentration (median 50 μ g/dm³) is similar to the average in Poland (median 54 μ g/dm³; Lis, Pasieczna, 1995) and Poznań and its surroundings (median 47 μ g/dm³; Lis, Pasieczna, 2005). With respect to barium concentration, the waters are classified into water quality classes I and II (<500 μ g/dm³). Elevated concentrations of this element were also found in the Kanał Henrykowski canal (up to 303 μ g/dm³), Łacha Potocka oxbow lake in Marymont (up to 217 μ g/dm³), Rów z Lewandowa ditch (up to 204 μ g/dm³), and some water bodies in Mokotów (Jeziorko Czerniakowskie lake, the moats of the Czerniakowski and Piłsudski forts, Bernardyńska Woda moat and Kanał Sielecki canal). Waters of these reservoirs are also conspicuous by high electrolytic conductivity values.

Anomalous concentrations of barium are recorded in single water samples from the tributaries of the Czarna and Mienia rivers, and its maximum concentration (453 μ g/dm³) was measured in the waters of a ditch crossing a forest area in the Świder drainage basin.

Br BROMINE

Waters: <u>Pl. 21</u>, <u>tab. 7</u>

Most of the waters show bromine concentrations below 0.1 mg/dm³. Concentrations >0.3 mg/dm³ are found at many places in the Vistula River; the contamination probably comes from long-distance transport from all over the drainage basin.

Bromine concentrations >0.2 mg/dm³ are recorded in the waters of the Kanał Henrykowski canal (accompanied by high electrolytic conductivity and high contents of many metals) and in the waters of small watercourses and ponds in the western part of the study area (Bemowo, Lachtorzew, Laski, Klaudyn, Mościska and Lipków). The elevated bromine concentrations may be an effect of surface runoff from the streets where salt is used as a de-icing agent.

A bromine concentration of 1.6 mg/dm³ was found in the ditch encircling the Radiowo landfill, abounding also in lithium (16.9 μ g/dm³), potassium (20.1 mg/dm³), hydrocarbonates (471 mg/dm³), manganese (1,280 μ g/dm³) and silica (27 mg/dm³).

The greatest bromine concentration (16.1 mg/dm³) is recorded in the waters of a ditch collecting municipal sewage from the village of Zagościniec (NE of Wołomin). These waters (with EC 2.3 mS/cm) also show the highest concentrations of bicarbonates (1,198 mg/dm³), total phosphorus (13.82 mg/dm³) and silica (27.5 mg/dm³), as well as elevated concentrations of sodium (175.4 mg/dm³) and chlorine (126 mg/dm³).

Corg TOTAL ORGANIC CARBON

Soils: <u>Pl. 22</u>, tab. <u>4</u>

The topsoil in the map sheet area is not rich in organic carbon. Over most of the study area (75%) the organic carbon content does not exceed 2.2%. Enrichment in this component of some soils from urban areas (2-4%), as compared with the soils of undeveloped land, can be the result of use of potting soil in urban lawns and greens, as well as accumulation, in urban soils, of products of incomplete combustion of carbon fuels by automobile engines.

Sandy soils of cropland are the poorest in organic carbon. Its greatest content was found in forest and grassland soils, often in wetlands, in areas of peat occurrence. The forest soils in the boundary area between the district of Wawer and the municipality of Wiązowna contain 19.2-47.8% of organic carbon, and in Wesoła near the Macierowe Bagno bog -41.0-44.3%.

Grassland peaty soils are also rich in organic carbon: in Białołęka (up to 22%), in the Raszynka valley (17.5%), in the Czarna drainage basin (up to 17.5%), and in the Długa valley upstream of Ossów (up to 14.4%).

Waters: Pl. 22, tab. 7

Organic carbon content in the surface waters is variable. About 86% of the waters meet the standards for water quality class I (\leq 15 mg/dm³), and 6% of the water samples represent class II (>15– \leq 20 mg/dm³).

Anomalous concentrations occur at single point sites and are mainly found in the waters of undeveloped land in the east and northeast of the map sheet area. The highest concentration of dissolved organic carbon (62.0 mg/dm³) is recorded in a forest lake of the Bagno Jacka nature reserve in Wesoła, where there are also elevated levels of lead ($3.02 \ \mu g/dm^3$) and zinc ($368 \ \mu g/dm^3$), and a high value of COD (117 mg/dm³). The water in a pond at Wólka Mlądzka is also rich in organic carbon (57.0 mg/dm³).

Ca CALCIUM

Soils: Pls. 23-24, tab. 4-5

Both the topsoil and subsoil of urban areas have higher calcium contents in comparison with the surrounding areas. The greatest average calcium contents are found in anthropogenic soils, soil of lawns, and soils of industrial and tall building areas. The poorest soils in this element are sandy forest soils. The main reason for the enrichment of soil in calcium in urban areas is dust emissions from coal combustion, and a large proportion of rubble in the soil.

The maximum calcium content (8.24%) in the topsoil is recorded in Warsaw in the premises of the already defunct Żerań cement plant. Calcium is also an abundant element in soils around a landfill of post-production waste of the ArcelorMittal steelworks (4.64%), currently being under elimination, and in the vicinity of the Polfa Tarchomin pharmaceutical company (2.50%).

Enrichment with calcium is also observed in soils on the outskirts of Ożarów. An anomaly in this area has a greater extent at a depth of 0.8–1.0 m than at the surface. Eluvial loess-like deposits are probably the source of calcium.

At a depth of 0.8–1.0 m, the greatest calcium content (and likely of natural origin) was found in peaty soils of the Raszynka valley (14.86%).

Sediments: Pl. 23, tab. 6

The calcium content in most of the sediments is below 1.19%. Elevated contents are observed mainly in water bodies of urban areas, which is undoubtedly due to the effect of anthropogenic factors.

Sediments markedly enriched in calcium were found in Mokotów (with a maximum of up to 9.15% in the sediments of Promenada pond, and slightly lower contents in the sediments of Arkadia pond, Sielecki Park pond, the ditch along Piaseczyńska Street, and the Piłsudski Fort moat).

Calcium-rich sediments are also found in the Łacha Potocka oxbow lake (up to 10.99%), the Bródnowski Górny (up to 7.80%), Henrykowski (up to 5.28%) and Wystawowy (up to 4.97%) canals,

and locally in the Vistula River and minor watercourses flowing across its flood terraces. The greatest average calcium contents are recorded in the Kanał Żerański canal (median 1.35%) and in the Vistula River (median 1.06%). The maximum calcium content (14.57%) was found in the Vistula sediments near the village of Kępa Falenicka.

The high levels of calcium are the result of both drainage from the basement that is naturally enriched in this element, and its influx from anthropogenic sources.

Waters: Pl. 24, tab. 7

Definitely, most of the waters are classified into water quality classes I and II with respect to the content of calcium. Its average concentration (median 71.3 mg/dm³) is similar to that measured in the waters of Poland (median 83 mg/dm³; Lis, Pasieczna, 1995) and much lower than in watercourses of Europe (median 40 mg/dm³; De Vos, Tarvainen, ed., 2006).

The greatest calcium concentrations are recorded in ditches from a forest area of Paluch (340.7 mg/dm³) and at the outskirts of the Bemowo forest (306.2 mg/dm³).

Anomalously high calcium concentrations (>127.1 mg/dm³) in the waters of agricultural areas are likely partly of natural origin, but they can as well result from runoff from limed soils. Elevated electrolytic conductivity values in these areas are due to largely high calcium contents.

As with sediments, high calcium concentrations are also common in water reservoirs and watercourses in the Mokotów area (up to 272.4 mg/dm³ in the ditch along the Piaseczyńska Street, but slightly lesser values in the Bernardyńska Woda moat, Piłsudski Fort moat and Kanał Sielecki canal).

Calcium is also abundant in the waters of the Rudawka River (up to 228.7 mg/dm³), Łacha Potocka oxbow lake (up to 182.7 mg/dm³), Kanał Henrykowski canal (up to 177.3 mg/dm³) and Żbikówka River (up to 167.8 mg/dm³). Increased calcium concentrations in these water bodies are caused by the emissions of industrial contaminants, surface runoff, dumping of rubble in ponds, and, in the case of the Kanał Henrykowski canal, by the influx of wastewater from the Polfa Tarchomin pharmaceutical company.

The Żbikówka River (also called the Konotopa canal) is contaminated by industrial plants, by the surface water drain system of Ursus, Piastów and Pruszków-Żbikowo, and by surface runoff from the A2 Motorway. Its waters are conspicuous by elevated concentrations of cadmium (up to 0.09 μ g/dm³), magnesium (up to 24.5 mg/dm³), molybdenum (up to 2.86 μ g/dm³), nickel (up to 5.8 μ g/dm³), nitrates (III) (up to 0.95 mg/dm³), nitrates (V) (up to 40 mg/dm³), sulphates (up to 185 mg/dm³), uranium (up to 14.01 μ g/dm³), vanadium (up to 3 μ g/dm³) and zinc (up to 46 μ g/dm³).

Cd CADMIUM

Soils: Pls. 25-26, tab. 4-5

Contamination of surface environments by cadmium is related primarily to human activity. In the soils of Warsaw and its surroundings, its content in 90% of the topsoil and in 97% of subsoil does not exceed 0.5 mg/kg, which is the geochemical baseline for soils in Poland (Pasieczna, 2003).

Local anomalies of cadmium concentration in the topsoil are associated with industrial and communication pollution. Its maximum concentration (95.6 mg/kg) was measured in Lazurowa Street in Jelonki.

The soils that are most polluted by cadmium are found in industrial and post-industrial areas. In the eastern flank of the former Służewiec Przemysłowy industrial area they contain 4–9 mg/kg of cadmium. In the industrial area of Białołęka the recorded cadmium values are 8.1 mg/kg, in the post-industrial area of Mokotów – 7.3 mg/kg, in the vicinity of the power plant and the former FSO automotive company in Żerań – 4.0 mg/kg, at the ArcelorMittal steelworks – 2–3 mg/kg, and in the Vistula River valley and its surroundings – 5–7 mg/kg.

Cadmium contamination of soils is found in some areas of the Vistula flood terraces (up to 4.8 mg/kg in the Łomianki region).

Outside of Warsaw, increased cadmium concentrations were found in Wołomin (3.6 mg/kg) near the Termisil glassworks, as well as in the meadows of Karczew (3.0 mg/kg), which are crossed by the Jagodzianka River, receiving wastewater from a sewage treatment plant in Otwock.

The maximum cadmium concentration (19.6 mg/kg) at a depth of 0.8–1.0 m was found in Targówek near the Kanał Bródnowski Górny canal close to the railway line. The soil also shows the maximum concentrations of silver (20 mg/kg) and cobalt (20 mg/kg). The contamination by these metals is associated probably with floods from the canal.

Sediments: Pl. 25, tab. 6

Cadmium contamination of sediments is caused primarily by the discharge of industrial wastewater. The greatest cadmium concentration (119.7 mg/kg) is recorded in the sediments of the Jeziorka River in the Spa Park of Konstancin-Jeziorna. The pollutants probably might originate from the discharge of sewage from the Thomson Technicolor Polska (former Polkolor) electronics company and from a sewage treatment plant in Piaseczno.

Anomalous concentrations of this element are also found in the sediments of the Kanał Bródnowski Górny canal (up to 58.9 mg/kg), Potok Służewiecki stream downstream of the airport (up to 6.9 mg/kg), and Struga Pogorzelska stream (up to 5.6 mg/kg). Contamination of the Kanał Bródnowski sediments is probably caused by the former industrial plants in Targówek, including the Warszawskie Zakłady Telewizyjne ELEMIS television equipment company, whereas the contamination of the Potok Służewiecki stream was likely caused in the past by sewage from numerous industrial plants (mainly

of the electronics industry), located in the Służewiec Przemysłowy industrial area (Cemi, Elwa, Cerad). Currently, the Potok Służewiecki stream is a receiver of rain sewage from the sewage treatment plant at the Chopin Airport, and of untreated rain sewage from the areas of Ursynów, Mokotów and Wilanów. In the case of the Struga Pogorzelska stream, the source of contaminating sewage is difficult to be determined.

Elevated cadmium levels (>1.6 mg/kg) are also found in the sediments of the Wilanówka River flowing across agricultural areas. The contamination can be associated with surface runoff from cropland where phosphatic fertilizers were used, containing considerable amounts of cadmium (Kabata-Pendias, Mukherjee, 2007).

Cadmium contamination (up to 4.1 mg/kg) is also locally observed in the sediments of the Vistula River (median 0.7 mg/kg).

Waters: Pl. 26, tab. 7

The cadmium concentration in 90% of the surface water samples does not exceed 0.05 μ g/dm³ (thus, all of the waters are classified into water quality class I, in accordance with the Directive 2013/39/EU).

The greatest cadmium concentration $(0.39 \ \mu g/dm^3)$ is recorded in a ditch in the village of Żanęcin, southeast of Wiązowna.

The cadmium concentrations of $0.07-0.30 \ \mu g/dm^3$ are common in the waters from the Struga Pogorzelska stream and its continuation – the Kanał Południowy canal crossing the Masovian Landscape Park. The enrichment of these waters also with aluminium, copper, lead, vanadium and zinc indicates a local sewage discharge.

Similar levels of cadmium concentrations were also found in the waters of the upper course of the Kanał Henrykowski canal, Żbikówka River, Czarna River and its tributaries, as well as in other minor watercourses.

COD CHEMICAL OXYGEN DEMAND

Waters: <u>Pl. 27</u>, <u>tab. 7</u>

Chemical oxygen demand is a conventional index of water contamination, which determines the amount of oxygen consumed from the oxidant to oxidize organic and some inorganic compounds present in the water.

With respect to the COD values, 83% of the samples meet the standards for water quality class I, and 4% for class II ($\leq 25 \text{ mg/dm}^3$ and $\geq 25 - \leq 30 \text{ mg/dm}^3$, respectively).

Elevated COD values are recorded locally in minor streams, mostly on the eastern side of the Vistula River. High average COD values are characteristic of the waters from the Czarna (median 19 mg/dm³) and Świder (median 15 mg/dm³) drainage basins. The highest COD values are recorded in stagnant water

reservoirs: in the pond at Wólka Mlądzka (118 mg/dm³) and in the lake of the Bagno Jacka bog (117 mg/dm³) in Wesoła.

CI CHLORINE

Waters: <u>Pl. 28</u>, <u>tab. 7</u>

The concentration of chlorine in the surface waters varies from 1.2 to 1,100 mg/dm³, and its distribution is similar to that of the EC. The average chlorine concentration (median 48.3 mg/dm³) is close to the average concentration of this element in the waters of the Poznań agglomeration (median 49.7 mg/dm³; Lis, Pasieczna, 2005).

The maximum chlorine concentration was found in the waters of a pond (marsh) in the village of Pólko (north of Marki).

High chlorine concentrations are typical of waters from urban areas. The water from Jeziorzec pond in Bemowo shows 1,010 mg/dm³ of chlorine, EC = 2.91 mS/cm, and considerable amounts of sodium (618.3 mg/dm³), molybdenum (8.66 g/dm³), and antimony (1.88 g/dm³).

Anomalous chlorine concentrations (>223 mg/dm³) are characteristic of water reservoirs in Mokotów (Bernardyńska Woda moat, moats of two forts: Czerniakowski and Piłsudski, Jeziorko Czerniakowskie lake, Kanał Czerniakowski canal, and Staw pod Królikarnią pond).

High amounts of chlorine were also found in the waters of the Potok Służewiecki stream, Kanał Henrykowski canal and Łacha Potocka oxbow lake. Considerable chlorine concentrations are observed in watercourses of the north-western districts of Warsaw and west of the city (in Laski, Mościska and Lachtorzew) – in a tributary of the Lipkowska Woda (flowing from the Wólka Węglowa and from the smelter area), in a right tributary of the Struga River (flowing from Bemowo), as well as in minor watercourses of this region.

Chlorine concentrations of up to 803 mg/dm³ occur in the waters of streams and ditches recharging the Raszynka River near Janki. The chlorine is derived from salting of roads.

94% of the analysed waters are included into water quality class I ($\leq 200 \text{ mg/dm}^3$ of chlorides), and 4% of waters are classified as class II ($\geq 200-\leq 300 \text{ mg/dm}^3$ of chlorides).

The Vistula River waters in the area of Warsaw are included mostly (95%) into water quality class I (median chlorine concentration is 63 mg/dm³). The greatest chlorine concentration was found in the Łasica drainage basin (median 72.6 mg/dm³), and the lowest one in the Świder drainage basin (median 20 mg/dm³).

Co COBALT

Soils: Pls. 29-30, tab. 4-5

The cobalt concentration in the topsoil of the map sheet area (median 2 mg/kg) is the same as in the soils of Poland (Lis, Pasieczna, 1995).

The cobalt concentration distribution in both of the soil depth ranges is similar. Elevated concentrations of this element (>4 mg/kg) are found in soils of the Vistula River valley and some areas in the western part of the city, which have developed on alluvial muds, glacial tills or eluvial deposits, rich in clay minerals. The cobalt content in these soils is of natural origin.

Anthropogenic contamination by cobalt in the topsoil is observed in the area of the ArcelorMittal smelter (up to 38 mg/kg), in the former Służewiec Przemysłowy industrial area (up to 17 mg/kg) and in the area of Polfa Tarchomin (8 mg/kg).

At a depth of 0.8–1.0 m the highest cobalt concentrations were found in Targówek and near the Kanał Bródnowski Górny canal, where the maximum concentrations of silver and cadmium are also recorded.

Sediments: Pl. 29, tab. 6

Most of the sediments contain below 10 mg/kg of cobalt, and elevated values are observed in the sediments of the Vistula River and the watercourses draining its flood terraces that are naturally enriched in cobalt.

Sediments contaminated by cobalt (up to 20 mg/kg) were also found in the Kanał Bródnowski Górny canal that starts near the Kawęczyn thermal power plant and flows around the eastern margin of the Targówek Fabryczny industrial area. Sediments of the Kanał Henrykowski canal, draining the area of Polfa Tarchomin pharmaceutical company, contain up to 14 mg/kg of cobalt, and those from the Rów z Lewandowa ditch in Białołęka – up to 12 mg/kg. The cobalt probably originates from the discharges of industrial sewage in the recent past.

Elevated cobalt concentrations are recorded in sediments of the Jagodzianka (14 mg/kg) downstream of the Otwock sewage treatment plant, and the greatest value (49 mg/kg) is recorded in an unnamed ditch in a forest area near Wiązowna.

Waters: Pl. 30, tab. 7

The cobalt concentrations in the waters of the study area are generally low and the lowest average values (median 0.13 μ g/dm³) are recorded in the Vistula River. All of the waters can be classified into water quality classes I and II (<50 μ g/dm³).

The greatest cobalt concentration (23.72 μ g/dm³) was found in a ditch of the Czarna River, and the lower one (15.63 μ g/dm³) in a ditch from the Potok Służewiecki drainage basin.

The water of a canal draining into the Czarna River in Wołomin contains $15.33 \ \mu g/dm^3$ of cobaltand $19 \ \mu g/dm^3$ of chromium. It also shows elevated concentrations of lithium($30 \ \mu g/dm^3$), nickel ($40.6 \ \mu g/dm^3$) and ammonium ions ($8.83 \ mg/dm^3$). The contamination originates from sewage and waste of former joinery manufacturers and currently operating chemical plants.

Elevated cobalt concentrations relative to the geochemical baseline are also recorded in the waters of the Kanał Henrykowski canal (up to $10.3 \ \mu\text{g/dm^3}$), Rów z Lewandowa ditch (up to $7.9 \ \mu\text{g/dm^3}$), Rów Miedzeszyński ditch (up to $6.0 \ \mu\text{g/dm^3}$), an oxbow lake (Lake Łacha) in Józefów (up to $6.0 \ \mu\text{g/dm^3}$), a ditch in a forested area at Radzymin ($4.39 \ \mu\text{g/dm^3}$), Kanał Zagoździański canal in Wawer (up to $3.0 \ \mu\text{g/dm^3}$), Magenta canal in Rembertów and in Zielonka (up to $2.6 \ \mu\text{g/dm^3}$). The amount of this element in the surface waters is strictly dependent on the amount of contaminants in industrial sewage.

Cr CHROMIUM

Soils: Pls. 31–32, tab. 4–5

The distributions of chromium concentration in the topsoil and subsoil are much the same. Elevated concentrations are found in soils of the Vistula River valley and in urban and industrial areas. The average content of chromium in the topsoil (median 7 mg/kg) is nearly twice as much as the geochemical background value in the soils of Poland (median 3 mg/kg; Pasieczna, 2003). The lowest chromium concentrations are typically found in forest soils.

Chromium concentrations >10 mg/kg in both soil depth ranges of the flood terraces of the Vistula River and in the area extending from the western outskirts of Warsaw to Ożarów are associated probably with a greater amount of chromium in the bedrock.

The greatest chromium concentrations (up to 785 mg/kg), found in the topsoil around the ArcelorMittal steelworks (active since 1957), are associated with dust emissions from this plant. The soils are also contaminated by arsenic (22 mg/kg), cadmium (2.8 mg/kg), cobalt (38 mg/kg), copper (123 mg/kg), nickel (272 mg/kg), lead (316 mg/kg), titanium (337 mg/kg), vanadium (63 mg/kg) and zinc (887 mg/kg). They are strongly alkaline and contain up to 14.06% of iron, up to 5,451 mg/kg of manganese, up to 4.64% of calcium and up to 1.39% of magnesium. The assessment survey of the degree of air pollution by heavy metals in the area of the steelworks, conducted in the years 1993–2008 using a bioindication method, showed a marked reduction in the emission of chromium by this plant as a result of its recent modernization (Dmuchowski *et al.*, 2011).

Anomalous chromium concentrations (93 mg/kg) are also recorded in the topsoil near the former Zakłady Ceramiki Radiowej ceramics company in Ursynów, in the premises of the Kawęczyn thermal power plant (up to 84 mg/kg), near the former Ursus Factory (59 mg/kg) and in a forest area near Zakręt (168 mg/kg).

At a depth of 0.8–1.0 m the maximum chromium concentration (112 mg/kg), accompanied by up to 74 mg/kg of nickel, was found in the Żerań industrial area.

Sediments: <u>Pl. 31</u>, <u>tab. 6</u>

Chromium concentrations in sediments in excess of the geochemical background value for Poland (median 5 mg/kg) are observed mainly in urban areas, indicating that the main source of chromium is industrial and municipal wastewater.

Anomalous chromium concentrations (>40 mg/kg) were found in the sediments of watercourses draining the modern and historical industrial areas: Kanał Bródnowski Górny canal, Kanał Henrykowski canal, Potok Służewiecki stream, Jeziorka downriver of Konstancin, and Rów Opaczewski ditch in Raszyn. The greatest concentration of chromium (983 mg/kg) is recorded in the sediments of the Żbikówka River near the A2 Motorway at Konotopa, and its lowest concentrations (4–5 mg/kg) are typically found in the sediments of the Świder, Czarna and Długa drainage basins.

Waters: Pl. 32, tab. 7

In most of the surface waters the chromium concentrations are below the detection limit (3 μ g/dm³). Greater concentrations were found in 17 samples, and the maximum value (19 μ g/dm³) is recorded in Wołomin in a canal draining an industrial area.

All of the analysed waters meet the standards for water quality classes I/II (chromium concentration $<50 \ \mu g/dm^3$).

Cu COPPER

Soils: Pls. 33-34, tab. 4-5

The average copper concentration in the topsoil (median 9 mg/kg) is three times greater than at a depth of 0.8–1.0 m (median 3 mg/kg), which indicates an anthropogenic origin of this metal. The distribution of anomalous concentrations at both depth ranges is very much alike, showing that the contaminants easily migrate from the ground surface into the soil profile. Soils in urbanized areas are clearly enriched in copper compared to the soils of undeveloped land. Soils of urbanized areas are markedly enriched in copper as compared with non-urbanized areas. The lowest average copper concentration (median 3 mg/kg), equal to the geochemical baseline value in non-urbanized areas of Poland (Pasieczna, 2003), is typically found in forest soils.

Anomalous copper concentrations (>50 mg/kg) mark some soils from the Targówek, Praga, Śródmieście, Wola, Ochota and Włochy areas as well as from the western peripheries of the city. These areas are located along major communication (railway and road) routes where, additionally, factories of various industries have been active since the mid-19th century. Copper in these areas originated mainly from dust emissions from industrial and power plants and communication sources.

In the topsoil the maximum copper concentration (4,477 mg/kg) was found in the Targówek Fabryczny industrial area. At a depth of 0.8–1.0 m the copper concentration is 200 mg/kg. The contamination is undoubtedly linked with industrial activity. From 1879 to the 1950s, a chemical

factory produced nitric acid, sulphuric acid, fertilizers, soda, ammonia, tannery fats, iron oxides and tile glaze in this area (Encyklopedia Warszawy, 1975; Targówek Fabryczny..., 2015). Before World War II the largest plants of this area included, e.g., steelworks, glassworks, a mint, and factories of machine tools, lamps, cosmetics, wire, welding equipment and ammunition. Many of these plants continued production after the war, but there were also new plants established: a television equipment factory, a telephone equipment factory, as well as machinery and furniture manufacturers.

Very high copper concentrations in the topsoil layer of Praga Południe (up to 1,489 mg/kg in Kozia Górka and 815 mg/kg in the Olszynka Grochowska area) as well as in Wawer (476 mg/kg), Wola (up to 310 mg/kg) and Bemowo (193 mg/kg) are found near railway tracks and railway stations. These can be associated with the use of herbicides and fungicidal preparations to impregnate railway sleepers.

Copper contamination (827 mg/kg) was detected in the topsoil in Kłopotowski Street, where a machinery and millstone factory operated from 1900, and, after World War II, machine and research equipment factories (Portal informacyjny..., 2015a).

Copper contamination in soils near the former Centrum Optyki in Ostrobramska Street (314 mg/kg), as well as in the premises of the ArcelorMittal steelworks (up to 123 mg/kg) and Polfa Tarchomin pharmaceutical company (100 mg/kg), and near the former Fabryka Kabli wire manufacturer in Ożarów (187 mg/kg) can be associated with industrial dust emission.

The maximum copper concentration in the subsoil (442 mg/kg) was found in Kamionek. The contamination is probably related to a long-time activity of a measuring equipment manufacturer (Encyklopedia Warszawy, 1975).

Higher copper concentrations compared with the topsoil are found in soils of railway premises of the former FSO automotive company in Żerań (279 mg/kg). They also contain up to 8.27% of iron, 1,524 mg/kg of manganese, 291 mg/kg of strontium and 379 mg/kg of titanium. The subsoil near Okęcie Chopin Airport contains 198 mg/kg of copper and 412 mg/kg of lead.

Sediments: <u>Pl. 33</u>, <u>tab. 6</u>

Copper-contaminated sediments occur predominantly in watercourses and reservoirs of urbanized areas. The median value of copper concentration (12 mg/kg) is slightly higher than that calculated in the 1990s – 9 mg/kg (Lis, 1992). The most copper-contaminated sediments include those from the Kanał Żerański drainage basin (median 31 mg/kg), and the lowest concentrations are found in the Świder drainage basin (median 3 mg/kg).

The greatest copper concentrations (383–2,131 mg/kg) are recorded in the sediments of the Rów Opaczewski ditch, rising near the WKD railway track at Salomea, which collects wastewater from part of the Włochy district area.

Anomalous copper concentrations in the sediments (>140 mg/kg) mark the Utrata River downstream of the confluence with the Raszynka (up to 367 mg/kg), in the Kanał Bródnowski Górny

canal downstream of the Targówek Fabryczny industrial area (up to 321 mg/kg), in the Kanał Henrykowski canal downstream of the Polfa Tarchomin pharmaceutical company (up to 225 mg/kg), and in a tributary of the Lipkowska Woda stream near Wólka Węglowa (up to 223 mg/kg). Sediments of the Wilanówka and Potok Służewiecki streams contain up to 106 mg/kg of copper.

The sediments are contaminated due to the discharge of sewage (largely industrial) and surface runoff.

Waters: Pl. 34, tab. 7

Copper concentrations in the surface waters ranges from 0.15 to 75.93 μ g/dm³. There was only one sample with the copper concentration above 50 μ g/dm³, which is the boundary limit for water quality classes I/II.

Anomalous concentrations (>5.45 μ g/dm³) are observed predominantly in watercourses and water reservoirs of the western part of the study area. The greatest concentrations of this element, as with sediments, are found in the Rów Opaczewski ditch (5.78–75.93 μ g/dm³) collecting wastewater from the S8 highway.

Copper also occurs abundantly in the waters of the tributaries of the Kanał Grabowski canal in Ursynów (up to 12.90 μ g/dm³), Lipkowska Woda stream that starts near the ArcelorMittal steelworks (up to 11.91 μ g/dm³), Struga River and its tributary from the area of Bemowo (up to 8.37 μ g/dm³), and Potok Służewiecki downstream of the Rów Wolica ditch (up to 6.39 μ g/dm³).

On the eastern side of the Vistula River valley, elevated copper concentrations are found in the waters of Struga Pogorzelska stream, Kanał Południowy canal and Kanał Henrykowski canal, as well as locally in the waters of the Rów Miedzeszyński ditch, Kanał Wawerski canal, and Czarna River and its minor tributaries. In the water of a ditch recharging the Czarna River in a forest area near Marki, the copper concentration is $14.19 \,\mu\text{g/dm}^3$.

The median value of copper concentration in the Vistula River waters $(2.32 \ \mu g/dm^3)$ is greater as compared with the values for other watercourses.

F FLUORINE

Waters: <u>Pl. 35</u>, <u>tab. 7</u>

In most of the samples (95%) the fluorine concentration does not exceed the detection limit (0.1 mg/dm³). Higher fluorine concentrations, found in the waters of the Lipkowska Woda and its tributaries, can be an effect of fluoride emissions by the ArcelorMittal steelworks, introduced into the atmosphere (and subsequently into the waters) as a result of steel-making technological processes (Dojlido, 1995). Anomalous fluorine concentrations are observed in the waters of the Kanał Henrykowski canal (also contaminated by a number of other chemical elements), Praga Port, Kamionkowskie Lake, Skaryszewski Park ponds, Old Vistula River and Łacha Kuligowska oxbow

lake in Wawer. Elevated values were also found in the tributaries of the Świder, Mienia, Czarna and Raszynka rivers. In areas used for agriculture, fluoride may originate from surface runoff from fields where phosphate fertilizers were applied.

With respect to fluorine concentration ($\leq 1.5 \text{ mg/dm}^3$) the analysed waters are classified into water quality class I. The maximum fluorine concentration (1.5 mg/dm³) is recorded in the waters of the Rów Wolica near the Ursynów Escarpment.

Fe IRON

Soils: Pls. 36–37, tab. 4–5

The distributions of iron content in both the topsoil and subsoil are similar. The lowest iron contents are found in sandy forest soils, whereas the greatest ones are recorded in soils of urban and industrial areas.

The anomalous contents of this element (>2%) probably originate from two sources. In the flood terraces of the Vistula River, where alluvial muds rich in clay minerals and aluminium are a common lithological component, the iron content is up to 4.35%, being likely of natural origin. Naturally iron-enriched soils (up to 5.98%), developed on peats and alluvial muds rich in organic matter, also occur in wetland areas of the Długa River valley downstream of Okuniew, as well as in Targówek and Białołęka (up to 6.23%). These soils are also enriched in arsenic.

Anthropogenic origin is suggested for iron contaminating the topsoil in the ArcelorMittal steelworks (up to 14.06%), in the railway premises of Wola (5.55%) and near the former Zakłady Mechaniczne Ursus Factory (3.59%). An anthropogenic source is also supposed for point anomalies in Bronisze and Kajetany, in the south-western part of the map sheet area.

The greatest iron content in the subsoil (20.76%) was found in the Henrykowski Park in Białołęka. Point anomalies of iron content (8.35% and 8.27%, respectively) are recorded in embankment soils near the Łazienkowska Thoroughfare in the Śródmieście district and in the railway premises of the FSO automotive company in Żerań – both are anthropogenic in origin.

Sediments: <u>Pl. 36</u>, <u>tab. 6</u>

The median value of iron content in the sediments (0.67%) is identical to that from earlier periods (Lis, 1992). The maximum iron contents (27.03%) in organic sediment of the Kanał Wolicki canal (Miasteczko Wilanów residential area) and Rów z Lewandowa ditch (up to 17.44%) may be the result of the discharge of iron-rich near-surface water from residential development areas into the watercourses.

Anomalous iron contents in the sediments of the Kanał Bródnowski Górny (up to 9.27%) and Kanał Henrykowski (up to 9.51%) canals are undoubtedly related to the activity of industrial plants in

Targówek and Tarchomin, while those in the canals of Białołęka (up to 8.55%) are probably of natural origin.

Clearly elevated iron contents (>3.82%) in the sediments of watercourses and water reservoirs on the flood terraces of the Vistula River (upriver of Zawady) are associated with drainage of the bedrock rich in iron compounds (in the Wilanówka sediments, the content is up to 9.25%).

Waters: <u>Pl. 37</u>, <u>tab. 7</u>

The iron concentrations in the surface waters of Warsaw and its environs range from <0.01 to 40.06 mg/dm³, and the median is 0.09 mg/dm³. As with aluminium, greater iron concentrations are common in the right-bank side of the Vistula River.

The greatest concentration (40.06 mg/dm³) was found in a ditch from the Raszynka River drainage basin. High iron concentrations are also recorded in the surface waters of forest ditches in Józefów (35.30 mg/dm³) and Radzymin (22.80 mg/dm³). In Radzymin there is also the greatest concentration of aluminium (4,209.6 μ g/dm³) in study area, and increased concentration of cobalt – 4.39 μ g/dm³.

Elevated concentrations (>1.60 mg/dm³) are also observed in the waters of some tributaries of the Czarna, Mienia and Świder rivers, Kanał Wawerski canal, canals in the area of Białołęka, Rów z Lewandowa ditch, as well as the Kanał Bródnowski Dolny canal, Kanał Zagoździański canal and Rów Miedzeszyński ditch.

In an oxbow lake of the Vistula River at Leg near Konstancin the iron concentration is 20.60 mg/dm³, and in the waters of a ditch crossing Wawer – 17.83 mg/dm³.

The lowest average iron concentration is typically found in the waters of the Utrata River drainage basin (median 0.05 mg/dm³), and the greatest values were calculated for the waters of the Świder River drainage basin (median 0.25 mg/dm³).

HCO₃ HYDROCARBONATES

Waters: <u>Pl. 38</u>, <u>tab. 7</u>

Over most of the map sheet area the hydrocarbonates concentrations are in the range of 12–325 mg/dm³. The highest average value is determined for the waters of the Łasica drainage basin (median 267 mg/dm³), whereas the lowest one was calculated in the Vistula River (median 171 mg/dm³). The median concentration for the waters of ponds and lakes is 193 mg/dm³.

The maximum concentration of HCO_3 (1,198 mg/dm³) is recorded in the waters of a ditch that receives municipal sewage from the village of Zagościniec (NE of Wołomin). The water of this ditch (with the EC value of 2.3 mS/cm) is also enriched in phosphorus, silica, sodium and chlorine.

Increased concentrations of hydrocarbonates are found in the waters of watercourses and reservoirs, which are also characterised by high EC value and high contents of boron, barium, calcium, chlorine, lithium, magnesium, sodium, sulphates, silica, strontium and uranium. In the Mokotów area

these are the waters of the Piłsudski and Czerniakowski fort moats, Bernardyńska Woda moat, Kanał Sielecki canal, Arkadia pond and Sielecki Park lake.

Hydrocarbonates (as well as barium, calcium, chlorine, lithium, magnesium, sodium and sulphates) are also abundant in the waters of the Łacha Potocka oxbow lake and Kanał Henrykowski canal.

Markedly anomalous bicarbonate concentrations (>378 mg/dm³) are observed in the waters of the Lipkowska Woda and Struga rivers and their tributaries (up to 681 mg/dm³) in the western part of the study area, in the waters of the Raszynka River and its tributaries (up to 540 mg/dm³) in the south, and in the waters of the Czarna River drainage basin in the northeast.

Hg MERCURY

Soils: Pls. 39-40, tab. 4-5

The mercury content is variable; in 50% of the analysed topsoil it does not exceed the geochemical baseline for the soils of Poland (median <0.05 mg/kg; Pasieczna, 2003).

Elevated mercury concentrations (of anthropogenic origin) occur mainly in the city centre of Warsaw: in Śródmieście, Wola, Żoliborz (Marymont), north Ochota, Praga Północ (Szmulki, Stara Praga, Nowa Praga) and Praga Południe (Kamionek). The extents of anomalies in both the topsoil and subsoil are similar, which indicates an easy migration of mercury into the soil profiles.

The greatest mercury concentrations in the city centre of Warsaw are found in the topsoil of parks (<0.05–2.74 mg/kg; median 0.11 mg/kg). Similar average mercury concentrations were also recorded in the city parks of Poznań (median 0.13 mg/kg; Lis, Pasieczna, 2005).

The maximum mercury concentrations (3.83 mg/kg in the topsoil and 4.98 mg/kg in the subsoil) were found near the Warsaw Wschodnia railway station. The source of the soil contamination along the railway track could be both emission from burning of coal that contains 0.06–0.39 mg/kg of mercury on average (Bojakowska, Sokołowska, 2001), and the use of mercury-containing chemicals for the maintenance of railway sleepers.

Mercury contamination is observed in soils of the Warsaw Escarpment (2.93 mg/kg in the topsoil and 4.01 mg/kg in the subsoil) near the Old Town. The topsoil in the Kazimierzowski Park contains 1.27 mg/kg of mercury, while in Marymont - 1.42 mg/kg. These soils represent anthropogenic grounds composed of different wastes that have been disposed of in the area of the Old and New Town since the Middle Ages.

Distinct anomalous mercury concentrations were encountered in the topsoil of the Moczydło Park (2.74 mg/kg), Bemowo Forest Park (2.49 mg/kg), allotment gardens in Targówek (2.07 mg/kg), near the former Powiśle thermal power plant (1.79 mg/kg), in the area of the Kawęczyn thermal power plant (1.52 mg/kg), in Koszykowa Street in the Śródmieście district (1.31 mg/kg) and in the Augustówek residential area in Białołęka (1.17 mg/kg).

Outside of Warsaw, small local mercury anomalies were observed close to the railway line at Duczki near Wołomin (2.49 mg/kg).

Mercury contamination was also found in cropland soils (1.98 mg/kg) of the village of Zamienie (Lesznowola municipality), in Jaworowo southeast of Raszyn (1.01 mg/kg), and near a sewage treatment plant between Karczew and Otwock (0.42 mg/kg). Mercury in these agricultural soils can origin from formerly used chemicals for seed treatment and plant protection preparations.

Sediments: Pl. 39, tab. 6

The mercury concentration in the sediments ranges from <0.05 to 3.57 mg/kg. Anomalous concentrations are typically found in the Kanał Bródnowski Górny canal that, for a long time, collected sewage from industrial plants of Targówek (up to 2.01 mg/kg), in the Kanał Henrykowski canal downstream of the Polfa Tarchomin pharmaceutical company (up to 1.11 mg/kg), and in the Wilanówka River (up to 0.55 mg/kg), where mercury originated from surface runoff from areas in which mercury preparations were used for plant protection.

Anomalous mercury concentrations were found locally in the sediments of the Rudawka in the Bielański Forest, Magenta canal in Rembertów, Jagodzianka (downstream of the sewage treatment plant), and some closed drainage reservoirs, e.g. Staw pod Królikarnią pond (3.46 mg/kg) and Radiowo Fort moat (0.70 mg/kg).

The maximum mercury concentration (3.57 mg/kg) is recorded in organic sediments of Jeziorko Wilanowskie lake, where considerable amounts of cadmium (6.7 mg/kg), cobalt (10 mg/kg), copper (105 mg/kg) and zinc (640 mg/kg) were also found. Previous analyses of the sediments from this lake, which is permanently contaminated by the waters of the Potok Służewiecki stream, revealed the mercury concentration of up to 1.870 mg/kg, as well as considerable amounts of cadmium, copper, lead and zinc (Tomassi-Morawiec *et al.*, 2007).

K POTASSIUM

Waters: Pl. 41, tab. 7

The potassium concentration in the waters varies from 0.1 to 58.3 mg/dm³. The median concentration of this element (5.7 mg/dm³) is lower than in the waters of Poland (median 6.5 mg/dm³; Lis, Pasieczna, 1995) and the Poznań agglomeration (median 7.9 mg/dm³; Lis, Pasieczna, 2005), but similar to the concentrations in the waters of Szczecin and its environs (median 5 mg/dm³; Lis, Pasieczna, 1998a).

On the western side of the Vistula River, anomalous potassium concentrations (>17.0 mg/dm³) are found in the waters of the Struga River and its tributary from the vicinity of Bemowo (up to 22.4 mg/dm³), watercourses in the Lipkowska Woda drainage basin (54.2 mg/dm³) and the surrounding trench of the Radiowo Landfill (20.1 mg/dm³).

Potassium-rich stagnant water bodies of urban areas include: Sadurka pond (45.6 mg/dm³), Łużek pond (44.3 mg/dm³), Jelonki pit ponds (44.0 mg/dm³), Jezioro Imielińskie lake (26.6 mg/dm³), Zbarż Fort moat (23.1 mg/dm³), Blizne Fort moat (22.8 mg/dm³), Stawy Młocińskie ponds (19.3 mg/dm³) and numerous unnamed ponds in agricultural areas in the Raszynka River drainage basin (up to 28.5 mg/dm³).

On the eastern side of the Vistula River, anomalous potassium concentrations are found in the waters of the Kanał Wawerski canal (up to 19.8 mg/dm³), in the waters of numerous tributaries of the Czarna River (up to 44 mg/dm³), and in ponds of its drainage basin.

The maximum potassium concentration (58.3 mg/dm³) accompanied by elevated lithium concentration (42.4 μ g/dm³) is recorded in the waters of a pond in Kobyłka, which is a former clay pit filled with rubble.

The highest average potassium concentrations (median 8.4 mg/dm³) are characteristic of the waters from dranaige basins of Nowa Ulga and Nowe Ujście canals as well of Łasica River (median 8.3 mg/dm³), while the lowest ones are observed in the Vistula River (median 4.2 mg/dm³).

The potassium concentration in the waters is caused by local sewage discharges as well as surface runoff. Agricultural areas are the source of potassium from fertilizers; while in urban areas, potassium comes from chemicals used for winter road maintenance.

Li LITHIUM

Waters: Pl. 42, tab. 7

The lithium concentration in the waters of the study area is highly variable ranging from <0.3 to 122.7 μ g/dm³. The median value (4.7 μ g/dm³) is lower than in the waters of Szczecin and its environs or in Poznań and its surroundings (median 6 μ g/dm³; Lis, Pasieczna, 1998a, 2005).

Elevated lithium levels $(5.6-17.3 \ \mu\text{g/dm}^3; \text{ median: } 8.5 \ \mu\text{g/dm}^3)$ are commonly found in the Vistula River. As with thallium, lithium probably originates from saline mine water of Upper Silesia.

Markedly anomalous lithium concentrations (>13.7 μ g/dm³) are found in the waters of numerous water reservoirs and ditches within the urban area of the left-bank side of Warsaw, commonly characterised also by high electrolytic conductivity values indicating a considerable degree of mineralisation.

The maximum lithium concentration (122.7 μ g/dm³) was found in the water from a ditch that flows from the area of ArcelorMittal steelworks.

High lithium concentrations are clearly marked in the waters of a ditch in Paluch (33.1 μ g/dm³), Morskie Oko pond (31.3 μ g/dm³) and the trench surrounding the Radiowo Landfill (16.9 μ g/dm³).

Lithium-enriched waters are found in the following water bodies: ponds in Łazienki, Staw Belwederski pond, Promenada pond, Jeziorko Czerniakowskie lake, Czerniakowski Fort moat, Piłsudski Fort moat, Bernardyńska Woda moat, Kanał Sielecki canal, Kanał Czerniakowski canal, Arkadia pond, Staw pod Królikarnią pond, the ditch along Piaseczyńska Street, a pond near Dolna Street, a pond in the Ujazdowski Park, Szczęśliwickie and Fajansowe clay pit ponds, Jelonki clay pit ponds, Okęcie and Blizne fort moats, Jeziorzec pond in Bemowo, Łacha Potocka oxbow lake, Rudawka River and, locally, Kanał Bródnowski Górny canal.

Outside of Warsaw, anomalous lithium levels were encountered in the waters of a tributary of Struga near Bemowo, which are also rich in other constituents (copper, potassium, magnesium, molybdenum, sodium, uranium, zinc, chlorine, fluorine, hydrocarbonates). Local enrichments in lithium are also found in the waters of the Kanał Ożarowski canal, Żbikówka and Raszynka rivers, and watercourses in the Czarna River drainage basin. High lithium concentrations are recorded in the waters of two ponds in Kobyłka (42.6 μ g/dm³ and 42.4 μ g/dm³, accompanied by the maximum potassium concentration of 58.3 mg/dm³).

The elevated lithium concentration in the water bodies can be associated with surface runoff and sewage discharges.

Mg MAGNESIUM

Soils: Pls. 43-44, tab. 4-5

The distribution of magnesium in the soils resembles that of iron, which indicates a co-occurrence of these elements in minerals of their parent rocks. Statistical parameters of the magnesium content for both soil depth ranges are very similar, so there is no evidence of significant enrichment of the topsoil as a result of human impact. The median magnesium content in the topsoil (0.07%) slightly exceeds the geochemical background level in the soils of Poland (0.04%; Pasieczna, 2003). The lowest magnesium contents in the map sheet area commonly occur in forest soils (median 0.02%).

Magnesium content in the soils mostly corresponds to the bedrock chemical composition. Increased contents (>0.12%) are observed in areas where the bedrock is rich in clay minerals and carbonates. These are glacial tills (in the left-bank side of Warsaw), alluvial soils (Vistula River flood terraces), as well as loess-like eluvial deposits (a belt extending from the western limits of Warsaw to Ożarów).

The topsoil in the area of Warsaw reveals also magnesium anomalies due to fallout of industrial particles. The maximum content of this element (1.39%) was encountered in the area of ArcelorMittal steelworks. Magnesium-rich soils occur around furnace waste landfills in Żerań (0.78%) and Zawady (0.48%) and near the Siekierki thermal power plant (up to 0.56%).

Dispersion of magnesium-rich dust also takes place around brick factories, resulting in 0.56% Mg in the topsoil in Marki and 1.23% Mg in the subsoil in Nowe Słupno in the north of the map sheet area. High magnesium contents are also found in the area of the former Fabryka Domów houses factory in Świderska Street (0.76%).

In the subsoil the maximum magnesium content (1.57%) was found in the immediate proximity to the composting plant of the Radiowo Landfill that received municipal waste till 1991. This anomaly

indicates that this element migrates into the soil profile. Enrichment with magnesium (up to 0.62%) in soils between Wieruchów and Ożarów is probably related to the lithology of parent rocks.

Sediments: Pl. 43, tab. 6

The magnesium content in sediments varies between <0.01 and 1.12%. The most Mg-rich sediments are those of the Vistula River (median 0.20%) and of the Wilanówka drainage basin (median 0.17%). The Vistula River sediments are naturally enriched in magnesium that is washed away from soils of the river terraces, and transported from the southern part of the drainage basin where weathered carbonate rocks are exposed at the surface. Draining of the Mg-enriched bedrock contributes to the accumulation of this element in sediments of reservoirs located on the Vistula flood terraces and near Ożarów. The maximum magnesium content (1.12%) was found in organic sediment of a pond in the village of Opacz. Enrichment in magnesium is also observed in a ditch in Stare Babice (1.06%), Kanał Bródnowski Dolny canal in Kąty Węgierskie (0.89%), Rów Miedzeszyński ditch (0.83%) and clay pit ponds in Nowe Słupno near a closed-down brickyard (0.68%).

Anomalous magnesium levels in the canals of Bródnowski Górny (up to 0.55%) and Henrykowski (up to 0.71%) are probably caused by the discharge of industrial sewage.

Waters: Pl. 44, tab. 7

The magnesium concentration in the analysed waters is highly variable. Elevated concentrations (>18.2 mg/dm³) are observed in the waters of both agricultural and urban areas. The average concentration of magnesium in the waters of Warsaw and surrounding areas (median 9.9 mg/dm³) is close to that in the waters of Szczecin (median 11.2 mg/dm³; Lis, Pasieczna, 1998a) and much lower than in the waters of Poznań (median 17.54 mg/dm³; Lis, Pasieczna, 2005). The lowest average magnesium concentration is characteristic of the waters of the Świder drainage basin (median 7.9 mg/dm³). The greatest values were found for the waters of the Łasica drainage basin (median 12.6 mg/dm³).

In urban areas, anomalous magnesium contents (>21.6 mg/dm³) are recorded in the waters of the Łacha Potocka oxbow lake and the Rudawka Stream in the Bielany Forest nature reserve, as well as in the watercourses and reservoirs of Mokotów (Kanał Czerniakowski canal, Bernardyńska Woda, Piłsudski Fort moat, Staw pod Królikarnią pond, Arkadia and Promenada ponds, and Kanał Sielecki canal). In the districts of Ochota and Włochy, Mg-rich waters are found in the Sadurka pond, Fajansowe and Szczęśliwickie clay pit ponds, and Żbikówka River.

Outside of Warsaw, Mg-rich waters are found in ponds of the town of Łomianki, in the Struga River and its tributaries, and in the watercourses of the Lipkowska Woda and Czarna River drainage basins. The magnesium is supplied to the waters with surface runoff from agricultural areas where magnesium-rich fertilizers were used or soil liming.

The maximum magnesium concentration (62.4 mg/dm³) was found in the waters of a pond in a forest at Piotrkówek Duży (municipality Ożarów Mazowiecki).

The waters of a forest ditch near Okęcie Chopin Airport contain 60.8 mg/dm³ of magnesium and 340.7 mg/dm³ of calcium. They are also rich in potassium (27.2 mg/dm³), lithium (33.1 μ g/dm³), hydrocarbonates (988 mg/dm³), sulphates (293 mg/dm³), silica (27.3 mg/dm³), strontium (1,067 μ g/dm³) and uranium (19.55 μ g/dm³). The contamination is caused presumably by leachate from illegal waste dumping.

With respect to the magnesium content the waters are categorised into water quality classes I or II (\leq 50 mg/dm³ and >50- \leq 100 mg/dm³, respectively).

Mn MANGANESE

Soils: Pls. 45-46, tab. 4-5

The ranges and distributions of manganese content in both the topsoil and subsoil layers are very similar. The greatest amounts of manganese are observed in soils of the Vistula River valley and the left-bank side of Warsaw, including its south-western peripheries. The lowest contents of this element were found in sandy and peaty forest soils.

The content of manganese in soils of urban areas is controlled mainly by its presence in the bedrock (Czarnowska *et al.*, 1983, 1992; Czarnowska, Walczak, 1988; Lis, Pasieczna, 1998b). Natural manganese anomalies (>500 mg/kg) are represented by those observed in alluvial muds of the Vistula flood terraces. In Siekierki and Zawady, the topsoil contains up to 1350 mg/kg of magnesium, and the concentrations of this element in the subsoil of the Powsinek area are up to 4,920 mg/kg.

Natural enrichment with manganese is observed in meadow soils that have developed on peats, alluvial muds and humic sands in the Dhuga River (up to 2,443 mg/kg) and in the area of an ancient meander of the Vistula River in Wawer (up to 1,128 mg/kg). These soils are also rich in iron and arsenic.

Soils from the area of Bemowo and Ożarów Mazowiecki, which are developed on eluvial sediments (sands, silts and loes-like silts) contain up to 1,050 mg/kg of manganese at both depth ranges.

The maximum manganese concentration (5,451 mg/kg) is recorded in the topsoil of anthropogenic soil near a waste landfill of the ArcelorMittal steelworks. Emission dust from the plant is the likely source of manganese here.

Of anthropogenic origin is also a small local anomaly near Karczew close to the Vistula River (1,161 mg/kg). It is evidenced by clearly increased concentrations of other elements, including arsenic, cadmium, cobalt, mercury and nickel in the soils periodically flooded by the Jagodzianka River waters, which receives wastewater from a sewage treatment plant.

Manganese is also abundant in the topsoil of Dziekanów Leśny and Łomianki (up to 1,501 mg/kg) near the highway to Gdańsk, and in Ożarów near the road to Poznań (up to 1,018 mg/kg), which is probably due to emissions from car engines, containing manganese tricarbonyl supplemented to the petrol as an anti-knock (Kabata-Pendias, Szteke, 2012).

At a depth of 0.8–1.0 m the greatest amount of manganese (5,452 mg/kg) was encountered in soils of Gocław near the Łazienkowska Thoroughfare and in the Rembielszczyzna area on both sides of the Kanał Żerański canal (3,000–4,920 mg/kg). These anomalies are probably lithogenic in origin.

Embankment soils in the railway premises of the former FSO automotive factory contain up to 2,013 mg/kg of manganese and other metals, maybe from anthropogenic sources. The considerable manganese concentration (1,524 mg/kg) in the subsoil of the Henrykowski Park in Tarchomin also seems to be anthropogenic in origin.

Sediments: Pl. 45, tab. 6

In Warsaw, the sediments are characterised by a wide range of manganese concentrations from 4 to 20,120 mg/kg. The average concentration of this element (median 183 mg/kg) is lower than the average in the rivers and streams of Poland and in sediments of the environs of Poznań (medians 274 and 203 mg/kg, respectively; Lis, Pasieczna, 1995, 2005), but greater than that calculated in the previous studies of this region (median 159 mg/kg; Lis, 1992).

The greatest amounts of manganese are found in sediments of the Kanał Żerański drainage basin (median 642 mg/kg), and the lowest ones are observed in the Długa River drainage basin (median 83 mg/kg). The maximum manganese concentration (20,120 mg/kg) is recorded in sediments of a ditch crossing a forest area near Wiązowna, which also contain much cobalt (49 mg/kg).

Anomalous manganese concentrations (>1,422 mg/kg) are characteristic of the sediments of watercourses flowing across the flood terraces of the Vistula River valley: Wilanówka (up to 8,581 mg/kg) and Rów Powsinkowy ditch (up to 2,407 mg/kg), draining the Mn-rich bedrock.

Mn-rich sediments are also known from the Rów z Lewandowa ditch (up to 7,029 mg/kg), Kanał Henrykowski canal (up to 6,510 mg/kg), Kanał Bródnowski Górny and Dolny canals (up to 5,043 mg/kg), lower course of the Nowa Ulga canal (up to 2,402 mg/kg), and Kanał Żerański canal downstream of the thermal power plant (up to 2,061 mg/kg). Anomalous manganese concentrations in these sediments should be linked mostly with the discharge of industrial sewage (in the past as well).

Waters: <u>Pl. 46</u>, <u>tab. 7</u>

The range of manganese concentrations in the waters around the world varies between 0.02 and 130 μ g/dm³, but in contaminated rivers it can exceed 1,000 μ g/dm³ (Kabata-Pendias, Szteke, 2012). In the waters of the study area the manganese concentration is highly variable, like in sediments, ranging from <1 to 12,495 μ g/dm³. In most of the waters (75%) it does not exceed 278 μ g/dm³. The average

manganese concentration (median 123 μ g/dm³) is similar to that from the Szczecin agglomeration (median 120 μ g/dm³; Lis, Pasieczna, 1998a).

The maximum manganese concentration (12 495 μ g/dm³) is recorded in the waters of a ditch running through arable land and paralleling the Kanał Habdziński canal in the village of Habdzin (municipality Konstancin-Jeziorna). The greatest average manganese concentration is recorded in the Kanał Żerański drainage basin (median 277 μ g/dm³), and the lowest one – in the Vistula River (median 230 μ g/dm³).

High manganese concentrations are observed in the waters of the Kanał Henrykowski canal $(1,498-5,578 \ \mu g/dm^3)$, strongly contaminated by other chemical elements, and in a ditch in the village of Klaudyn, municipality Izabelin (6,488 $\mu g/dm^3$).

Anomalous manganese concentrations (4,065 μ g/dm³) were found in the waters of a ditch draining the area of ArcelorMittal steelworks (containing also up to 47.37 μ g/dm³ of molybdenum).

Waters of the surrounding trench around the Radiowo Landfill contain 1280 µg/dm³ of manganese.

Anomalous levels of manganese are typically found in minor tributaries of the Lipkowska Woda and in numerous small watercourses and reservoirs in the Czarna River, Świder and Kanał Wawerski drainage basins. Considerable manganese concentrations are also observed in the waters of ponds in Łomianki, in the Kanał Bródnowski canal, ditches recharging the Kanał Żerański canal, Rów z Lewandowa ditch, Wilanówka River, and locally in the Vistula River and its oxbow lakes.

Mo MOLYBDENUM

Waters: Pl. 47, tab. 7

The molybdenum concentration in the waters of the study area ranges from <0.05 to 47.37 μ g/dm³; 90% of the samples show the concentrations below 2.41 μ g/dm³. Excepting the sample with the maximum concentration of this element, all the remaining samples represent water quality classes I/II with respect to molybdenum content (\leq 40 μ g/dm³).

Elevated (>2.41 μ g/dm³) and anomalous (>3.50 μ g/dm³) molybdenum concentrations are observed mainly in the watercourses and reservoirs of urban areas.

The maximum concentration of molybdenum is recorded in the waters of a ditch draining the area of ArcelorMittal steelworks. High levels of this element (and also of lead) are found in the waters of two ditches recharging the Lipkowska Woda, resulting in the contamination of Lipkowska Woda waters up to 9.67 μ g/dm³. Waters of a ditch in the Wólka Węglowa area contain 7.62 μ g/dm³ of molybdenum, and the waters of the Kanał Henrykowski canal – up to 5.21 μ g/dm³.

Anomalous molybdenum concentrations $(3.52-20.68 \ \mu\text{g/dm}^3)$ are characteristic of the waters of the Kanał Bródnowski Górny canal. This contamination originates probably from coal burning in the Kawęczyn thermal power plant as well as emissions from the Municipal Solid Waste Treatment Plant in Gwarków Street. It is evidenced by the molybdenum concentrations in the waters of the nearby

Kanał Kawęczyński canal (4.19–5.07 μ g/dm³) and of Kozia Górka pond (4.06 μ g/dm³), where an additional source of contamination may be the sewage from the Grochów rolling-stock repair workshop.

Distinct anomalous molybdenum concentrations are recorded in the waters of some reservoirs in the Bemowo district: Jelonki clay pit ponds 16.43 μ g/dm³, Jeziorzec pond 8.66 μ g/dm³, and Blizne Fort moat – 6.30 μ g/dm³.

Molybdenum contamination is also found in the waters of the Górznik Stream, which is a tributary of the Czarna River (6.63–8.16 μ g/dm³), where high amounts of antimony were also noted (up to 7.88 μ g/dm³).

As regards minor watercourses, considerable molybdenum concentrations were found in the waters of a ditch recharging Jeziorko Dziekanowskie lake in Łomianki (up to 6.09 μ g/dm³), in the waters of streams draining the Blizne Łaszczyńskiego and Wieruchów areas (up to 4.91 μ g/dm³), and in the waters of the Rudawka River (up to 4.74 μ g/dm³).

Elevated molybdenum concentrations are also locally observed in the waters of the Raszynka River, Jeziorka ditch, Rów Miedzeszyński ditch, Kanał Żerański canal, Żbikówka, Wolica ditch and canal, and some other water reservoirs (Stawy Kacze ponds in the Skaryszewski Park, Jeziorko Czerniakowskie lake and Czerniakowski Fort moat).

Na SODIUM

Waters: <u>Pl. 48</u>, <u>tab. 7</u>

The sodium concentration in the waters of the map sheet area varies from 0.8 to 714.1 mg/dm³, and its distribution is similar to that of chlorine. The median value (30.1 mg/dm³) is twice as much as that in the surface waters of Poland (median 14 mg/dm³; Lis, Pasieczna, 1995) and is similar to the corresponding value in the waters from the Poznań agglomeration (median 26.6 mg/dm³; Lis, Pasieczna, 2005). The lowest sodium concentration was found in the waters of the Świder drainage basin (median 13.3 mg/dm³), while the greatest one – in the Łasica drainage basin (median 39.3 mg/dm³).

Waters of the Vistula River contain 8.9–123.2 mg/dm³ of sodium. The values are slightly lower than those determined in the study from 1992 (40–156 mg/dm³; Dojlido, 1995). The sodium originates both from Upper Silesia's discharges of saline mine waters subsequently transported by rivers (Pasieczna, ed., 2010b), and from surface runoff of sodium chloride used for winter road maintenance.

Anomalous sodium concentrations (>111.7 mg/dm³) are found mainly in the waters of the left-bank side of Warsaw, particularly in closed drainage reservoirs of urban areas, and are associated with the discharge of wastewater or surface runoff.

Highly contaminated waters occur in the reservoirs along the Trasa AK (Home Army Thoroughfare). The sodium concentration in Jeziorzec pond (Bemowo) is 618.3 mg/dm³, and in the

Blizne Fort moat -395.7 mg/dm^3 . There are also considerable amounts of chlorine, potassium, lithium and molybdenum in these water bodies.

Sodium concentrations >111.7 mg/dm³ (as well as high EC and considerable proportions of other constituents) are recorded in the following water bodies: Bernardyńska Woda moat, Czerniakowski and Piłsudski fort moats, Jeziorko Czerniakowskie lake, Jelonki clay pit ponds, Glinianki Sznajdra clay pit ponds, Staw Koziorożca pond, Kanał Czerniakowski canal and Łacha Potocka oxbow lake.

High sodium concentrations are characteristic of the waters of streams in the Lipkowska Woda drainage basin. In the waters of a ditch flowing from the Wólka Węglowa area the sodium concentration is 281.5 mg/dm^3 , while in those running from Bemowo – 266.7 mg/dm^3 .

The sodium concentration in a stream from the Struga drainage basin (Lachtorzew area) is 190.7 mg/dm³, and in the waters of the Kanał Henrykowski canal -218.1 mg/dm³.

Local elevated sodium concentrations are recorded in the waters of the Regułka, streams recharging the Raszynka River, and the lower course of the Czarna Struga River.

The maximum sodium concentration of 714.2 mg/dm³ (and 1,100 mg/dm³ of chlorine) is recorded in the waters of a pond (marsh) at a village of Pólko, near the Warsaw–Wyszków road.

NH₄ AMMONIUM ION

Waters: <u>Pl. 49</u>, <u>tab. 7</u>

The ammonium ion concentration varies from <0.05 to 29.2 mg/dm³. Waters quality class I is represented by 56% of the analysed waters ($\leq 0.78 \text{ mg/dm}^3$), and 35% of the waters is included in class II (>0.78– $\leq 1.56 \text{ mg/dm}^3$).

The maximum ammonium ion concentration is recorded in the waters of the Kanał Henrykowski canal, downstream of the sewage discharge from Jabłonna.

There are few point anomalies in the area. Elevated ammonium ion concentrations were found in the waters of a ditch near Pęcice (19.6 mg/dm³), Magenta canal downstream of the Rembertów sewage treatment (13.6 mg/dm³), a ditch in Michałówek (12.4 mg/dm³) and a ditch in Wołomin (11.8 mg/dm³). The ammonium ion concentration of 5.5 mg/dm³ in the waters of the Jagodzianka River is probably related to the sewage discharge from the Otwock sewage treatment plant.

Increased ammonium ion concentrations in the watercourses of the Czarna and Utrata drainage basins may originate from runoff of nitrate fertilizers in agricultural areas.

In Warsaw, elevated levels of NH₄ ion are recorded in the waters of the Kamionkowski (5.26 mg/dm³) and Gocławski (2.15 mg/dm³) canals, and locally in the waters of a ditch recharging the Kanał Grabowski canal in Pyry, as well as in the waters of the Nowa Ulga and Nowe Ujście canals, Kanał Kawęczyński canal, Kanał Żerański canal, Rów Miedzeszyński ditch, Rów Natoliński ditch and moat near the Radiowo Fort.

Elevated concentrations of NH₄ point to recent pollution by household or industrial wasterwater. In closed or weak flow-through reservoirs the abundance of ammonium ion can suggest decay of organic matter under anaerobic conditions.

Ni NICKEL

Soils: Pls. 50-51, tab. 4-5

The distribution of nickel content in the soils resembles those of iron, magnesium and manganese – the elements whose occurrence is highly dependent on the bedrock chemical composition. Nickel occurs abundantly in alluvial muds of the Vistula River valley and in soils that developed on rocks rich in clay minerals: glacial tills and eluvial sediments of the left-bank side of Warsaw.

The median nickel concentration in the topsoil (5 mg/kg) is slightly greater than the geochemical baseline for the soils of Poland (3 mg/kg; Pasieczna, 2003). The distribution images on the maps for both soil depth ranges are very similar and the topsoil concentrations are only slightly greater than the subsoil concentrations. This proves an insignificant human impact on the nickel propagation.

The highest nickel concentrations are found in alluvial muds of the Vistula flood terraces upstream of Siekierki. In the topsoil the concentration is 37–38 mg/kg, whereas in the subsoil – up to 53 mg/kg. Enrichment with this element can be linked with redeposition of fine-grained material from higher-elevated areas of the drainage basin in ancient river meanders.

The topsoil shows local anthropogenic anomalies. The largest one (32–272 mg/kg of nickel) is located in the premises of the ArcelorMittal steelworks. Between the Wisłostrada Thoroughfare and the Vistula River valley in Marymont the nickel concentration is 152 mg/kg, near the closed-down PZL Wola engine factory – 127 mg/kg, and near the Kawęczyn thermal power plant – 55 mg/kg.

The origin of the nickel point anomaly in the soil of a lawn in Mysiadło (165 mg/kg) is difficult to explain.

At a depth of 0.8–1.0 m the maximum nickel concentration (74 mg/kg; also 112 mg/kg of chromium) is recorded in an industrial area between the Żerań thermal power plant and the former FSO automotive factory.

Sediments: Pl. 50, tab. 6

The median nickel concentration in the water sediments (7 mg/kg) is almost identical to the geochemical baseline value for the sediments of rivers and streams of Poland (6 mg/kg; Lis, Pasieczna, 1995) and to the results of previous studies of the sediments from the area of Warsaw and its environs (median 6 mg/kg; Lis, 1992).

The distribution of nickel concentration is similar to those of iron and manganese, which may indicate binding of part of nickel by hydroxides of these metals.

The highest average nickel concentration value is characteristic of the sediments of the Kanał Żerański canal (median 13 mg/kg), while the lowest values were measured in the sediments of the Długa and Świder rivers (median 3 mg/kg). The maximum concentration (146 mg/kg) is recorded in the sediments of the Radiowo Fort moat in Bemowo.

Anomalous concentrations of nickel are characteristic of the sediments of watercourses flowing across flood terraces of the Vistula River valley, which drain the bedrock enriched in this element: Wilanówka (up to 36 mg/kg), Rów Powsinkowy ditch (up to 32 mg/kg), Jeziorka (up to 38 mg/kg), Nowa Ulga canal (up to 48 mg/kg), and other minor streams and closed drainage reservoirs.

The recent and historical discharge of sewage is the source of elevated nickel concentrations in the sediments of the Kanał Bródnowski Górny (up to 69 mg/kg) and Kanał Henrykowski (up to 35 mg/kg) canals as well as the Jagodzianka River (up to 71 mg/kg). Sewage discharges are probably also responsible for sediment contamination in the Vistula River (locally containing up to 20–30 mg/kg of nickel).

Waters: <u>Pl. 51</u>, <u>tab. 7</u>

The nickel concentration in the waters of the map sheet area varies between <0.5 and $41.2 \ \mu g/dm^3$. The median value (1.7 $\mu g/dm^3$) is similar to the geochemical baseline value in the waters of Europe (1.91 $\mu g/dm^3$; De Vos, Tarvainen, ed., 2006). There were only two samples with the concentration exceeding the maximum permissible limit (34 $\mu g/dm^3$) specified in the Directive 2013/39/EU.

75% of the analysed waters show the concentration of nickel $<2.3 \ \mu g/dm^3$, and its maximum concentration is recorded in the water of a ditch in Miedzeszyn, which also abounds in manganese, iron, cobalt and copper.

Elevated nickel concentrations are also characteristic of the waters of the Czarna River and its tributaries – up to $40.6 \ \mu g/dm^3$ in a canal crossing an industrial area in Wołomin, which is additionally contaminated by ammonium ions, lithium, cobalt and chromium.

The waters of Lake Łacha (oxbow lake) in Józefów contain from 7.5 to 26.8 μ g/dm³ of nickel that probably originates from sewage discharges. The high nickel concentrations in the waters of the Kanał Henrykowski canal (4.9–12.1 μ g/dm³) and in the waters of a minor ditch recharging the canal (5.7 μ g/dm³) are likely caused by a periodic discharge of wastewater from a residential area in Dąbrówka Szlachecka.

On the right-bank side of the Vistula River, nickel contamination is found in the waters of the Rów z Lewandowa ditch (9.6–19.4 μ g/dm³), which is also rich in iron and cobalt, in the Kanał Bródnowski Górny (11,0 μ g/dm³) and Kanał Zagoździański canals, Rów Miedzeszyński ditch, and Nowe Ujście canal (up to 8,0 μ g/dm³).

Considerable nickel concentrations on the left-bank side of the Vistula were also encountered in the Struga River and its tributaries, in the watercourses of the Lipkowska Woda and Żbikówka drainage basins, and locally in the tributaries of the Raszynka and Utrata rivers.

In the waters of the Kanał Młociński canal the nickel concentrations are 20.1 μ g/dm³, and in the waters of a ditch in Łomianki Dolne (also containing 474 mg/dm³ of sulphates) – 19.1 μ g/dm³.

The primary source of nickel in many water samples is industrial sewage (Kabata-Pendias, Szteke, 2012).

NO₂ NITRATES (III)

Waters: Pl. 52, tab. 7

The concentration of NO₂ ions in the water samples from the map sheet area ranges from <0.01 to 11.10 mg/dm³. The average concentrations (median 0.07 mg/dm³) are similar to those in the waters of the Poznań agglomeration (median 0.05 mg/dm³; Lis, Pasieczna, 2005).

Elevated and anomalous levels of NO_2 ions occur predominantly in agricultural areas: in the waters of the Utrata and Raszynka rivers, and in the Jeziorka ditch and its tributaries, as well as in the Struga and Czarna rivers (including their tributaries). They are associated mostly with surface runoff and local household wastewater discharges.

The maximum concentration of NO_2 ions (11.10 mg/dm³) is recorded in the village of Dawidy in the waters of a stream recharging the Raszynka, into which sewage is discharged from a sewage treatment plant in Zamienie.

In urban areas, elevated concentrations of NO₂ ions are found in the waters contaminated by municipal and industrial sewage. Such origin is attributed to the concentrations of 0.94–2.04 mg/dm³ in the waters of the Magenta canal that receives wastewater from the Rembertów sewage treatment plant. The waters also contain considerable amounts of aluminium (up to 647 μ g/dm³), cobalt (up to 2.6 μ g/dm³), nitrates (V) (up to 40.50 mg/dm³), phosphorus (up to 3.62 mg/dm³), vanadium (up to 2 μ g/dm³) and ammonium ions (13.60 mg/dm³).

Anomalous levels of NO_2 ions (up to 1.29 mg/dm³) are present in the waters of the Kanał Bródnowski Górny canal that receives rainwater from the Trasa AK (Home Army Thoroughfare) and nearby allotment gardens.

Contamination by NO₂ ions in the waters of Lake Gocławskie and the Kanał Wystawowy ditch (up to 1.01 mg/dm^3) can be attributed to surface runoff from allotment gardens, and the one in the waters of the Żbikówka River (up to 0.95 mg/dm^3) – to rainwater from the motorway.

Elevated concentrations of NO_2 ions are also common in the waters of the Kanał Żerański canal and the Długa River downstream of Ossów.

NO₃ NITRATES (V)

Waters: <u>Pl. 53</u>, <u>tab. 7</u>

The concentration of NO₃ ions in the waters ranges from 0.01 to 89.50 mg/dm³, and the distribution is similar to that for the concentration of NO₂ ions. The average concentration of NO₃

ions (median 2.24 mg/dm³) is lower than in the waters in Poznań and its environs (median 3.21 mg/dm³; Lis, Pasieczna, 2005) and in the waters of Europe (median 2.82 mg/dm³; De Vos, Tarvainen, ed., 2006). Half of the samples meet the standards for water quality class I (\leq 2.2 mg/dm³ NO₃), and approximately 17% of the samples represent water quality class II (>2.2– \leq 5 mg/dm³ NO₃).

Distinct anomalous concentrations of NO_3 ions are typically found in the waters of agricultural areas in the Łasica (Struga and its tributaries), Utrata (Żbikówka, Kanał Ożarowski canal, Raszynka and their tributaries) and Jeziorka (Jeziorka ditch) drainage basins.

The greatest concentration of NO₃ ions is recorded in the waters of streams in the municipality of Lesznowola, near Dawidy, Nowe Jeziorki and Nowa Wola (up to 89.5 mg/dm³ in a tributary of the Raszynka River). The concentrations of NO₃ ions up to 56 mg/dm³ were found in the waters of the Jeziorka ditch, up to 45.3 mg/dm³ in the waters of the Struga River, up to 40 mg/dm³ in the waters of the Żbikówka River, and 29.8 mg/dm³ in the waters of the Kanał Ożarowski canal near the Centrum Bronisze wholesale market.

In the vicinity of Falenty the concentration of NO_3 ions in the waters of minor watercourses is up to 42.5 mg/dm³.

In the right-bank side of the Vistula River drainage basin, anomalous concentrations of NO_3 ions occur at point sites. In a watercourse recharging the Długa River in Sulejówek, the concentration of NO_3 ions is 60.7 mg/dm³, and considerable levels were also found in the waters of the Wawerski, Nowe Ujście, Nowa Ulga and Magenta canals.

P PHOSPHORUS

Soils: Pls. 54-55, tab. 4-5

The phosphorus geochemical background level in the analysed topsoil is in the range of 0.003–0.106%. The average concentration of this element (median 0.036%) is similar to the average value in Poland (median 0.034%; Lis, Pasieczna, 1995) and in the Poznań agglomeration (median 0.039%; Lis, Pasieczna, 2005). Comparison of the median phosphorus concentrations in both soil depth ranges indicates that the topsoil concentration is twice as much as the subsoil concentration.

The lowest amounts of phosphorus are typically found in forest soils (median 0.017%), greater amounts in cropland soils (median 0.046%), and the greatest ones in soils of urban areas (median 0.053%).

The concentration of phosphorus in the analysed soils is mostly affected by their origin. Its spatial distribution at both soil depth ranges is clearly dependent on the chemical composition of parent rocks. The greatest amounts of phosphorus occur in soils developed on glacial tills in the western part of Warsaw, on loess-like deposits of the Ożarów region, and on alluvial muds in the Vistula River valley. The smallest concentrations are typical of soils developed on sandy sediments. This observation is

confirmed by the median values: 0.052% in loamy soils, 0.050% in peaty soils and 0.026% in sandy soils.

The maximum phosphorus concentration (0.500%) is recorded in the topsoil of peaty soil in Rembertów near the railway line and a municipal waste treatment plant, and in soils of a wetland area in Białołęka – 0.492%.

Phosphorus anomalies in peaty soils (which are also rich in arsenic, iron and manganese) occur in the Długa (up to 0.429%) and Utrata (up to 0.264%) river valleys. The source of phosphorus was probably surface runoff from arable land where phosphatic fertilizers were used.

An anthropogenic phosphorus anomaly occurs in the Jeziorka valley in Konstancin, where sewage was discharged to the river from the paper mill (0.344% in the topsoil and 0.127% in the subsoil).

The maximum phosphorus concentration in the subsoil (0.880%) was found in the Henrykowski Park in Tarchomin, accompanied by the maximum concentration of iron (20.76%), 39 mg/kg of arsenic, 1,524 mg/kg of manganese, and 0.429% of sulphur.

Sediments: Pl. 54, tab. 6

The average phosphorus concentration in the sediments (median value) is 0.045%, and the highest values are recorded in organic muds. The greatest average concentration is characteristic of the sediments of the Kanał Żerański drainage basin (median 0.180%), while the lowest are found in the Świder drainage basin (median 0.028%).

Clearly elevated concentrations of phosphorus (>0.301%) are found in the sediments of watercourses and reservoirs of the Vistula flood terraces in the Konstancin-Jeziorna–Zawady region, which are covered with soils rich in this element. Sediments of the Wilanówka (containing up to 1.133% of phosphorus) can be additionally enriched due to surface runoff from nearby agricultural areas as well as the sewage discharge from the inactive paper mill and from the sewage treatment plant in Konstancin-Jeziorna.

High phosphorus concentrations (up to 1.164%) were also found near the border of Warsaw in Targówek, particularly in the watercourses flowing through meadows with iron bog deposits. Anomalous phosphorus levels in the sediments of the Kanał Bródnowski Górny (up to 0.627%) and Henrykowski (up to 0.601%) canals are additionally caused by municipal and industrial sewage discharges.

Elevated phosphorus concentrations (0.601%) are recorded in the sediments of the Rudawka River in the Bielany Forest nature reserve.

Sewage discharges from the Otwock sewage treatment plant are the source of phosphorus contamination of sediments in the Jagodzianka (up to 0.491%) and Utrata (up to 0.564%) rivers.

Waters: <u>Pl. 55</u>, <u>tab. 7</u>

The phosphorus concentrations in the waters of the map sheet area are variable (<0.05-13.82 mg/dm³), although half of the samples show values below 0.07 mg/dm³. 80% of the waters meet the standards for water quality class I (≤ 0.2 mg/dm³), and 10% represent water quality class II ($>0.2-\le 0.4$ mg/dm³). The median phosphorus concentration (0.07 mg/dm³) is lower than that for the waters of the Poznań agglomeration (median 0.10 mg/dm³; Lis, Pasieczna, 2005) and for the waters of Poland (median 0.16 mg/dm³; Lis, Pasieczna, 1995). The lowest phosphorus concentrations are found in the waters of the Vistula River and the Kanał Żerański drainage basin (median <0.05 mg/dm³), and the highest ones were determined in the Jeziorka (median 0.15 mg/dm³) and Utrata (median 0.13 mg/dm³) drainage basins.

Anomalous phosphorus concentrations (>0.67 mg/dm³) occur primarily in the waters of agricultural areas, in the Raszynka, Mienia, Czarna and Długa drainage basins. The source of phosphorus is surface runoff of excess phosphatic fertilizers from arable soils.

However, the greatest phosphorus levels are due mainly to discharges of various types of sewage. The maximum phosphorus concentration (13.82 mg/dm³) is recorded in the village of Zagościniec (Wołomin municipality) in the water of a ditch collecting municipal wastewater.

The greatest phosphorus concentrations are recorded in watercourses receiving household and municipal sewage from local sewage treatment plants: 4.17 mg/dm³ in the waters of a ditch in the village of Janina (municipality Wołomin), 3.62 mg/dm³ in the waters of the Magenta canal in Rembertów, 1.40 mg/dm³ in the waters of the Kanał Wawerski canal in Stara Miłosna, 1.23 mg/dm³ in the waters of a canal collecting wastewater from the Toruńska Thoroughfare, and 0.76 mg/dm³ in the waters of the Kanał Ożarowski canal.

Elevated phosphorus concentrations are characteristic of the waters of ponds and lakes receiving local sewage effluent: 2.06 mg/dm³ in a pond at Dobczyn (Klembów municipality), 1.93 mg/dm³ in a pond in Łużek (Dawidy), 1.62 mg/dm³ in the Śmiardki marsh near Wesoła, 1.39 mg/dm³ in Lake Imielińskie, 0.90 mg/dm³ in Lake Torfowisko in Powsin, and 0.83 mg/dm³ in the Czerniakowski Fort moat.

In the waters of a pond that was formed in a peat extraction area near the village of Duchów, Wiązowna municipality, the phosphorus concentration is up to 6.56 mg/dm³.

Pb LEAD

Soils: Pls. 56-57, tab. 4-5

The lead concentrations from both of the soil depth ranges are similar (from <2 to 2,784 mg/kg). Anthropogenic contamination is evidenced by the four-times greater median value recorded in the

topsoil as compared with the values for the subsoil (15 and 4 mg/kg, respectively) and for geochemical background in non-urbanized areas of Poland -10 mg/kg (Pasieczna, 2003).

Soil contamination by lead is found throughout Warsaw, but primarily in urbanized areas located along major roads and railway tracks.

The highest lead anomalies (>100 mg/kg) cluster in industrial areas that have been developing since the mid-19th century (Śródmieście, Wola and the boundary zone between Targówek, Praga Północ and Praga Południe) and near the ArcelorMittal steelworks.

The highest lead concentration (2,784 mg/kg) was found in an anthropogenic soil of a postindustrial area in Kamionek. The potential sources of lead in this region could be the already closeddown manufacturers of lead and tin products, which operated here before World War II (Krasucki, 2009), a telephone equipment factory, and a printer factory built on the site of a pre-war car factory (Portal informacyjny..., 2015b).

Particulate matter emissions from the ArcelorMittal steelwork have resulted in strong soil contamination of the nearby grounds of the "Hutnik" sports club in Bielany, where 1,196 mg/kg of lead were recorded in the topsoil and 2,574 mg/kg in the subsoil. Near a landfill of smelting waste the lead concentration in soils is up to 316 mg/kg, and at a slightly greater distance it is 140–200 mg/kg.

Considerable lead contamination is found in soils near the Średnicowy rail bridge along Wybrzeże Szczecińskie Street (675 mg/kg), in Śródmieście (up to 370 mg/kg), and in the Skaryszewski (332 mg/kg) and Wilanowski (325 mg/kg) parks.

A small-area lead anomaly (up to 229 mg/kg) on the outskirts of the former Służewiec Przemysłowy industrial area is found in soils that are additionally contaminated by barium and cadmium. The contamination by metals is likely the result of activity of numerous electronics manufacturers that operated in this area in the past.

High lead concentrations (513 mg/kg) are also recorded in soils of arable land in the Salomea area, Włochy district.

Outside of Warsaw, anomalous lead concentrations are observed in Jabłonna (334 mg/kg), between Ożarów and Bemowo (up to 319 mg/kg) and in Piastów (up to 256 mg/kg). The contamination is probably caused by the proximity to heavy traffic roads (emission from the period when petrol was supplemented with lead anti-knocks) and by the dispersion of particulate matter from industrial plants located presently and in the past in Ożarów Mazowiecki (former cable manufacturer), Piastów (lead-acid battery manufacturer) and Pruszków (thermal power plant and the former machine tools manufacturer).

The extent of lead anomalies in the subsoil is similar to that observed in the topsoil. The anomalies are most strongly accentuated in the city centre of Warsaw and near the steelworks in Bielany, which proves their anthropogenic origin. In the peripheries of Warsaw, lead concentrations do not exceed 10 mg/kg.

Sediments: Pl. 56, tab. 6

In sediments of the area of Warsaw and its surroundings the lead concentration varies from <2 to 382 mg/kg. The highest levels are found in the Kanał Żerański drainage basin (median 29 mg/kg), while the lowest ones in the Świder drainage basin (median 6 mg/kg).

The maximum lead concentration (382 mg/kg) is recorded in the sediments from the Żbikówka River, near the site of wastewater discharge from the motorway at Konotopa.

In the south of the map sheet area, anomalous lead concentrations are found in the sediments of the Jeziorka, downstream of Konstancin (up to 300 mg/kg), and in the Wilanówka River (up to 122 mg/kg). Despite separation of these rivers in the 1950s, they have remained permanently connected by ditches and canals, and the source of lead was probably wastewater from the sewage treatment plant of the paper mill.

Considerable lead concentrations are typically found in the Henrykowski (up to 263 mg/kg) and Bródnowski Górny (up to 166 mg/kg) canals, which are contaminated by industrial wastewater.

Elevated lead concentrations are also observed in the sediments of the Kanał Młociński canal (up to 164 mg/kg) and in the tributaries of the Lipkowska Woda, which flow from the Wólka Węglowa region (up to 102 mg/kg) and from the area of ArcelorMittal steelworks (97 mg/kg).

Highly contaminated sediments are also found in closed reservoirs: a pond in the village of Duczki (381 mg/kg), a pond in Marki (214 mg/kg), Radiowo Fort moat (192 mg/kg), Fajansowe clay pit pond (185 mg/kg) in Włochy, and a pond in Pruszków (160 mg/kg), located between Aleje Jerozolimskie Street and the WKD (Warsaw Commuter Railway) rail line.

Lead contamination is related predominantly to the discharge of industrial wastewater and surface runoff. Sediments of not contaminated waters commonly show lead concentrations in the range of 30–45 mg/kg, but sediments of the contaminated waters can contain up to several thousand mg/kg of lead (Pasieczna, ed., 2010b; Kabata-Pendias, Szteke, 2012).

Waters: <u>Pl. 57</u>, <u>tab. 7</u>

The range of lead concentrations in the waters of the study area ($<0.05-7.32 \ \mu g/dm^3$) is similar to that in the waters Europe ($<0.005-6.37 \ \mu g/dm^3$; De Vos, Tarvainen, ed., 2006). The median values are 0.06 $\mu g/dm^3$ and 0.093 $\mu g/dm^3$, respectively. The analysed waters are not contaminated by lead. There was no sample with exceeded permissible limit of lead concentration in inland waters, specified in the Directive 2013/39/EU – 14 $\mu g/dm^3$, neither with exceeded permissible concentration in drinking water in Poland – 10 $\mu g/dm^3$ (Rozporządzenie, 2010).

Clearly elevated lead concentrations are characteristic of the waters of closed reservoirs. The maximum concentration (7.32 μ g/dm³) is recorded in the waters of a pond located in wasteland near Babice Nowe.

Anomalous levels of this metal (4.55 μ g/dm³) are recorded in the Radiowo Fort moat in Bemowo near allotment gardens, where the waters abound in copper as well.

Lead contamination is also observed in the following water bodies: a pond/marsh in a forest area at Zagórze, municipality Wiązowna ($3.08 \ \mu g/dm^3$), a lake in the Bagno Jacka marsh ($3.02 \ \mu g/dm^3$), the Biały Ług marsh ($2.09 \ \mu g/dm^3$) in Wesoła, Kądziołeczka pond ($2.62 \ \mu g/dm^3$) in Ursynów, Fort Bema moat ($1.50 \ \mu g/dm^3$) and a pond in the Młociny Forest ($1.39 \ \mu g/dm^3$).

In the waters of two ponds near the village of Zabraniec, the lead concentrations are 0.90 μ g/dm³ and 0.86 μ g/dm³.

Elevated lead concentrations (>0.61 μ g/dm³) occur locally in the waters of the Czarna River and its tributaries. Acidic waters (pH 4.62) of a ditch draining the Horowe Bagno bog (peat lake) in a forest area near Marki show the lead concentration of 5.13 μ g/dm³, and the waters of a ditch in Radzymin (contaminated also by aluminium, iron and cobalt) – 3.51 μ g/dm³.

Lead contamination is also observed in the waters of minor watercourses recharging the Mienia, Świder (up to 2.35 μ g/dm³) and Utrata (up to 1.07 μ g/dm³) rivers, and in the Rów Miedzeszyński ditch (up to 0.65 μ g/dm³) and Struga Pogorzelska (up to 0.92 μ g/dm³), which are additionally characterised by increased concentrations of aluminium, cadmium, copper, vanadium and zinc.

The lead concentration of $1.29 \,\mu\text{g/dm}^3$ is recorded in the waters of a ditch flowing from the ArcelorMittal steelworks area.

Elevated lead concentrations typically occur in the waters of the Vistula River, downstream of the Kanał Młociński canal.

The greatest lead concentrations are found in the waters of the Łasica (median $0.12 \ \mu g/dm^3$) drainage basins and Vistula River (median $0.10 \ \mu g/dm^3$), while the lowest ones in the Utrata, Świder and Kanał Żerański drainage basins (median <0.05 $\ \mu g/dm^3$).

S SULPHUR

Soils: Pls. 58–59, tab. 4–5

The sulphur content in the topsoil varies from <0.003 to 0.565%, while in the subsoil from <0.003 to 0.616%. Comparison of the median values indicates that the average sulphur content in the topsoil is four times greater than in the subsoil (0.016% and 0.004%, respectively). The lowest contents (at both depth ranges) are found in sandy soils, while the highest ones in peaty soils. The median sulphur content in the topsoil of the map sheet area is greater than the geochemical baseline for the soils of Poland (0.009%; Pasieczna, 2003).

Comparison of the maps of sulphur content distribution in the topsoil and subsoil indicates that this element originates from anthropogenic sources – the highest amounts of sulphur are found in soils of urban and industrial areas. Sulphur is dispersed as a result of sulphur dioxide emissions due to fossil

fuel combustion, mainly the burning of coal that can contain even up to 5% of this element (Bojakowska, 1994; Szuflicki *et al.*, ed., 2014).

Natural sulphur enrichment of alluvial soils is observed in the Vistula River valley. The major sulphur anomalies of that area are related to the occurrence of soils developed on peats and alluvial muds rich in organic matter.

The greatest sulphur content (0.566%) is typically found in peaty soils from both depth ranges in the Raszynka River valley, which also contain high amounts of strontium (up to 203 mg/kg). Considerable amounts of sulphur were also found in the topsoil of peaty soils of meadows in Białołęka (up to 0.255%), Długa River valley (up to 0.149%) and east of Wołomin (up to 0.093%).

High sulphur contents in soils of swampy forest areas are recorded in Bemowo (up to 0.222%), Góraszka (up to 0.162%) and Wesoła (up to 0.159%).

The presence of 0.224% of sulphur in the topsoil and 0.247% in the subsoil around the Tarchomin cement plant (inactive since 2004) is supposed to be the result of its dispersion during the latest activity of this plant. The sulphur content of 0.073% in the topsoil near the Polfa Tarchomin pharmaceutical company may also be related to the activity of the company.

Anthropogenic sulphur enrichments are observed in the topsoil between Pruszków and Piastów (up to 0.177%) and in Konstancin-Jeziorna, in the area of the former paper mill (0.075%).

In the subsoil the greatest sulphur content (0.616%) is recorded near the Siekierki thermal power plant.

High sulphur content is also recorded in an anthropogenic soil of the Henrykowski Park (0.429%), where the elevated concentrations of arsenic (39 mg/kg) and manganese (1,524 mg/kg) as well as the map sheet's maximum contents of iron (20.76%) and phosphorus (0.880%) are observed.

Sediments: <u>Pl. 58</u>, <u>tab. 6</u>

The sulphur content in the sediments is highly variable (from <0.003 to 5.031%), although 75% of the sediments show the contents below 0.163%. The median sulphur content in the sediments from the Warsaw area and its surroundings (0.066%) is markedly lower than in the Poznań agglomeration (median 0.096%; Lis, Pasieczna, 2005) but greater than in the Szczecin agglomeration (median 0.040%; Lis, Pasieczna, 1998a).

In the north of the map sheet area the greatest amounts of sulphur are found in the sediments of the Kanał Żerański drainage basin (median 0.184%). The maximum content (5.031%) is observed in the sediments of this canal in Białołęka, while the sediments of the Kanał Bródnowski canal contain up to 2.583% of this element. Sulphur contamination in the sediments of this region is probably caused by sewage discharges from industrial plants of Targówek, and by surface runoff from the busy Trasa AK (Home Army Thoroughfare). The concentrations of sulphur (up to 1.904%) in the sediments of the Kanał Markowski drainage basin (near the north-eastern border of Warsaw) is likely natural in origin

and associated with the drainage of waterlogged area with soils containing considerable amounts of this element.

Municipal sewage is the main source of sulphur in the sediments of a ditch in the village of Zagościniec, northeast of Wołomin (2.822%), and in the sediments of the Jagodzianka River (2.794%) and Kanał Henrykowski canal (1.456%) downstream of the discharge site.

Concentrations of sulphur, which are typical of the sediments of watercourses and water reservoirs of the Vistula flood terraces in the south of the map sheet area, are related to drainage of bedrock enriched in this element (alluvial muds). The greatest sulphur contents were found in organic sediments of a ditch recharging the Kanał Habdziński canal in the village of Opacz (3.251%), as well as in the sediments of the Wilanówka (2.283%) and Rów Powsinkowy (1.560%).

Anomalous sulphur contents in the sediments of the Raszynka River (up to 1.261%) are also linked with the lithology.

High sulphur contents are usually found in the sediments of some closed reservoirs: the Keller ponds (1.493%), Łacha Potocka oxbow lake (0.810%) near the Trasa AK (Home Army Thoroughfare), Lake Łosice in Natolin (1.426%), Lake Łacha in Józefów (1.340%) and Piłsudski Fort moat in Mokotów (1.327%).

Of natural origin are probably the elevated sulphur contents observed locally in the watercourses and reservoirs in Kampinos. Most of them are organic slurry.

Waters: <u>Pl. 59</u>, <u>tab. 7</u>

The concentration of sulphates in the surface waters of Warsaw ranges from <0.5 to 650.0 mg/dm³. The median concentration (47.5 mg/dm³) is much lower than that for the waters of the agglomerations of Szczecin (median 92 mg/dm³; Lis, Pasieczna, 1998a) and Poznań (median 116 mg/dm³; Lis, Pasieczna, 2005), but similar to the median concentration in the waters of Poland – 56 mg/dm³ (Lis, Pasieczna, 1995). In the surface waters of Europe the sulphate concentration varies between <0.3 and 1400 mg/dm³ (median 16 mg/dm³; De Vos, Tarvainen, ed., 2006).

As regards the sulphate content, the standards for water quality class I are met by 94.4% of the analysed waters from the Warsaw agglomeration; for class II – 4.3%. For 16 samples the permissible limits are exceeded.

The distribution of sulphate content in the surface waters is similar to that of calcium content. Elevated concentrations of sulphates (>111.0 mg/dm³) are observed predominantly in the watercourses of the left-bank side of Warsaw, and the least contaminated waters flow in the Vistula River.

The maximum sulphate concentration (650.0 mg/dm³) is recorded in the waters of a pond in the village of Lęg in the Wilanówka drainage basin. In the left-bank side of Warsaw, distinct anomalies of sulphate concentrations are also found in the waters of the Struga (up to 246.0 mg/dm³) and its tributary

flowing from Bemowo (up to 205.0 mg/dm³), in the Rudawka (up to 235.0 mg/dm³), Łacha Potocka oxbow lake (up to 215.0 mg/dm³) and Raszynka (up to 223.0 mg/dm³).

In the Łomianki area the concentration of sulphates in the waters of the ditch running under Wiślana Street is up to 474.0 mg/dm^3 , and in a pond – 222.0 mg/dm^3 .

Considerable sulphate concentrations were identified in the waters of the Żbikówka (185.0 mg/dm³), Kanał Ożarowski canal (183.0 mg/dm³) and Rów Opaczewski ditch (165.0 mg/dm³).

Sulphate contamination was also found in the waters of the Jelonki clay pit ponds, Keller ponds, Jezioro Powsinkowskie lake, a ditch in Paluch near the Chopin Airport, and in the reservoirs and watercourses in Mokotów (up to 214.0 mg/dm³ in the waters of a pond near Dolna Street).

In the right-bank side of the Vistula River drainage basin, anomalous concentrations of sulphates are characteristic of the waters of reservoirs in the drainage basins of the Czarna River (up to 438.0 mg/dm³) in the former clay pit in Kobyłka), Kanał Henrykowski canal (up to 278.0 mg/dm³), Rów z Lewandowa ditch (up to 170.0 mg/dm³), and locally in the Kanał Zagoździański canal (up to 236.0 mg/dm³).

Sulphate contamination in the waters is probably due to various sewage effluents, surface runoff and fallout of dust from the thermal power plant and other industrial plants.

Sb ANTIMONY

Waters: <u>Pl. 60</u>, <u>tab. 7</u>

The antimony concentration in the analysed waters is highly variable ranging from <0.05 to 9.07 μ g/dm³, and the median concentration (0.34 μ g/dm³) is much greater than the average for the waters of Europe (median 0.07 μ g/dm³; De Vos, Tarvainen, ed., 2006).

The antimony concentration in the river waters is commonly $<1 \ \mu g/dm^3$, and it may reach a few $\mu g/dm^3$ in the premises of plants of metal processing as well as coal and municipal waste combustion (Niedzielski *et al.*, 2015).

The lowest antimony concentration is characteristic of the waters of the Świder drainage basin (median $0.24 \ \mu g/dm^3$), and the highest one is observed in the Łasica drainage basin (median $0.57 \ \mu g/dm^3$). The Vistula River waters show insignificant contamination ($0.12-0.35 \ \mu g/dm^3$).

Very high antimony concentrations $(2.08-4.05 \ \mu g/dm^3)$ are found in the waters of a ditch in Łomianki Fabryczne, near a sewage treatment plant. Local anomalies are observed in the waters of the Kanał Młociński canal (1.63 $\mu g/dm^3$), Lipkowska Woda drainage basin (up to 1.26 $\mu g/dm^3$) and Potok Służewiecki stream (up to 1.84 $\mu g/dm^3$).

In the waters of the Kanał Bródnowski Górny canal, where the antimony concentration reaches $1.19 \,\mu\text{g/dm}^3$, the potential contamination source can be dusts from coal burning in the Kawęczyn thermal power plant and waste from the nearby waste treatment plant, since the hard coal from Polish deposits contains up to 4.1 mg/kg of antimony (Bojakowska *et al.*, 2007).

Anomalous antimony concentrations are recorded in the waters of the Rów Miedzeszyński ditch (up to 2.21 μ g/dm³) and Kanał Henrykowski canal (up to 1.97 μ g/dm³).

Antimony contamination was also found in the waters of closed drainage reservoirs in Bemowo (Jelonki clay pit ponds – 2.76 μ g/dm³, Jeziorzec pond – 1.88 μ g/dm³, Blizne Fort moat – 1.05 μ g/dm³) and in the waters of the Staw na Kosku pond (1.89 μ g/dm³) and Stawy Kacze ponds (1.80 μ g/dm³) in the Skaryszewski Park.

Outside of Warsaw, anomalous antimony concentrations are characteristic of the waters of the Czarna River tributaries – up to 9.07 μ g/dm³ in the Górznik stream, 2.94 μ g/dm³ in a ditch in Kobyłka, and 1.97 μ g/dm³ in a ditch in the northern part of Marki.

Anomalous antimony concentrations were also encountered in the waters of ponds in the Czarna Struga drainage basin (up to $2.10 \ \mu g/dm^3$) and in the waters of a tributary of the Struga River (up to $2.03 \ \mu g/dm^3$) with high electrolytic conductivity values, containing also elevated levels of sodium, lithium, potassium, magnesium, molybdenum, strontium, uranium, chlorine, nitrates and sulphates.

Considerable antimony concentrations are recorded in the waters of the Rów Opaczewski ditch recharging the Raszynka River (up to $1.27 \ \mu g/dm^3$) near the Opacz road junction of the southern bypass of Warsaw.

Increased antimony concentrations (>0.56 µg/dm³) are locally found in the waters of the Kanał Wawerski canal, Jeziorka ditch, Kanał Grabowski canal, and Wilanówka and Regułka rivers.

At many localities, elevated levels of antimony occur in the waters contaminated also by molybdenum and other metals, which indicates its anthropogenic origin.

SIO₂ SILICA

Waters: Pl. 61, tab. 7

The range of silica concentrations in the waters in Warsaw and its surroundings is from <0.1 to 27.1 mg/dm³. The median concentration value (9.6 mg/dm³) is slightly lower than that for the waters of Poland (median 12.5 mg/dm³; Lis, Pasieczna, 1995) and the Poznań agglomeration (median 10.6 mg/dm³; Lis, Pasieczna, 2005). In the waters of Europe the median concentration value for silica is 8 mg/dm³ (De Vos, Tarvainen, ed., 2006).

Elevated and anomalous concentrations of SiO_2 in the waters are observed in areas of various land use types and can be associated either with drainage of sandy bedrock that occur over much of the map sheet area, or with sewage discharges.

The greatest silica concentration is characteristic of the waters from the Łasica drainage basin (median 11.9 mg/dm³), while the lowest one in the waters of lakes and ponds (3.4 mg/dm³). The median silica concentration in the waters of the Vistula River is 8.6 mg/dm³.

The maximum silica concentration (and elevated concentrations of a number of other constituents) is found in the waters of a ditch in the village of Zagościniec, which receives municipal sewage.

The silica concentration of 27.3 mg/dm³ (accompanied by increased contents of many other constituents) is recorded in the waters of the polluted ditch in Paluch and in the trench surrounding the Radiowo Landfill (27.0 mg/dm³).

The waters of ditches in a forest area near Marki contain 26.7 mg/dm³ of silica, and near the Natolin Park -25.9 mg/dm³.

In the left-bank side of the Vistula River drainage basin, increased (>14.3 mg/dm³) and anomalous (>16.2 mg/dm³) silica concentrations are found in the waters of the Struga, Lipkowska Woda and Raszynka rivers and their tributaries, Rudawka and, locally, in the waters of watercourses in the Utrata, Potok Służewiecki, Wilanówka and Jeziorka drainage basins.

On the eastern side of the Vistula River valley, SiO_2 occurs abundantly in the waters of the Rów z Lewandowa ditch (up to 19.2 mg/dm³) and in numerous tributaries of the Czarna River (up to 20.4 mg/dm³ in the waters of a ditch in the village of Krym, downstream of the sewage treatment plant).

Silica is also a common constituent of the waters in the Kanał Henrykowski canal, in the canals recharging the Nowy Kanał canal in Białołęka, and locally in the tributaries of the Mienia and Świder rivers.

Sr STRONTIUM

Soils: Pls. 62-63, tab. 4-5

The strontium concentration in the topsoil varies from <1 to 556 mg/kg. The enrichment in strontium of the topsoil is almost three times greater when compared to the subsoil (median values 11 and 4 mg/kg, respectively), which indicates the strontium originates in great part from anthropogenic factors. It is also confirmed by the lowest strontium concentrations (at both depth ranges) in forest soils, and the greatest ones in industrial and urban areas. In urban areas, strontium comes from coal burning, while, in the central districts of Warsaw, also from carbonate rubble in anthropogenic embankments.

The spatial distributions of strontium content in the topsoil and subsoil are similar. Soils of the western districts of the city and of the Vistula flood terraces are richer in this element. Its higher concentration can be linked with the occurrences of glacial tills as well as weathering mantles, aeolian sediments and alluvial muds.

The strontium anomalies in soils commonly show small extents at the surface, but they often occur at both soil depth ranges. The greatest strontium concentration (556 mg/kg in the topsoil and 182 mg/kg in the subsoil) is observed in the vicinity of Kobyłka, near a number of brickyards.

Strontium accumulation near Jeziorko Czerniakowskie lake (312 mg/kg) is probably related to the fallout of particulate matter from the Siekierki thermal power plant.

Elevated strontium concentrations (>200 mg/kg at both soil depth ranges) are characteristic of soils from the Tarchomin industrial areas (also containing 8.24% of calcium).

Near furnace waste landfills the strontium levels in the topsoil and subsoil are 196 mg/kg and 173 mg/kg in Zawady, and 159 mg/kg and 235 mg/kg in Żerań, respectively.

Local enrichments in strontium are observed in soils along railway tracks (up to 180 mg/kg in the topsoil layer of Bemowo, and 291 mg/kg in the subsoil of Żerań), which are probably caused by coal burning in steam locomotives in the past years.

Elevated strontium concentrations are also recorded in industrial areas: 178 mg/kg in the Służewiec Przemysłowy industrial area, and 254 mg/kg in Mysiadło, where 165 mg/kg of nickel was also determined.

Sediments: <u>Pl. 62</u>, <u>tab. 6</u>

In the sediments the strontium concentration varies from 1 to 329 mg/kg, and the highest amounts are found in the Kanał Żerański drainage basin (median 46 mg/kg) and in the Vistula River (median 28 mg/kg). In most of the samples (75%) the strontium concentration does not exceed 32 mg/kg. The average strontium concentration in the sediments of the map sheet area (median 16 mg/kg) is slightly lower than the average value for Poland (median 20 mg/kg; Lis, Pasieczna, 1995). Sediments of the Vistula River are naturally enriched in strontium that is washed out from soils of the flood terraces and supplied from the southern part of the drainage basin, where weathered carbonate rocks crop out at the surface.

Strontium is an abundant element in some watercourses of the Wilanówka drainage basin. In the sediments of the ditches and canals around the sewage treatment plant of the former paper mill in Konstancin-Jeziorna the strontium concentration is 230–329 mg/kg, undoubtedly coming from sewage discharges.

Anomalous strontium concentrations, linked with the discharge of various types of sewage, are found in the sediments of the Kanał Bródnowski Górny canal (199 mg/kg near the Toruńska Thoroughfare), Kanał Henrykowski canal (120 mg/kg) and Żerański canal (154 mg/kg), as well as in the sediments of the Rów z Lewandowa ditch (138 mg/kg).

Locally increased strontium levels are observed in the sediments of watercourses in the Czarna River drainage basin (up to 111 mg/kg), Łacha Potocka oxbow lake (up to 101 mg/kg), Rudawka River (79 mg/kg) and Raszynka River (96 mg/kg).

The elevated strontium concentrations are in many cases associated with sewage discharge or rubble disposal into watercourses and closed reservoirs. In urbanized areas the strontium enrichment of waters and sediments can be the effect of surface runoff of road maintenance chemicals in winters, whereas in agricultural areas – with surface runoff after soil liming treatment.

Waters: <u>Pl. 63</u>, <u>tab. 7</u>

The strontium concentration in the surface waters ranges from 10 to 1,269 μ g/dm³ (median 202 μ g/dm³). As regards the waters of the whole of Poland the median strontium concentration is 243 μ g/dm³ (Lis, Pasieczna, 1995).

The highest concentration of this element is characteristic of the Vistula River (median 327 μ g/dm³), and half of the value was measured in the Czarna and Świder drainage basins (155 μ g/dm³). The surface waters in Warsaw and its surroundings are poorer in strontium as compared with the

waters in the Szczecin (median 311 µg/dm³; Lis, Pasieczna, 1998a) and Poznań agglomerations (median 276 µg/dm³; Lis, Pasieczna, 2005).

In the right-bank side of the Vistula River drainage basin, anomalous strontium concentrations (>438 µg/dm³) are characteristic of the sewage-polluted waters of the Kanał Henrykowski canal in Tarchomin, Kanał Bródnowski Górny canal, Rów z Lawendowa ditch in Białołęka and locally, the watercourses and reservoirs in the Czarna River drainage basin.

In the left-bank side of the Vistula River drainage basin, clearly strontium-enriched waters are found in the ditches and ponds of Łomianki, Rudawka River, Raszynka River, Kanał Ożarowski canal and some watercourses and reservoirs in Mokotów.

The greatest strontium concentrations are recorded in the waters of clay pit ponds of the former brickyard in Kobyłka (1,269 μ g/dm³) and in the waters of the Kanał Ożarowski canal in Bronisze (1,129 μ g/dm³).

In addition, anomalous strontium concentrations (>1,000 μ g/dm³) are recorded in the waters of a ditch on the outskirts of the Bemowo Forest in Lachtorzew (1,022 μ g/dm³), in the waters of the Kanał Henrykowski canal (1,025 μ g/dm³), a pond in Kolonia Opacz (1,410 μ g/dm³) and a ditch in Paluch near the Chopin Airport (1,067 μ g/dm³).

Ti TITANIUM

Soils: Pls. 64-65, tab. 4-5

The distributions of titanium content in the topsoil and subsoil are very similar. Almost identical are also the statistical parameters of titanium concentrations for both soil depth ranges, like with the soils of Europe, where the ratio of median titanium concentrations in the topsoil and subsoil is 1.021 mg/kg (De Vos, Tarvainen, ed., 2006).

Greater titanium amounts are found in soils developed on glacial tills, eluvial sediments and anthropogenic embankments. Anthropogenic soils from both soil depth ranges are characterised by the highest titanium concentrations (medians 79 and 80 mg/kg, respectively). Anomalous levels commonly occur at both depth intervals.

The maximum titanium concentration in the topsoil was found in the premises of the Polfa Tarchomin pharmaceutical company (736 mg/kg), where the element was used in the production of medicines.

The sources of titanium are furnace waste and emission from thermal power plants. In the topsoil and subsoil, near the landfills, the titanium concentrations are 569 and 751 mg/kg in Żerań and 430 and 353 mg/kg in Zawady, respectively. Soils from the immediate proximity to the Siekierki thermal power plant contain 535 and 490 mg/kg of titanium. In the storage area in Siekierki the value is 516 mg/kg, whereas near Jeziorko Czerniakowskie lake – 478 mg/kg

The titanium contamination is caused by the activity of the former Warsaw cement plant (328 and 258 mg/kg of titanium in the topsoil and subsoil, respectively).

Anthropogenic contamination by titanium is also observed in the premises of ArcelorMittal steelworks (337 mg/kg and 275 mg/kg - in both soil depth ranges), former Ursus Factory (279 mg/kg), and storage and industrial areas of Ursynów (up to 252 mg/kg). The last-mentioned area is contaminated by titanium (as well as by barium and lead) likely as a result of long-term activity of the Zakłady Ceramiki Radiowej ceramics factory, wherein lead titanate was used in the production of piezoelectric ceramic materials.

Elevated titanium concentrations occur in soils along railway tracks (up to 276 mg/kg near a railway siding in Bemowo).

The titanium concentrations in Janki near numerous warehouses are 289 mg/kg in the topsoil and 351 mg/kg in the subsoil, while in Otwock the concentration is 244 mg/kg.

At a depth of 0.8–1.0 m, 472 mg/kg of titanium is recorded in soils developed on aeolian sediments near Kobyłka, 325 mg/kg in the Raszynka River valley (developed on kame sands), and up to 207 mg/kg between Ursus and Ożarów (developed on loess-like sediments). In these cases the titanium contamination is probably of lithogenic origin.

Anthropogenic origin is suggested for the presence of titanium (214 mg/kg) in the subsoil near the junction of Wolska, Kasprzaka and Prymasa Tysiąclecia streets, which is an area of heavy road and railway traffic. Anthropogenic soil in the railway premises near the former FSO automotive factory, which is also characterised by elevated concentration of other metals, contains 379 mg/kg of titanium.

Sediments: Pl. 64, tab. 6

Most of the analysed sediments (75%) contain below 84 mg/kg of titanium. Elevated concentrations are found in various areas of the map sheet, whereas clearly anomalous values (>170 mg/kg) are associated mainly with urban areas. The median titanium concentration in the sediments from the Warsaw area and its surroundings (58 mg/kg) is more than twice as much as that in the Szczecin agglomeration (median 24 mg/kg; Lis, Pasieczna, 1998a) but lower than in the sediments of Poznań area (median 105 mg/kg; Lis, Pasieczna, 2005).

The lowest amounts of titanium are found in the sediments of the Vistula River and in the Długa River drainage basin (median 48 mg/kg), while the greatest ones are observed in the Kanał Żerański drainage basin (median 79 mg/kg).

The maximum titanium concentration (469 mg/kg) is recorded in the sediments of a watercourse in the area of Łomianki.

Titanium-enriched sediments occur in the Rów Miedzeszyński ditch in Wawer (up to 436 mg/kg), and in the Kanał Henrykowski canal near Mehoffera Street (310 mg/kg).

Anomalous titanium concentrations are characteristic of the sediments of the Potok Służewiecki stream and Rów Wolica ditch (up to 390 mg/kg). The latter also receives untreated sewage from Ursynów and Natolin, while the Potok Służewiecki stream is contaminated by rainwater from the Chopin Airport. Part of the contaminants can also come from industrial plants that operated in the past in the Służewiec Przemysłowy area.

Strong titanium contamination of the sediments in the Kanał Bródnowski Górny (198–276 mg/kg) and Kanał Żerański (191–257 mg/kg) canals can be due to surface runoff from nearby industrial areas, railway premises and residential areas under development.

Anomalous titanium concentrations are locally recorded in organic sediment of a pond in the village of Opacz (418 mg/kg), in a ditch in the Lipkowska Woda drainage basin (400 mg/kg), and in the sediments of the tributaries of the Czarna (316 mg/kg) and Jeziorka (211 mg/kg) rivers.

TI THALLIUM

Waters: <u>Pl. 66</u>, <u>tab. 7</u>

The geochemical baseline for thallium in the surface waters of Poland was determined at 0.006 μ g/dm³ (Salminen ed., 2005), while in the waters of the study area the values vary from <0.05 to 0.24 μ g/dm³ (median <0.05 μ g/dm³).

The thallium concentration is much lower than the boundary limit for water quality classes I/II (2 μ g/dm³) in all of the samples. 90% of the waters in the map sheet area show the thallium concentrations below 0.06 μ g/dm³.

Evidently elevated thallium levels relative to the baseline value are observed in the waters of the Vistula River: >0.06 μ g/ dm³ (median 0.08 μ g/dm³). The likely source of this element is the Upper Silesian area of mining and processing of Zn-Pb ores, from which it is transported by the Vistula River and its tributaries. The strongly thallium-contaminated Biała Przemsza River is recharged by the Biała and Sztoła tributaries carrying mine waters from the Pomorzany Zn-Pb mines as well as sewage from the ZGH Bolesław mine in Bukowno and from a sewage treatment plant in Olkusz. Waters of the Biała Przemsza River further flow into the Przemsza River which is a tributary of the Vistula River. The thallium concentration in the waters of the Biała Przemsza is 8.73–17.89 μ g/dm³, and in the waters of the Przemsza up to 3.81 μ g/dm³ (Pasieczna, ed., 2010a, c). Waters of the Vistula River in Warsaw consequently show much lower concentrations of this element.

Besides the above-mentioned areas, thallium contamination was encountered only in 16 water samples collected from other reservoirs. The maximum thallium concentration $(0.24 \,\mu\text{g/dm}^3)$ was found in the waters of a ditch draining the Horowe Bagno marsh in a forest area at Marki.

U URANIUM

Waters: Pl. 67, tab. 7

The uranium concentration in the river waters across the world varies from 0.02 to 5.0 μ g/dm³, and the average value is 0.37 μ g/dm³ (Gaillardet *et al.*, 2003 w: Kabata-Pendias, Szteke, 2012). In the waters of Europe the uranium concentrations range between <0.002 and 11.100 μ g/dm³, and the median is 0.320 μ g/dm³ (De Vos, Tarvainen, ed., 2006).

In the waters of the Warsaw area and its surroundings the uranium concentrations are in the range from <0.05 to 19.55 μ g/dm³ (median 0.53 μ g/dm³).

In the left-bank side of the Vistula drainage basin the waters are much richer in uranium compared with the area on the eastern side of the river, which is likely caused by the differences in the geological structure of the basement. On the western side the watercourses drain areas composed of glacial tills, loess-like weathering mantles and aeolian sediments, and alluvial muds rich in uranium-binding clay minerals, whereas on the eastern side, sandy deposits, rich only in silica, are predominant.

Uranium-contaminated waters are found in the Utrata drainage basin (median 1.77 μ g/dm³), and the lowest amounts of this element were encountered in the waters of lakes and ponds (median 0.27 μ g/dm³). Waters of the Vistula River are characterised by intermediate concentrations in the range of 0.26–0.98 μ g/dm³ (median 0.50 μ g/dm³).

The maximum uranium concentration (19.55 μ g/dm³) is recorded in the waters of a ditch in a forest area in Paluch. The waters are also conspicuous by high electrolytic conductivity and elevated concentrations of many other constituents.

Uranium contamination (>2.49 μg/dm³) is observed in the waters of the Struga and Lipkowska Woda rivers and their tributaries, Rudawka, Kanał Ożarowski canal, Żbikówka, Raszynka, Rów Opaczewski ditch, Utrata drainage basin, Regułka, Jeziorka ditch, Kanał Wolacki canal and Potok Służewiecki stream, as well as some reservoirs and watercourses in Mokotów.

The following uranium concentrations are recorded in the waters: in a tributary of the Lipkowska Woda – 18.63 μ g/dm³, in Żbikówka – 14.01 μ g/dm³, in the ditch paralleling the Piaseczyńska Street in Mokotów – up to 13.41 μ g/dm³.

On the right-bank side of the Vistula River, elevated uranium levels (>1.17 μ g/dm³) are characteristic of the waters of some canals: Henrykowski, Wystawowy, Gocławski and Nowa Ulga, and locally of the Czarna River and its tributaries.

V VANADIUM

Soils: Pls. 68-69, tab. 4-5

Statistical parameters of the concentration and distribution of vanadium in both the topsoil and subsoil are very similar. The median vanadium concentration in the topsoil (8 mg/kg) is similar to the geochemical baseline level for Poland (7 mg/kg; Lis, Pasieczna, 1995). As regards land use types, the

greatest vanadium concentrations in the topsoil are found in the areas of parks (median 11 mg/kg), and the lowest ones in forests (median 3 mg/kg).

The vanadium concentration at both soil depth ranges is clearly linked with the chemical composition of parent rocks. Greater amounts of vanadium are observed in soils developed on alluvial sediments (muds of the Vistula flood terraces), weathering mantle and aeolian sediments, glacial tills, and locally alluvial muds.

At both soil depth ranges the vanadium concentrations are manifested by a number of anomalies (>20 mg/kg).

In the topsoil the maximum vanadium concentration (119 mg/kg) is recorded in meadows of Białołęka, which are also enriched in iron, arsenic and sulphur. In this area, vanadium is probably bound with iron oxides. Similar lithogenic enrichments are found in meadow soils developed on alluvial muds in the area of an ancient meander of the Vistula River in Wawer (32–42 mg/kg), in the Długa River valley – in Okuniew (43 mg/kg) and in Ossów (26 mg/kg). Naturally increased vanadium concentrations are observed in soils of the Vistula flood terraces (30–50 mg/kg).

Anthropogenic contamination of soils by vanadium (63 mg/kg) is recorded in the area of ArcelorMittal steelworks, where the element is used for steel production.

The anomalies found in the area of Augustówka (up to 80 mg/kg), Siekierki (49 mg/kg) and Jeziorko Czerniakowskie lake (36 mg/kg) are probably a result of emission from the Siekierki thermal power plant.

Elevated vanadium concentrations are recorded at both soil depth ranges near the landfills of furnace ashes in Żerań (50–60 mg/kg) and Zawady (30–70 mg/kg).

The vanadium anomalies detected near railway tracks are probably caused by smoke emissions from steam locomotives.

Local anthropogenic anomalies are found near the Polfa Tarchomin pharmaceutical company (23 mg/kg), former Ursus Factory (29 mg/kg) and in the area of inactive glassworks in Ożarów (24 mg/kg).

The maximum vanadium concentration (84 mg/kg) in the subsoil was observed near some brickyards at Kobyłka, where elevated titanium (472 mg/kg) and strontium (182 mg/kg) levels were also detected.

Sediments: <u>Pl. 68</u>, <u>tab. 6</u>

The range of concentrations of vanadium in the sediments is much the same as the range of its levels in the topsoil, and the median value (8 mg/kg) is identical as in the soils. In most of the sediments the vanadium concentration does not exceed 25 mg/kg. Anomalous concentrations (>25 mg/kg) occur predominantly in the sediments of watercourses and reservoirs draining areas composed of vanadium-enriched alluvial and fluvial muds.

Considerable amounts of vanadium are found in the sediments of the Wilanówka (up to 44 mg/kg) and a pond in the village of Opacz (38 mg/kg).

The vanadium levels in the sediments of watercourses recharging the Kanał Markowski canal in Białołęka are up to 32 mg/kg, and in the Nowa Ulga canal – 29 mg/kg.

Elevated vanadium concentrations in the sediments of the Kanał Bródnowski Górny (up to 40 mg/kg) and Kanał Henrykowski (up to 39 mg/kg) canals result probably from the discharge of sewage from industrial plants of Targówek and Tarchomin, active both currently and in the past.

Vanadium contamination of the sediments from the Rów Miedzeszyński ditch in Wawer (up to 40 mg/kg) is likely anthropogenic in origin. The sediments also typically show considerable levels of titanium (up to 436 mg/kg) and zinc (up to 1,171 mg/kg).

Elevated vanadium concentrations are locally observed in the sediments of watercourses and reservoirs in the Czarna River drainage basin. The maximum vanadium concentration (214 mg/kg) is recorded in a forest pond near the village of Stanisławów Pierwszy (municipality Nieporęt). High amounts of vanadium were also found in the sediments of Krzewiny pond in Dąbrówka near Mysiadło (36 mg/kg), Staw Młociński pond (33 mg/kg) in a gated residential community, and in the sediments of a minor branch of the Vistula River (up to 30 mg/kg) in Młociny.

Waters: Pl. 69, tab. 7

The vanadium concentrations in the surface waters in Warsaw and its surroundings vary from <1 to $15 \ \mu g/dm^3$ (median <1 $\mu g/dm^3$). In the waters of Poland the vanadium concentrations are found in the range of <8–1,848 $\mu g/dm^3$ (Lis, Pasieczna, 1995), while in the waters of Europe – <0.05–19.5 $\mu g/dm^3$; median 0.46 $\mu g/dm^3$ (De Vos, Tarvainen, ed., 2006).

All of the analysed water samples meet the standards for water quality classes I/II in terms of vanadium concentration ($\leq 50 \ \mu g/dm^3$).

The vanadium concentration distribution indicates that elevated levels (>1 µg/dm³) relative to the baseline value are typical primarily of the waters from the area located to the west of the Vistula River, which is probably associated with the abundance of clay minerals in the bedrock. Vanadium-enriched waters are found in the Kanał Młociński canal, Struga and Lipkowska Woda and their tributaries, Żbikówka, Raszynka and Utrata rivers and their tributaries, Jeziorka ditch, and Potok Służewiecki stream and its tributaries.

To the east of the Vistula River, anomalous vanadium concentrations are observed in the waters of the canals: Henrykowski, locally Żerański and Markowski, Magenta, Wawerski, Nowe Ujście and Zagoździański, as well as in the Struga Pogorzelska, Mienia and Czarna drainage basins.

Water enrichment in vanadium is also observed at some sections of the Vistula River.

The highest vanadium concentration was found in the waters of the Kanał Młociński canal in the Młociny Forest ($15 \mu g/dm^3$), which are also characterised by high levels of arsenic ($13 \mu g/dm^3$), antimony ($1.63 \mu g/dm^3$) and thallium ($0.10 \mu g/dm^3$).

Anomalous vanadium concentration was also observed in the waters of a ditch in a forest area of the Radzymin municipality. These waters are additionally conspicuous by considerable amounts of other constituents discussed in the section on aluminium. A considerable vanadium concentration (8 μ g/dm³) was detected in a pond located in a forest area at Stanisławów Pierwszy.

Anomalous vanadium concentrations were also found in the waters of a tributary of the Raszynka River (6 μ g/dm³), in Pozytywka pond in Ursynów (5 μ g/dm³), a ditch recharging the Jeziorka ditch in Dąbrówka near Mysiadło (4 μ g/dm³), Jelonki clay pit ponds (4 μ g/dm³), Rów Opaczewski ditch (4 μ g/dm³) and Regułka River (4 μ g/dm³).

TOTAL SUSPENDED SOLIDS

Waters: <u>Pl. 70</u>, <u>tab. 7</u>

The concentration of total suspended solids is among the major proxies of surface water quality. Suspended solids are a carrier of contaminants whose content is often greater than in bottom sediments (Barbusiński *et al.*, 2012). In the surface waters in Warsaw and its surroundings the concentration of total suspended solids was determined in one third of the samples collected. The values range from <5 to 194 mg/dm³. 16% of the analysed samples meet the standards specified for water quality class I as regards the concentration of suspended solids (≤ 25 mg/dm³), 38.5% of the samples are categorised into class II (>25 mg/dm³), and 45.5% of the samples show exceeded boundary limits. The highest concentration of suspended solids is observed in the waters of Czarna River drainage basin (median 68 mg/dm³), while the lowest one – in the the waters of Utrata drainage basin (median 38 mg/dm³).

Greater amounts of suspended solids are recorded in water bodies outside of Warsaw, commonly in forests east of the Vistula River. The highest concentration of suspended solids (194 mg/dm³) is observed in the waters of a ditch crossing meadows near the village of Stare Grabie (municipality Wołomin). Distinct anomalous concentrations are found in a ditch recharging the Rządza River in the village of Pasek (190 mg/dm³) andin Białe Błota pond in Wołomin (186 mg/dm³).

To the west of the Vistula River the greatest amounts of suspended solids are recorded in the waters of a ditch recharging the Kanał Grabowski canal in Pyry (178 mg/dm³) and in the waters of the Raszynka River that drains cropland in the village of Lesznowola (166 mg/dm³).

Zn ZINC

Soils: Pls. 71-72, tab. 4-5

The zinc concentration in soils of the study area varies within a wide range from 2 to 7,019 mg/kg in the topsoil and from 2 to 4,290 mg/kg in the subsoil. Comparison of the median zinc concentrations for both soil depth ranges (44 and 12 mg/kg) indicates an anthropogenic zinc enrichment of the topsoil, although the geochemical baseline value for the topsoil of Poland – 35 mg/kg (Lis, Pasieczna,

1995) – is exceeded only insignificantly. A comparison with the study of soils from the area of Warsaw and its surroundings, carried out 25 years ago (Lis, 1992), shows that the topsoil was less contaminated by zinc at that time (median 34 mg/kg).

In terms of topsoil use types the lowest average zinc concentrations are typically found in forest soils (median 10 mg/kg), and the highest ones are observed in soils of allotment gardens (median 102 mg/kg) and parks (median 91 mg/kg). Zinc enrichment of soils in urban green areas is probably due to the use of plant protection products containing this element.

In the environs of Warsaw and its eastern outskirts the most common soils are those showing zinc concentration values within the limits of geochemical background (70–90 mg/kg). In the western peripheral districts of Warsaw and on the Vistula flood terraces the soils that are developed on glacial tills and loess-like sediments, as well as fluvial muds, contain more zinc (100–200 mg/kg).

Clearly anomalous zinc concentrations (>348 mg/kg in the topsoil and >171 mg/kg in the subsoil) are observed in the city centre (Śródmieście, Wola, border area of Targówek, Praga Północ and Praga Południe). A similar extent of anomalies and concentrations of zinc were determined in Warsaw in the late 1970s (Czarnowska, Gworek, 1991). This leads to a conclusion about a slow rate of increasing soil contamination in the urbanized area.

The maximum zinc concentration in the topsoil (7,016 mg/kg) was found in Białołęka near the Polfa Tarchomin pharmaceutical factory whose history dates back to the early 19th century. Chemical plants that existed in this place since 1849 produced vinegar, fertilizers, processed chemicals, paints, cosmetics and pharmaceutical products using zinc-containing compounds (Historia zakładów Polfy Tarchomin..., 2015). The potential zinc-contamination source could also be the plastics factory, not existing any more. Zinc compounds are used in the production of fertilizers, pharmaceutical products, cosmetics, paints and plastics (Kabata-Pendias, Pendias, 1999).

Strongly zinc-contaminated soils (at both depth intervals) are found in the Augustówka area: 3,961 mg/kg in the topsoil and 3,768 mg/kg in the subsoil. The topsoil near Jeziorko Czerniakowskie lake contains 677 mg/kg of zinc. The zinc concentrations are comparable to those in soils of areas of Zn-Pb ore mining and processing (Pasieczna, ed., 2010a, b) and their occurrence in the study area is somewhat enigmatic. Part of the zinc may origin from emissions of particulate matter during coal combustion in the Siekierki thermal power plant, but the primary source is certainly different.

In the topsoil a strong zinc anomaly is found in an area (from Kamionka through Szmulki to Nowa Praga) that has been highly industrialized since the second half of the 19th century. The highest zinc concentration within the anomaly (2005 mg/kg) is observed in the premises of the former high-voltage switchgear plant which is the successor of an electrical equipment plant (since 1921). In the subsoil the zinc concentration also shows an anomalous value (556 mg/kg), and the soil additionally contains 442 mg/kg of copper. Within the same anomaly, a value of 1,296 mg/kg of zinc is recorded in the topsoil near the former cosmetics factory as well as close to or within the nearby allotment gardens

(1,132 mg/kg in Kozia Górka in Grochów) and along railway tracks (977 mg/kg near the Warszawa Wschodnia station).

Zinc-contaminated soils are found in the area of ArcelorMittal steelworks (476 mg/kg) and near the landfill of its waste (887 mg/kg). Currently, the plant uses technologies that successively reduce emissions of metals, including zinc (Dmuchowski *et al.*, 2011).

An anthropogenic zinc anomaly (552 mg/kg) occurs near the former Służewiec Przemysłowy industrial area, in place of high concentrations of barium, lead and titanium.

Outside of Warsaw, soil contaminations by zinc were encountered in Piaseczno: 808 mg/kg in the topsoil and 1,099 mg/kg in the subsoil.

In the subsoil, the greatest amounts of zinc (>171 mg/kg) are found within a more compact but smaller area as compared with the topsoil. The highest zinc concentration (4,290 mg/kg) is recorded in soil of the anthropogenic embankment along Wybrzeże Gdańskie Street in Śródmieście.

Sediments: <u>Pl. 71</u>, <u>tab. 6</u>

The zinc concentration in the sediments ranges from 4 to 3,237 mg/kg. Contaminated sediments are observed mainly in the watercourses draining urban areas.

Sediments strongly contaminated by zinc were found in the Kanał Henrykowski canal (3,237 mg/kg) downstream of the Polfa Tarchomin pharmaceutical company, which has received wastewater from the plant for many years (Encyklopedia Warszawy, 1975).

Highly anomalous zinc concentrations (2,361 mg/kg) are observed in the sediments of the Kanał Bródnowski Górny canal that has received wastewater from the Targówek Fabryczny industrial area since the 19th century.

Contaminated sediments are found in a ditch flowing from the Wólka Węglowa area to the Lipkowska Woda (999–1,056 mg/kg).

Anomalous zinc levels (>474 mg/kg) also occur in the sediments of the Jeziorka downstream from Konstancin-Jeziorna (623 mg/kg), and in the Wilanówka (1,054 mg/kg). Contamination of the sediments in both these rivers may date back to the period when the rivers were a single watercourse and received municipal and industrial sewage from the Konstancin-Jeziorna area.

High zinc concentrations are locally found in the sediments of the Wolica ditch (739 mg/kg) and Wolica canal (778 mg/kg), both recharging the Potok Służewiecki stream, and in the sediments of the stream itself (544 mg/kg near the airport) and of Jeziorko Wilanowskie lake (640 mg/kg), which the river drains into. Slightly lower zinc concentrations (up to 458 mg/kg) in the sediments of the Potok Służewiecki stream were reported in the years 2009–2010 (Bojakowska *et al.*, 2012).

Point anomalies of zinc were also encountered, e.g., in the sediments of the Rów Opaczewski ditch, Rów Miedzeszyński ditch, Łacha Potocka oxbow lake, Piłsudski Fort moat and Nowa Ulga canal. Outside of Warsaw, worth noting is the very high amount of zinc (1584 mg/kg) in the sediments of a pond in Hipolitowo and in the tributaries of the Czarna River in Nadma, Kobyłka and Wołomin.

Waters: <u>Pl. 72</u>, <u>tab. 7</u>

The zinc concentration in the surface waters of Warsaw is highly variable, ranging from <3 to 544 μ g/dm³ (median <3 μ g/dm³), but there is no sample with the value exceeding the boundary limit for water quality classes I/II (1,000 μ g/dm³). In the waters of the Poznań agglomeration the range of zinc concentrations is similar: <3–539 μ g/dm³ (Lis, Pasieczna, 2005). The geochemical baseline value for the waters of Poland is much greater (33 μ g/dm³), which results mainly from anomalous zinc levels in the watercourses of Upper Silesia (Lis, Pasieczna, 1995).

Elevated zinc concentrations (>9 µg/dm³) are typically found in the waters of the Kanał Młociński canal, Lipkowska Woda and Struga rivers and their tributaries, Kanał Ożarowski canal, Żbikówka, Rów Opaczewski ditch, Potok Służewiecki stream and its tributaries (Kanał Grabowski and kanał Wolica), tributaries of the Czarna River, Magenta canal, Kanał Wawerski canal (downstream from the sewage treatment plant in Stara Miłosna), tributaries of the Mienia and Świder rivers, Struga Pogorzelska and Rów Miedzeszyński ditch.

Anomalous zinc concentrations (>59 μ g/dm³) were found in the contaminated waters of the Kanał Henrykowski canal (378 μ g/dm³), Potok Służewiecki stream (95 μ g/dm³) and, locally, in many minor watercourses and closed reservoirs in the Czarna, Długa, Kanał Wawerski, Świder, Struga and Łasica drainage basins.

The highest zinc concentration (544 μ g/dm³) is recorded in the waters of the Struga River near Stare Babice. High zinc levels (368 μ g/ dm³) are a characteristic feature of Bagno Jacka lake at Wesoła, which is also conspicuous by the maximum concentration of DOC (62 mg/dm³) and a considerable amount of lead (3.02 μ g/dm³).

The highest zinc levels are typically found in the waters of the Łasica (median 11 μ g/dm³) drainage basin, while the lowest ones in the Vistula River (<3 μ g/dm³).

PERSISTENT ORGANIC POLLUTANTS IN SOILS AND SEDIMENTS

Persistent organic pollutants are organic compounds characterised by high resistance to chemical, photolytic and biological degradation in the environment. These compounds, due to their stability, lipophilic properties and bioaccumulatability, may have a negative impact on the biosphere, including human health. Most of the compounds classified as POPs are man-made and are currently or were in the past used as pesticides, solvents, pharmaceuticals and industrial chemicals. Some of the POP compounds may arise naturally, for example during volcanic emissions and by biosynthesis pathways. Organic compounds that are persistent in sediments and soils, posing the greatest threat to the environment, include, among others, polychlorinated biphenyls (PCBs), organochlorine pesticides and polycyclic aromatic hydrocarbons (PAHs).

Geochemical maps have been developed for a number of selected pesticides (DDTs, HCHs, dieldrin, endosulfan I, which have been widely used in Poland), mineral oils, PCBs and PAHs.

Organochlorine pesticides are chlorinated hydrocarbons widely used in agriculture as insecticides in the years 1940–1960. In many countries, due to harmful effect on animal cells and very low susceptibility to degradation in the environment, most of the organochlorine pesticides were withdrawn from the production and use. However, they are still produced and applied in some developing countries.

Some of the pesticides that were spread over agricultural fields and plantations in tropical countries, especially in soils with very low concentration of organic matter and subject to strong solar radiation, penetrate into the atmosphere and are transported by air masses over long distances toward the poles, and finally, with precipitation, again go to the soils in the temperate climate zone (Ramamoorthy, Ramamoorthy 1997; Grynkiewiczet al., 2003).

Modern sediments of water reservoirs in different regions of the world contain organochlorine pesticides at a level of several hundred thousand μ g/kg (extreme concentrations are noted, for example, in sediments of some ports). In general, even in highly contaminated sediments, the concentration of these compounds does not exceed 1,000 μ g/kg (Kannan *et al.*, 1997; Sivey Lee, 2007; Lin *et al.*, 2009). The highest concentrations of these compounds are found in sediments dated for the period of 1950–1970.

Among the 20 organochlorine pesticides analysed for the study, the following have been found in the sediments: α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, α -chlordane, γ -chlordane, endosulfan I, endosulfan II, endosulfan sulphate, dieldrin, p,p'-DDE, p,p'-DDD, p,p'-DDT, endrin and endrin aldehyde.

Mineral oils in the soils and sediments are a mixture of aliphatic hydrocarbons (paraffins), cycloparaffins (naphthenes) and aromatics (arenes) containing 10 to 40 and more carbons in the molecule. Mineral oils are widely distributed in the environment and their background concentrations can be up to 100 mg/kg. Elevated concentrations of mineral oils are mostly anthropogenic, but in forest and peat bog soils they may be of natural origin. In urban areas the primary sources of mineral oils are road transport, storage and processing of liquid fuel, oil spills due to car accidents, and the use of wastewater sludge for soil fertilization (Riffaldi *et al.*, 2006; Pathak *et al.*, 2011; Akpan, Udoh, 2013).

Polychlorinated biphenyls (PCBs), chlorinated biphenyl derivatives, are synthetic compounds which in the past were used as dielectric liquid for capacitors and transformers, working fluids in hydraulic cylinders and heat exchangers, additives for paints and varnishes, and plasticizers for plastics and wood impregnators. Currently, the PCBs are released to the environment during the combustion of coal in power plants, incineration of hospital wastes, combustion of hard coal and wood for household and municipal purposes, and as a result of leaks of grease from vehicles, damage of heat exchangers and transformers, and emission of contaminants in some technological processes.

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds widespread in the environment. Under natural conditions, PAHs are formed by high-temperature pyrolysis of organic matter during the fires of vegetation, volcanic eruptions, and especially during the diagenesis and catagenesis of organic matter in the processes of oil and coal formation (Capaccioni *et al.*, 1995; Harvey 1998; Oros, Simoneit 2001; Alves *et al.*, 2010). PAHs are introduced into the environment mainly by the processing of hard coal in coking plants, coal combustion in households and power plants, oil processing in refineries, combustion of liquid fuels in car and aircraft engines, extraction, transportation and storage of liquid fuels, incineration of municipal waste, as well as by metallurgical processes (Howse, Jones, 1998; Grynkiewicz *et al.*, 2003).

DIELDRIN

Soils: <u>Pl. 73</u>, <u>Tab. 8</u>

The presence of dieldrin at a concentration exceeding the determination limit was found in 24.39% of the analysed soils. The largest area of soils contaminated by this compound (>2 μ g/kg) extends from Piastów and Włochy in the south to Ożarów and Blizne in the north. Its eastern boundary approaches the area of Ochota. In this area, the maximum dieldrin concentration (41.0 μ g/kg) is recorded near the streets of Połczyńska and Synów Pułku in the district of Bemowo. The soil is also conspicuous by high concentrations of DDT. At some other sites of this extensive anomaly the dieldrin concentrations exceed 10 μ g/kg (near Mszczonowska Street, and in the areas of Konotopa and Ożarów).

Elevated dieldrin concentrations are also recorded in Wilanów (27.1 μ g/kg), Tarchomin near the TEKNO factory and the former houses factory (8.4 μ g/kg), and in Targówek (8.1 μ g/kg).

Sediments: Pl. 73, Tab. 9

Dieldrin concentrations in the sediments are low (up to 2.7 μ g/kg) and recorded only in 13.25% of the samples. At three locations the concentrations were slightly higher than the TEC (Threshold Effect Concentration) value (1.9 μ g/kg): in the sediments of a canal in an industrial area of Wołomin, in a ditch running across cropland at Raszyn, and in the Radiowo Fort moat.

DDT

Soils: <u>Pl. 74</u>, <u>Tab. 8</u>

As regards the analysed organochlorine pesticides, the most commonly detected contaminants in the topsoil were DDT compounds and their metabolites. The maximum concentration of p,p'-DDT is 4,000 μ g/kg, p,p'-DDE – 1,700 μ g/kg, and p,p'-DDD – 800 μ g/kg. The average concentration (arithmetic mean) of the sum of DDT and its metabolites is 57.6 μ g/kg.

Over large areas there are anomalies of DDT concentrations with values permissible only for industrial soils, and at some localities the concentrations are even greater.

The lowest levels of the sum of DDT (<10.2 μ g/kg) are recorded in the east of the map sheet area – in the areas of Okuniew, Sulejówek, Wesoła and Wiązowna, whereas high or elevated concentrations of these compounds are observed across almost the whole remaining area.

In the largest, Praga Południe anomaly the concentrations of the sum of DDT exceed 100 μ g/kg, and in its central part, covering the area of Skaryszewski Park and allotment gardens near the Waszyngtona Street, the concentrations are >200 μ g/kg (even up to 5,400 μ g/kg).

Similar levels of the sum of DDT (>100 μ g/kg) are recorded in areas adjoining the railway line to Piastów (in the districts of Ochota and Ursus) and in the Ożarów region. Measurements performed within these anomalies revealed up to 2,580 μ g/kg of DDT compounds in Mszczonowska Street of the Wola district, and up to 530.0 μ g/kg near Zapustna Street in the Ursus district. Near the railway track in Wola (in Prądzyńskiego Street) the concentration of DDT compounds is 1,900 μ g/kg, and in Jelonki (near Batalionu Zośka Street) – 1,302 μ g/kg. In the Gołąbki residential area the maximum DDT concentration is 1,140.8 μ g/kg.

At some other localities (near Łomianki, Henryków, Marki, and in the Vistula River valley) the anomalies are not so extensive in area, and the DDT concentrations are commonly in the range of $500-1,100 \mu g/kg$. Worth noting is the distinct predominance of concentrations of p,p'DDT over its metabolites, indicating that the compounds have been introduced into the soil relatively recently.

Depending on the soil use and management there is variability in the occurrence of DDT, although extremely high levels were detected in areas of different land use types. The greatest mean geometric concentrations of the sum of DDT are distinctive for arable fields (59.5 μ g/kg) and allotment gardens (19.3 μ g/kg), while the lowest ones are found in forests (4.1 μ g/kg) and meadows (9.6 μ g/kg). The DDT concentrations in the soils of arable fields are much greater that the average concentration for arable fields for the whole of Poland – 29.57 μ g/kg (Maliszewska-Kordybach *et al.*, 2014).

Compared to other urbanized areas across the world, the soils of Warsaw are characterised by similar mean geometric concentration of DDT ($10.9\mu g/kg$) as the soils of the city of Kurukshetra in India – 7.9 $\mu g/kg$ (Kumar *et al.*, 2013), but much lower than in the soils of Beijing – 68.1 $\mu g/kg$ (Yang *et al.*, 2010).

Sediments: Pl. 74, Tab. 9

DDT compounds and their metabolites were found in 97% of the sediment samples, including p,p'-DDT found in 45.25% of the samples, p,p'-DDD in 84% of the samples, and p,p'-DDE in 96.75% of the samples. The maximum concentration of p,p'-DDT is 770.0 μ g/kg, p,p'-DDE – 277.3 μ g/kg, and p,p'-DDD – 860.0 μ g/kg.

The extremely high concentration of the sum of DDT (1,900.0 μ g/kg) is recorded in the sediments of a drainage ditch running across arable fields north of Marki. The sediments of the Wilanówka (up to 430,1 μ g/kg), an unnamed stream in Sokołów (up to 202.9 μ g/kg), and ditches in Latchorzew (up to 174.8 μ g/kg), Radiowo (up to 111.1 μ g/kg) and Raszyn (up to 105.3 μ g/kg) are also highly contaminated.

The calculated geometric mean values show considerable contamination of the sediments in the Raszynka (13.1 μ g/kg), Łasica (10.3 μ g/kg), Wilanówka (8.6 μ g/kg) and Jeziorka (7.0 μ g/kg) drainage basins, but lower in the Świder (1.0 μ g/kg), Czarna (1.5 μ g/kg) and Długa (1.6 μ g/kg) drainage basins.

p,p'-DDT levels higher than the TEC values (1.19 μ g/kg) were measured for 116 of the sediment samples, and the concentrations greater than the PEC (Probable Effect Concentration) value (62.9 μ g/kg) were found only in the sediments of a ditch in Nadma (north of Marki).

As regards the p,p'-DDE metabolite, its concentrations lower than the TEC value ($3.2 \mu g/kg$) were observed in 73.25% of the samples, whereas its concentrations greater than the PEC value ($31 \mu g/kg$) were detected in 2.75% of the samples.

Concentrations of p,p'-DDD lower than the TEC value (4.9 μ g/kg) were found in 78% of the samples, whereas concentrations greater than the PEC value (28 μ g/kg) – in 4% of the samples.

The lowest levels of DDT and its metabolites, like other POPs, were encountered in sandy sediments (geometric mean 1.5 μ g/kg), while the highest ones in organic slurry (12.8 μ g/kg).

Abundance of DDT and its metabolites in the sediments is primarily the result of their common use in the past in parks, allotment gardens, arable fields and forests. Part of the compounds may originate from distant atmospheric transport.

While estimating the contamination level of the sediments by DDT it is important to consider the interdependence between DDT and its metabolites. Low value of the (DDE+DDD)/DDT ratio (<1) indicates close proximity to the contamination source and relatively recent use of the compound. High value of the DDE+DDD/DDT ratio (6.5) calculated for the analysed sediments proves that the compounds were introduced into the natural environment of Warsaw and its surroundings long ago.

ENDOSULFAN I

Soils: <u>Pl. 75</u>, <u>Tab. 8</u>

Endosulfan I was found in 13.71% of the topsoil samples. Areas of its elevated concentrations (>2 μ g/kg) generally coincide with the DDT anomalies. The maximum concentration (23.6 μ g/kg) is recorded in the area of allotment gardens in Waszyngtona Street.

Relatively high levels of endosulfan I were also observed in anthropogenic soil near Mszczonowska Street in the Wola district (19.4 μ g/kg), near the Siekierkowska Thoroughfare (15.5 μ g/kg), near Kanał Bródnowski canal (9.0 μ g/kg), and in the vicinity of Batalionu Zośka Street (7.2 μ g/kg). In arable fields of countries where the pesticide is still in use, its concentrations are greater by

three orders of magnitude. Soils of the Jordan River valley contain up to 185.4 mg/kg of endosulfan, and in India up to 384 mg/kg (Batta *et al.*, 2006; Sunitha *et al.*, 2011). In China, its concentration in arable soils is 160 μ g/kg, and in urban areas – 83 μ g/kg, while the geochemical baseline value is 38 μ g/kg (Jia *et al.*, 2010).

Sediments: Pl. 75, Tab. 9

The maximum concentration of endosulfan I (10.9 μ g/kg) is recorded in the sediments of a ditch in Nadma north of Marki, and its presence was detected in 12.25% of the samples.

Endosulfan concentration in excess of $1 \mu g/kg$ (TEC value) was found in the sediments of the Wilanówka, in a canal crossing an industrial area in the north-eastern outskirts of Wołomin, and in a left-bank side canal-tributary of the Raszynka River (cropland area).

Endosulfan II was found in a single sample from the Wilanówka ($0.6 \mu g/kg$), while endosulfan sulphate – in the sediments of the Raszynka ($2.6 \mu g/kg$) and Wilanówka ($1.2 \mu g/kg$) rivers.

HCH HEXACHLOROCYCLOHEXANE

Soils: Pl. 76, Tab. 8

HCH isomers were detected only in 6% of the soil samples. The most common isomer, observed at highest concentrations, is γ -HCH. The maximum concentration of the sum of HCH isomers is 5 μ g/kg.

The highest HCH levels were found in the Bemowo-Lotnisko region, near Wrocławska Street and Powstańców Śląskich Street (5 μ g/kg), in a post-industrial area near Wołoska Street and Woronicza Street (5 μ g/kg), in Bartycka Street (4 μ g/kg), and in Żytnia Street (4 μ g/kg).

For comparison, the average concentration of the sum of HCH in agricultural soils of Poland is 2.85 μ g/kg (Maliszewska-Kordybach *et al.*, 2014), and in agricultural soils of the Czech Republic – 0.91 μ g/kg (Holubek *et al.*, 2009).

The presence of HCH in soils is associated mainly with the use of lindane as an insecticide in the past, in which γ -HCH was the main component. Currently, it is still used in the pharmaceutical and veterinary industries, and as an impregnant.

None of the analysed samples contains δ -HCH, γ -chlordane, α -chlordane, endrin, endosulfan II, endosulfan sulphate and heptachlor epoxide. Other pesticides were detected sporadically and at low concentrations.

Sediments: Pl. 76, Tab. 9

At least one HCH isomer was found in each of the 33 sediment samples (8.25%), including lindane (γ -HCH) which was detected in 14 samples. The maximum concentration of the sum of HCH isomers is 5 μ g/kg. HCH isomers were detected predominantly in the sediments of the Vistula River between Tarchomin and Jabłonna and in the sediments of the Wilanówka River.

MINERAL OILS

Soils: <u>Pl. 77</u>, <u>tab. 10</u>

Over much of the study area the concentration of mineral oils in the topsoil is below 40 mg/kg. An extensive anomaly with the concentrations >40 mg/kg (and a maximum value of 3,050 mg/kg) covers the central districts of the city. Smaller areas of elevated concentration of mineral oils are found in Żerań, in the vicinity of Dąbrówka Szlachecka and Gołąbki, between the Kanał Markowski canal and Czarna River valley, near Ząbki and Kobyłka, and in the Aleksandrów–Stara Miłosna–Boryszew and Karczew–Otwock regions.

The highest concentrations of mineral oils were detected in soils of lawns, near fuel stations, and in forests. Lawn soils in the district of Praga Południe contain up to 678 mg/kg of mineral oils, in Służewiec up to 665 mg/kg, in Kobyłka up to 489 mg/kg, and in Ząbki near the railway track – up to 442 mg/kg. The maximum concentration of mineral oils (3,050 mg/kg) was discovered in lawn soil near Żwirki i Wigury Street. In forest soils of Wesoła the concentration of mineral oils is up to 2,350 mg/kg.

Geometric mean values show that the highest concentrations of mineral oils occur in industrial (25 mg/kg) and tall building areas (28 mg/kg), and the lowest ones in rural areas (11 mg/kg).

Sediments: <u>Pl. 77, Tab. 11</u>

The concentration of mineral oils in the sediments varies between <10 and 7,940 mg/kg. High levels, >3,000 mg/kg, are recorded only in four sediment samples, and very high values, >5,000 mg/kg, in three samples. The greatest concentrations of mineral oils were detected in the sediments of the Rów Miedzeszyński ditch in the Borkowo area (7,940 mg/kg), Rów Opaczewski ditch in Raszyn (6,280 mg/kg), Kanał Bródnowski canal in Białołęka (3,040 mg/kg), and in a ditch flowing into the Czarna River (6,820 mg/kg).

The pattern of contamination by mineral oils in the sediments demonstrates considerable variability. Contamination is found in the sediments of the Kanał Henrykowski (950 mg/kg) and Kanał Bródnowski (337 mg/kg) canals, Jeziorka (149 mg/kg) and Wilanówka (289 mg/kg) rivers, and in the Utrata (56 mg/kg) and Łasica (93 mg/kg) drainage basins. Much lower levels are observed in the sediments of the Świder (12 mg/kg) and Długa (23 mg/kg) drainage basins.

The elevated concentrations of mineral oils in the sediments are caused primarily by the emission of these compounds by vehicles, as well as by the discharge of storm wastewater and household and municipal sewage. Locally increased concentrations of mineral oils are the result of water transport, runoff from the area of garages and petrol stations (spills of oils and lubricants) and from the sites where wood is impregnated and mineral oils are used (strengthening of river embankments).

PCB POLYCHLORINATED BIPHENYLS

Soils: <u>Pl. 78</u>, <u>Tab. 8</u>

Polychlorinated biphenyls are exclusively anthropogenic contaminants in the environment. In the analysed soils, PCBs occur at low concentrations, most commonly $<3.4 \mu g/kg$, although the presence of at least one of the PCB congeners was detected in 71.10% of the samples.

The largest PCB anomaly is located in the right bank of the Vistula River, extending from Gocław to Żerań and Ząbki. The maximum concentrations of the sum of PCBs are recorded in the Blizne residential area near Hubala-Dobrzańskiego Street (221.8 µg/kg) and in Gocław (180.6 µg/kg).

Smaller areas of soils contaminated by PCB compounds (>6 μ g/kg) comprise part of the districts of Wola, Ochota and Anin. Local anomalies are also found elsewhere in the city.

Outside of Warsaw, PCB anomalies occur in Piaseczno and Kobyłka.

Contamination by PCB compounds was found in soils of different use types. However, higher average PCB concentrations (geometric means) are characteristic of soils from industrial (1.6 μ g/kg) and urban areas (1.2 μ g/kg) as compared to rural areas (<0.7 μ g/kg). For comparison, worth quoting are the research results from London, wherein soils contain up to 750 μ g/kg PCB, 22 μ g/kg on average (Vane *et al.*, 2010).

The presence of PCBs in the soils of Warsaw and its surroundings is primarily the result of their atmospheric deposition from local sources – the burning of coal and municipal and hospital waste.

The contamination of soils by PCBs can also originate from uncontrolled leaks from stationary transformers and trains (Bentum *et al.*, 2012; Wiłkomirski *et al.*, 2012; Vane *et al.*, 2014), leaks at sites of their production and storage (Kalinovich *et al.*, 2008; Danielovič *et al.*, 2014), and due to their use in construction sealants (Herrick *et al.*, 2007).

Sediments: Pl. 78, Tab. 9

The concentration of PCBs in the sediments ranges from <0.7 to $118.7 \mu g/kg$. The presence of at least one of the PCB congeners was detected in 61.75% of the analysed sediments.

Concentrations lower than 20 µg/kg are found in 98.50% of the samples. Concentrations higher than 60 µg/kg (TEC value) are recorded only at two sites: in the sediments of the Stara Wisła oxbow lake in Gocław (118.7 µg/kg) and in the Kanał Zagoździański canal west of Falenica (63.3 µg/kg).

Elevated concentrations of PCBs were measured in the sediments of the Rów Opaczewski ditch (4.1 μg/kg), Wilanówka (4.1 μg/kg), Raszynka (3.4 μg/kg) and Kanał Żerański canal (3.0 μg/kg).

Sediments of the watercourses in the Utrata, Łasica and Jeziorka drainage basins are characterised by the more frequent occurrence of increased PCB concentrations compared to the sediments in the Świder, Długa and Czarna drainage basins.

The lowest concentrations of polychlorinated biphenyls are found in sandy sediments (<0.7 μ g/kg), while the highest ones in organic slurry (2.0 μ g/kg).

PAHS POLYCYCLIC AROMATIC HYDROCARBONS

Soils: Pl. 79, Tab. 10

The concentrations of PAHs in soils of the study area range from <41 to 77,143 μ g/kg (median 818 μ g/kg).

Most of the soil types in the left-bank side of Warsaw and much of them in the right-bank districts are characterised by elevated or high PAH concentrations (>2,110 μ g/kg).

Very high PAH concentrations were found near the railway track in Wola (47,451–77,143 μ g/kg), in soils that are also contaminated by mineral oils, near the intersection of Okopowa and Dzielna streets (23,170 μ g/kg), and in Redutowa Street (21,042 μ g/kg). Soils in the vicinity of Jeziorko Wilanowskie lake contain up to 53,190 μ g/kg PAH, in Żwirki i Wigury Street – up to 23,288 μ g/kg, and near the Włochy railway station – up to 20,784 μ g/kg.

In some industrial and post-industrial areas of Praga Północ the PAH concentrations in soils reach a level of 38,775 µg/kg.

Outside of Warsaw, high PAH concentrations were found in Łomianki (up to 40,769 μ g/kg), Babice (up to 31,980 μ g/kg) and Marki (up to 17,162 μ g/kg).

PAH concentrations lower than 1,000 μ g/kg were detected in 56.79% of the samples, while the concentrations of 1–250 μ g/kg – in 43.20%.

As with mineral oils, very high concentrations of PAHs are recorded in soils of different use types. The highest values were measured in anthropogenic soils of built-up and industrial areas, while the lowest ones in rural areas.

The average concentration of PAHs in agricultural soils of Poland is 395 μ g/kg (Maliszewska-Kordybach *et al.*, 2008), and in soils of industrial areas (near power plants, copper and aluminium smelters, coking plants and old gasworks) it may attain up to several tens of thousand μ g/kg (Wcisło, 1998; Lis *et al.*, 1999; Bojakowska, 2005).

The concentrations of PAHs in soils of the area of Warsaw are higher than in soils in Glasgow, but similar to those in Valasske Mezirici in the Czech Republic and in London (Morillo *et al.*, 2007; Placha *et al.*, 2009; Vane *et al.*, 2014).

PAHs in soils of urban areas are of natural and anthropogenic origin. In soils of the study area they commonly come from the combustion of liquid fuels in car and aircraft engines, and from leaks while transported and stored.

Sediments: Pl. 79, Tab. 11

In the sediments, PAH concentrations below 1,610 μ g/kg (TEC value) were characteristic of 76.70% of the samples, while at six localities the measured concentrations were higher than the PEC (Probable Effect Concentration) value (22,800 μ g/kg).

The maximum concentration of PAHs (33,158 µg/kg) was detected in the sediments of a pond in Józefów. The contamination was also found in the Kanał Królewski canal (in the Czarna River drainage basin) in a post-industrial area (29,085 µg/kg), a small pond in the Jeziorka drainage basin north of the village of Opacz (25,493 µg/kg), Staw Raszyński pond (24,448 µg/kg), Rów Natoliński ditch (24,973 µg/kg) and Kanał Czerniakowski canal in Ujazdów (23,826 µg/kg).

The greatest PAH concentrations are typical of sediments rich in organic matter. The mean geometric concentration in organic slurry is 1,753 μ g/kg, in muddy sediments 898 μ g/kg, and in sandy sediments 234 μ g/kg.

The main reason for the elevated concentrations of PAHs is the emission of these compounds due to coal burning by households and power plants, as well as combustion of fuels in car and aircraft engines.

SUMMARY

Soils. The attempt to assess the summary contamination of soils was undertaken to draw attention to the areas that should be subjected to remediation, after having been additionally studied. The sampling density should be appropriate for such actions (detailed scales). Accumulation of certain elements in soils, even in relatively small amounts, can cause both damage to the plants that receive nutrients, and diseases in humans and animals due to absorption of dust particles through their digestive and respiratory systems.

Analysis of grain-size composition, pH and concentrations of chemical elements and compounds in soils from two depth ranges has allowed to estimate the influence of natural (geological) and/or anthropogenic factors on their accumulation in the area of Warsaw and its surroundings.

The main natural factors include: the type and chemical composition of parent rocks, chemical properties of individual elements, topography and hydrogeological conditions of the area. The most important anthropogenic factors leading to soil contamination include industrial and communication emissions, storage and incineration of waste materials, and sewage discharge.

Throughout the whole map sheet area the chemical composition of soils depends primarily on the lithology of parent rocks and is clearly different in its eastern and western parts.

In the eastern and northern area, sandy soils predominate. They have developed either on sands and gravels of the fluvial over-flood terraces and the Warsaw-Błonie cut-fill terrace of the Vistula River, or on aeolian and fluvial sands. A considerable proportion of sandy soils are overgrown by forest communities. The soils are usually characterised by acidic pH and by concentrations of most determined constituents close to the regional geochemical background.

In wetland areas, covered with peaty soils, natural enrichment of soils with organic carbon and sulphur is observed. This soil group includes forest soils on the border between the Wawer district and

Wiązowna municipality and between Wawer and Góraszka (Biały Ług marsh), in Wesoła (Macierowe Bagno), and locally in forest areas of Bemowo.

Meadow soils in Białołęka, Targówek, Wawer and the Długa River valley (near Okuniew and Ossów), which developed on peats and alluvial muds rich in organic matter, are naturally enriched in arsenic, iron, manganese, phosphorus and sulphur.

A special soil group is represented by alluvial muds that developed mainly from Holocene alluvial sediments of the flood terraces in the Vistula River valley. They are characterised by increased concentrations of many chemical elements. Their pH is neutral in the topsoil and alkaline in the subsoil. Enrichment of alluvial soils in aluminum, barium, calcium, cobalt, chromium, iron, magnesium, manganese, nickel, sulphur, strontium, vanadium and zinc is natural. To a small extent they are contaminated by anthropogenic arsenic and cadmium.

The western and south-western parts of the map sheet area are dominated by loamy and loamysandy soils that developed on glacial tills, glaciofluvial and eluvial sediments, and alluvial muds. Most of these soils (at both soil depth ranges) are remarkably enriched in aluminium, arsenic, calcium, cobalt, chromium, magnesium, manganese, nickel, strontium, titanium and vanadium, derived from the parent rocks. The greatest amounts of these elements are accumulated in alkaline soils that formed from loess-like weathering and aeolian covers stretching in a wide belt from the western peripheries of Warsaw toward Ożarów Mazowiecki.

In industrial and urbanized areas (Warsaw and smaller towns) there are anthropogenic anomalies of barium, cadmium, copper, chromium, mercury, lead and zinc in the topsoil layer. The main contamination sources are fallouts of particulate matter emitted by industry and energy sectors, transportation by rail and road, and landfill leachates.

A significant role in soil contamination in Warsaw was played by numerous industrial plants, no longer existing, that were active at a time when environmental protection was in its infancy. In the topsoil, copper, mercury, lead and zinc occur at the greatest amounts in Śródmieście, Wola and on the border of Praga Północ, Praga Południe and Targówek (Kamionek, Targówek Fabryczny, Nowa and Stara Praga). In the subsoil the extents of anomalous concentrations of these metals are very similar, which indicates an easy migration of the contaminants into the soil profile.

In industrial areas and near communication routes occur local anthropogenic anomalies. In the topsoil, the most significant of them include the following:

- arsenic, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, nickel, lead, titanium, vanadium and zinc in the premises of ArcelorMittal steelworks,
- barium, calcium, cobalt, copper, strontium, titanium and zinc near the Polfa Tarchomin pharmaceutical company,
- barium, cadmium, cobalt, chromium, lead, strontium, titanium and zinc in the industrial and storage area of the former Służewiec Przemysłowy,

- barium, magnesium, strontium and vanadium near the furnace waste landfills of the thermal power plant in Żerań and Zawady,
- calcium, strontium, sulphur and titanium in the premises of the former Warszawa cement works.

In the subsoil the following anomalies have been detected:

- chromium and nickel in the Żerań industrial area (near the former FSO automotive factory and thermal power plant),
- arsenic, iron, manganese, phosphorus and sulphur in the Henrykowski Park in Tarchomin.

The topsoil of industrial and urbanized areas are locally contaminated by mineral oils and PAHs from car engines as well as from storage, transportation and liquid fuel processing sites.

A characteristic feature of the soils of Warsaw is alkaline pH mainly due to the fallout of particulate matter emitted by industrial plants. The much wider extent of strongly alkaline soils at a depth of 0.8–1.0 m compared to the topsoil is related both to the migration of manganese and calcium compounds into the soil profile and to the occurrence of anthropogenic embankments that contain much rubble (in the city centre of Warsaw).

Local soil contaminations occur in parks and allotment gardens. These areas are conspicuous by the highest concentrations of barium, chromium, copper, iron, mercury, nickel, phosphorus, lead, sulphur, zinc and organochlorine pesticides. Their presence in soils is a result of both agrotechnical measures (fertilization and use of plant protection products) and the fallout of particulate matter from industrial and communication sources.

Particularly noteworthy is soil contamination by DDT in parks, allotment gardens and cultivated fields. The most extensive anomaly of the concentrations of the sum of DDT is observed in Praga Południe (in the Skaryszewski Park and nearby allotment gardens). In arable field near Łomianki, Henryków and Marki and in the Vistula River valley, p,p'DDT predominates over its metabolites in concentration, indicating that the compounds were introduced into the soil relatively recently.

Soil classification indicating proper soil use. The topsoil was analysed for the assessment of the degree of contamination by metals and organic compounds, categorizing them into soil use groups A, B and C, based on permissible concentrations (Rozporządzenie..., 2002). For the summary classification, the principle of categorizing the soil into particular group was used if the concentration of at least one element/compound was greater than the lower permissible value for the group.

In terms of the concentration of metals the result of categorization is pretty optimistic. As much as 72.47% of the analysed soils have been classified into group A, 20.11% into group B, and 6.77% into group C. Exceedances of permissible concentrations of metals for group C (mainly zinc, copper and lead) were found in 0.65% of soils (<u>Tab. 12</u>). Soils classified into groups A or B comply with the requirement for multifunctional use and are mostly used properly. There is a considerable proportion of soils categorized into group A, even in urbanized areas (<u>Pl. 80</u>). Soils of the forest areas (including the Kampinos National Park) mostly meet the standards specified for protected areas. Soils that are

included into group C, and those showing exceeded permissible concentrations of metals for this group, occur locally in industrialized districts (currently or in the past) and in densely built-up areas.

Much less optimistic is the result of categorization of the topsoil layer as regards the concentration of organic compounds. Only 16.74% of the analysed soils have been categorised into group A, 22.22% into group B, and 57.04% into group C (<u>Tab. 13</u>). Exceedances of permissible concentrations of organic compounds for group C have been found in 4.05% of soils (predominantly due to the concentration of the sum of DDT compounds and its metabolites). Soils that are classified into group C (or those showing exceeded permissible concentrations specified for this group) occur in areas with dense development, industrial areas or near communication routes. Point contaminations are found in low-rise and sparsely built-up urban areas, urban lawns, arable fields and forests. In many cases the high concentration of organic compounds (DDT, PAHs and mineral oils) inclines to categorize the soil into group C, although it meets the standards specified for groups A or B in terms of concentrations of metals.

Sediments. Bottom sediments of the watercourses and reservoirs in the area of Warsaw and its surroundings are characterised by highly variable chemical composition dependent on both bedrock lithology and anthropogenic factors.

Sediments of the reservoirs and watercourses draining the flood terraces of the Vistula River (including the Wilanówka, which is the major tributary) are conspicuous by considerable contents of aluminium, barium, calcium, cobalt, iron, magnesium, manganese, nickel, phosphorus, sulphur and vanadium – natural elements abundant in alluvial sediments. Barium and phosphorus concentrations in these sediments are also a result of human impact.

Sediments of the Jeziorka and Wilanówka (which were a single river until the mid-1950s) were contaminated anthropogenically by silver, barium, cadmium, lead and zinc. Contaminants in these sediments originate from household and municipal sewage discharged from the area of Konstancin and Jeziorna and from the Piaseczno sewage treatment plant, as well as industrial wastewater from the Thomson electronic factory (formerly Polkolor) and the paper mill that operated for over 250 years.

In the western peripheries of Warsaw, covered with weathering mantles and aeolian (partly loesslike) sediments, the sediments of watercourses and reservoirs are characterised by naturally elevated concentrations of calcium and magnesium.

Anthropogenic origin is attributed to the anomalous concentrations of the analysed constituents in the sediments of many watercourses and stagnant-water reservoirs, supplied by various types of industrial and household sewage.

Among strongly contaminated by many chemical elements (mainly in the past) are sediments of the Kanał Bródnowski Górny and Kanał Henrykowski canals. The Kanał Bródnowski Górny canal, which has received sewage from industrial plants of the Targówek Fabryczny industrial area since the mid-19th century until the present, is also under the influence of emissions from the Kawęczyn thermal power plant and the waste incineration plant. The Kanał Henrykowski canal received industrial

pharmaceutical wastewater from the Polfa Tarchomin company (with its 150-year history) untill the mid-1970s, and probably from nearby located factories of plastics, cosmetics and food flavours.

Contamination by metals (silver, cadmium, chromium, copper, titanium and zinc) of the sediments in the Potok Służewiecki stream is probably the effect of electronics and electrical engineering factories in the former Służewiec Przemysłowy industrial area, which operated over several tens of years. Furthermore, the sediments are being still contaminated by rainwater from the Chopin Airport treatment plant and untreated rainwater from Ursynów, Mokotów and Wilanów. To the Potok Służewiecki stream are also discharged contaminants from the developing area of Miasteczko Wilanów.

Elevated concentrations of arsenic, barium, cobalt, iron, manganese, phosphorus and strontium in the sediments of the Rów z Lawendowa ditch in Białołęka may be partly natural (caused by drainage of meadow soils in wetland areas), and partly originate from sewage and runoff from developing residential areas.

The sediments of the Rów Opaczewski ditch, with anomalous concentrations of chromium and zinc (and the maximum copper concentration recorded), were likely contaminated by surface runoff from railway tracks of the WKD Warsaw Commuter Railway and by rainwater from the Włochy district.

The contents of chemical elements in the sediments of watercourses draining rural areas (Świder, Długa and Czarna drainage basins) are close to the geochemical baseline values.

Slightly contaminated sediments are found in the Vistula River. They contain elevated amounts of magnesium, calcium, cadmium, cobalt, manganese and strontium.

Most of the sediments commonly contain DDT compounds and their metabolites as a result of their intense use on arable fields, in forests, parks and allotment gardens in the past. As regards DDT, the most strongly contaminated sediments are found in the Łasica, Wilanówka and Jeziorka drainage basins (which are also contaminated by PCBs, PAHs and mineral oils) and in the Raszynka River drainage basin.

Waters. The chemical composition of surface waters in the study area is controlled by both the bedrock chemistry and the land use within the drainage basin.

Most of the waters (79.8%) show slightly alkaline pH. Acidic, slightly acidic and neutral waters occur mainly in the southern part of the study area (Wilanów, Ursynów, Konstancin-Jeziorna and Raszyn) and in forested areas (Kampinos Forest, forests near Rembertów and Otwock).

Electrolytic conductivity values point to an insignificant degree of water salinity and contamination (87% of the waters meet the standards for water quality class I, while 9% fall into class II). The highest average electrolytic conductivity distinguishes the waters of the Łasica drainage basin.

The distribution of concentrations of the analysed chemical elements shows regional variability. In the watercourses and reservoirs of the western part of the Vistula drainage basin, where the bedrock includes deposits rich in clay minerals, the waters are enriched in boron, uranium and vanadium. To the east of the Vistula River (in the Świder, Czarna and Nowe Ujście canal drainage basins) the waters contain much aluminium and iron, including those originating from natural sources.

High electrolytic conductivity values and elevated concentrations of many elements are characteristic of the waters of ponds in abandoned clay pits, and of moats of the 19th-century forts in the left-bank side of Warsaw. They are usually enriched in boron, barium, calcium, chlorine, hydrocarbonates, lithium, magnesium, sodium, sulphates, silica, strontium and uranium. Especially highly contaminated waters are found in the Bernardyńska Woda moat and in the moats of the Piłsudski and Czerniakowski forts in Mokotów. Jeziorzec pond in Bemowo is contaminated by sodium, chlorine, molybdenum and antimony.

In the left-bank side of the Vistula drainage basin, considerably contaminated waters occur locally in minor ditches and canals. The waters of a ditch in Paluch contain elevated concentrations of calcium, potassium, lithium, hydrocarbonates, magnesium, sulphates, silica, strontium and uranium. Considerable concentrations of bromine, lithium, potassium, hydrocarbonates, manganese and silica were found in the waters of the trench surrounding the Radiowo Landfill.

In the northern part of Warsaw, elevated concentrations of many constituents are recorded in the waters of the Rudawka River and Łacha Potocka oxbow lake, as well as of the tributaries of the Lipkowska Woda near the ArcelorMittal steelworks and the Wólka Węglowa environs. The waters of the Kanał Młociński canal are marked by the maximum concentration of vanadium and high contents of arsenic, antimony and thallium.

The greatest concentrations of copper, as in the case of sediments, are characteristic of the waters of the Rów Opaczewski ditch.

In the right-bank side of Warsaw, considerable concentrations of some constituents are recorded in the waters of a number of canals. The waters of the Kanał Henrykowski canal (supposed to be contaminated predominantly by industrial sewage) contain high amounts of arsenic, barium, bromine, calcium, cadmium, chlorine, cobalt, copper, fluorine, hydrocarbonates, manganese, molybdenum, sodium, ammonium ions, nickel, sulphates, antimony, silica, strontium, uranium, vanadium and zinc. The waters of the Kanał Bródnowski Górny canal show elevated concentrations manganese, molybdenum, nickel, antimony and strontium, which come from emissions of the Kawęczyn thermal power plant and the waste incineration plant. Contamination of the waters of the Magenta canal in Rembertów, resulting from the wastewater discharge from the sewage treatment plant, is manifested by high concentrations of aluminium, cobalt, nitrates, phosphorus, vanadium and ammonium ions.

To the west of Warsaw, increased concentrations of chemical elements distinguish the tributaries of the Struga and Lipkowska Woda (in the Łasica drainage basin). The waters of a tributary of the Struga near Bemowo contain much copper, potassium, lithium, magnesium, molybdenum, sodium, uranium, zinc, chlorine, fluorine and hydrocarbonates.

The waters of the Żbikówka River (previously known as the Konotopa canal) are contaminated by sewage from industrial plants, storm sewer systems in Ursus, Piastów and Pruszków, and surface

runoff from the A2 Motorway. They contain considerable amounts of cadmium, magnesium, molybdenum, nickel, nitrates, sulphates, uranium, vanadium and zinc.

The waters of the southern and western peripheries of Warsaw (agricultural and post-agricultural areas) in the Utrata, Jeziorka and Łasica drainage basins are contaminated by nitrates and phosphorus.

The waters of the Vistula River contain much copper, lithium and strontium. They show elevated concentrations of bromine, manganese, nickel, lead, sodium and chlorine, and are also significantly contaminated by thallium. The sources of the contamination are probably distant discharges of mine waters and sewage of industrial plants in the upper part of the Vistula drainage basin (mainly in Upper Silesia).

The vast majority of the surveyed waters meet the standards for water quality class I or class II in terms of the concentrations of aluminum, organic carbon, calcium, chlorine, copper, magnesium, ammonium ions, phosphorus and sulphates and as regards the COD index. And all the of waters belong to water quality class I in terms of the concentrations of arsenic, barium, boron, chromium, cobalt, fluorine, molybdenum, thallium, vanadium and zinc.

REFERENCES

- AKPAN G.U., UDOH B.T., 2013 Evaluation of some properties of soils affected by diesel oil pollution in Uyo, Niger Delta Area, Nigeria. *Journal of Biology, Agriculture and Healthcare*, **3**, 8.
- ALVES C., GONÇALVES C., EVTYUGINAM., PIOC., MIRANTEF., PUXBAUMH., 2010 Particulate organic compounds emitted from experimental wildland fires in a Mediterranean ecosystem. *Atmospheric Environment*, **44**,23: 2750.
- BARANIECKA M.D., 1975 Szczegółowa Mapa Geologiczna Polski 1:50 000, ark. Otwock (561). Inst. Geol., Warszawa.
- BARANIECKA M.D., 1976 Objaśnienia do Szczegółowej Mapy Geologicznej Polski 1:50 000, ark. Otwock (561). Inst. Geol., Warszawa.
- BARBUSIŃSKI K., NOCOŃ W., NOCOŃ K., KERNERT J., 2012 Rola zawiesin w transporcie metali ciężkich w wodach powierzchniowych na przykładzie Kłodnicy. *Ochr. Środ.*, **34**, 2: 33–39.
- BATTA Y., ZATAR N., SADEQ N., 2006 Detection of endosulfan residues in the soil of Western Jordan Valley. *Jordan J. Agricult. Sci.*, **2**, 1: 57–64.
- BAZA danych. Osady, GIOŚ. Dane za lata 2010–2013.
- BENTUM J.K., DODOO D.K., KWAKYE P.K., 2012 Accumulation of metals and polychlorinated biphenyls (PCBs) in soils around electric transformers in the Central Region of Ghana. *Advances in Appl. Sci. Res.*, 3, 2: 634–643.
- BOJAKOWSKA I., 1994 Wpływ czynnika antropogenicznego na procesy geochemiczne w powierzchniowych warstwach litosfery. *Instr. Met. Bad. Geol.*, **53**.
- BOJAKOWSKA I., 2005 PAH spectrum in soils of industrial areas. Pol. Geol. Inst. Sp. Papers, 17: 9-16.
- BOJAKOWSKA I., LECH D., JAROSZYŃSKA J., 2012 Metale ciężkie w osadach Potoku Służewieckiego w Warszawie (Polska). Górnictwo i Geologia, 7, 2: 71–83.
- BOJAKOWSKA I., LECH D., PASIECZNA A., 2007 Arsen i antymon w węglach kamiennych i brunatnych ze złóż polskich. *Ochr. Środ. Zas. Nat.*, **31**: 522–527.
- BOJAKOWSKA I., SOKOŁOWSKA G., 2001 Rtęć w kopalinach wydobywanych w Polsce jako potencjalne źródło zanieczyszczenia środowiska. *Biul. Państw. Inst. Geol.*, 349: 5–54.
- CAPACCIONI B., MARTINI M., MANGANI F., 1995 Light hydrocarbons in hydrothermal and magmatic fumaroles: hints of catalytic and thermal reactions. *Bull. Volcanol.*, **56**, 8: 593–600.
- CZARNOWSKA K., GWOREK B., 1991 Stan zanieczyszczenia cynkiem, ołowiem i miedzią gleb Warszawy. *Rocz. Glebozn.*, 42, 1/2: 49–56.

- CZARNOWSKA K., GWOREK B., KOZANECKA T., LATUSZEK B., SZAFRAŃSKA E., 1983 Heavy metals in soils as indicator of urbanization. *Pol. Ecol. Stud.*, **9**: 63–70.
- CZARNOWSKA K., GWOREK B., MAJCHRZAK B., 1992 Spatial distribution of lead, zinc, cooper and manganese in Pabianice soils. *Ann. Warsaw Agricult. Univ. SGGW Agricult.*, **24**: 27–32.
- CZARNOWSKA K., WALCZAK J., 1988 Distribution of zinc, lead and manganese in soils of Łódź city. *Rocz. Glebozn.*, **39**, 1: 19–27.
- DANE o Warszawie. Urząd Statystyczny w Warszawie. Internet: http://warszawa.stat.gov.pl/dane-o-wojewodztwie/stolica-wojewodztwa/
- DANE powiatowe województwo mazowieckie. Podregiony, powiaty, gminy, 2014. Urząd Statystyczny w Warszawie. Internet: http://warszawa.stat.gov.pl/dane-o-wojewodztwie/powiaty
- DANIELOVIČ I., HECL J., DANILOVIČ M., 2014 Soil contamination by PCBs on a regional scale: the case of Strážske, Slovakia. *Pol. J. Environ. Stud.*, 23, 5: 1547–1554.
- DE VOS W., TARVAINEN T. (red.), 2006 Geochemical atlas of Europe. Part II. Geological Survey of Finland, Espoo.
- DMUCHOWSKI W., GWOREK B., GOZDOWSKI D., BACZEWSKA A., MACIASZEK D., 2011 Ocena zmian zanieczyszczenia powietrza ołowiem, cynkiem i chromem w rejonie huty stali w Warszawie w latach 1993–2008. Przem. Chem., 90, 2: 218–221.
- DOJLIDO J., 1995 Chemia wód powierzchniowych. Wyd. Ekonomia i Środowisko, Białystok.
- DYREKTYWA Parlamentu Europejskiego i Rady 2013/39/UE z dnia 12 sierpnia 2013 r. zmieniająca dyrektywy 2000/60/WE i 2008/105/WE w zakresie substancji priorytetowych w dziedzinie polityki wodnej. Dziennik Urzędowy Unii Europejskiej, 24.8.2013.
- ENCYKLOPEDIA Warszawy, 1975. PWN, Warszawa.
- EUROPEJSKA SIEĆ NATURA 2000, 2015. Internet: http://zielona.um.warszawa.pl/tereny-zielone/obszary-i-obiekty-chronione/europejska-siec-natura-2000
- FRANKOWSKI Z., BAŻYŃSKI J., ZAWADZKI R., LEWKOWICZ M., SMAGAŁA S., WYSOKIŃSKI L., MAJER E., ŁUKASIK S., FILIPOWICZ A., SOBIECH J., 2000 — Atlas geologiczno-inżynierski Warszawy. NAG PIG-PIB, Warszawa.
- GRYNKIEWICZ M., POLKOWSKA Z., GÓRECKI T., NAMIEŚNIK J., 2003—Pesticides in precipitation from an urban region in Poland (Gdańsk–Sopot–Gdynia Tricity) between 1998 and 2000. *Water Air Soil Poll.*, 149, 1/4: 3–16.
- HARVEY R., 1998 Environmental chemistry of PAHs. W: PAHs and related compounds. Springer-Verlag Berlin Heidelberg.
- HERRICK R.F., LEFKOWITZ D.J., WEYMOUTH G.A., 2007 Soil contamination from PCB-containing buildings. *Environ. Health Perspect.*, **115**, 2: 173–175.
- HISTORIA zakładów Polfa Tarchomin S.A., 2015. Internet: http://www.polfa-tarchomin.com.pl/index.php/ofirmie/historia/
- HOLOUBEK I., DUSEK L., SÁNKA M., HOFMAN J., CUPR P., JARKOVSKÝ J., ZBÍRAL J., KLÁNOVÁ J., 2009 — Soil burdens of persistent organic pollutants — their levels, fate and risk. Part I. Variation of concentration ranges according to different soil uses and locations. *Environ. Poll.*, 157, 12: 3207–3217.
- HOWSAM M., JONES K., 1998 Sources of PAHs in the environment. *W*: PAHs and related compounds: 137–174. Springer-Verlag Berlin Heidelberg.
- JIA H., LIU L., SUN Y., SUN B., WANG D., SU Y., KANNAN K., LI Y.F., 2010 Monitoring and modeling endosulfan in Chinese surface soil. *Environ. Sci. Technol.*, **44**, 24: 9279–9284.
- KABATA-PENDIAS A., MUKHERJEE A.B., 2007 Trace elements from soil to human. Springer, Berlin.
- KABATA-PENDIAS A., PENDIAS H., 1999 Biogeochemia pierwiastków śladowych. PWN, Warszawa.
- KABATA-PENDIAS A., PIOTROWSKA M., MOTOWICKA-TERELAK T., MALISZEWSKA-KORDYBACH B., FILIPIAK K., KRAKOWIAK A., PIETRUCH C., 1995 — Podstawy oceny chemicznego zanieczyszczenie gleb. Metale ciężkie, siarka i WWA. Bibl. Monit. Środ., Warszawa.
- KABATA-PENDIAS A., SZTEKE B., 2012 Pierwiastki śladowe w geo- i biosferze. IUNG-PIB, Puławy.
- KALINOVICH I., RUTTER A., POLAND J.S., CAIRNS G., ROWE R.K., 2008 Remediation of PCB contaminated soils in the Canadian Arctic: excavation and surface PRB technology. *Sci. Total Environ.*, 407: 53–66.
- KANNAN K., MARUYA K., TANABE S., 1997 Distribution and characterization of polychlorinated biphenyl congeners in soil and sediments from a superfund site contaminated with Aroclor 1268. *Environ. Sci. Technol.*, **31**, 5: 1483–1488.
- KLECZKOWSKI A.S., RÓŻKOWSKI A. (red.), 1997 Słownik hydrogeologiczny. TRIO, Warszawa.
- KONDRACKI J., 2009 Geografia regionalna Polski. Wyd. Nauk. PWN, Warszawa.

- KOSTRZ-SIKORA P., BOJAKOWSKA I., WOŁKOWICZ S., DOBEK P., LECH D., NARKIEWICZ W., 2015 — Anthropogenic sediments from facultative lagoons of the Konstancin-Jeziorna sewage treatment facility and their usability for soil recultivation. *Geol., Geoph. Environ.*, 41, 2: 177–185.
- KRASUCKI M., 2009 Katalog warszawskiego dziedzictwa postindustrialnego. Fundacja Heritas, Warszawa. Internet: http://www.fundacja-hereditas.pl/files/katalog_warszawa_1.pdf
- KRZYWICKI T., 2013 Skarpa Warszawska. W: Zrozumieć Ziemię. Konspekt lekcyjno-ćwiczeniowy: 140– 185. PIG-PIB, Warszawa.
- KUMAR B., MISHRA M., VERMA V.K., KUMAR S., SHARMA C.S., 2013 Distribution of dichlorodiphenyltrichloroethane and hexachlorocyclohexane in urban soils and risk assessment. J. Xenobiotics, 3.
- LIN T., HU Z., ZHANG G., LI X., XU W., TANG J., LI J., 2009 Levels and mass burden of DDTs in sediments from fishing harbors: the importance of DDT-containing antifouling paint to the coastal environment of China. *Environ. Sci. Technol.*, **43**, 21: 8033–8038.
- LIS J., 1992 Atlas geochemiczny Warszawy i okolic 1:100 000. Państw. Inst. Geol., Warszawa.
- LIS J., PASIECZNA A., 1995 Atlas geochemiczny Polski 1:2 500 000. Państw. Inst. Geol., Warszawa.
- LIS J., PASIECZNA A., 1998a Atlas geochemiczny aglomeracji szczecińskiej 1:200 000. Cz. I. Państw. Inst. Geol., Warszawa.
- LIS J., PASIECZNA A., 1998b Atlas geochemiczny aglomeracji łódzkiej 1:100 000. Cz. I. Państw. Inst. Geol., Warszawa.
- LIS J., PASIECZNA A., 2005 Atlas geochemiczny Poznania i okolic 1:100 000. Państw. Inst. Geol., Warszawa.
- LIS J., PASIECZNA A., BOJAKOWSKA I., GLIWICZ T., FRANKOWSKI Z., PASŁAWSKI P., POPIOŁEK E., SOKOŁOWSKA G., STRZELECKI R., WOŁKOWICZ S., 1999 Atlas geochemiczny legnickogłogowskiego okręgu miedziowego. Państw. Inst. Geol., Warszawa.
- MACDONALD D., INGERSOLL C., BERGER T., 2000 Development and evaluation of consensus-based sediment development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch. Environ. Contamin. Toxicol.*, **39**: 20–31.
- MALISZEWSKA-KORDYBACH B., SMRECZAK B., KLIMKOWICZ-PAWLAS A., 2014 Evaluation of the status of contamination of arable soils in Poland with DDT and HCH residues; national and regional scales. *Pol. J. Environ. Stud.*, **23**, 1: 139–148.
- MALISZEWSKA-KORDYBACH B., SMRECZAK B., KLIMKOWICZ-PAWLAS A., TERELAK H., 2008 Monitoring of the total content of polycyclic aromatic hydrocarbons (PAHs) in arable soils in Poland. *Chemosphere*, **73**, 8: 1284–1291.
- MONITORING jakości gleb i ziemi na terenie powiatu wołomińskiego, 2006. PIG-PIB, Warszawa.
- MONITORING rzek w latach 2010-2014, 2015. Internet: www.wios.warszawa.pl
- MORAWSKI W., 1979 Szczegółowa Mapa Geologiczna Polski 1:50 000, ark. Warszawa Zachód (523). Inst. Geol., Warszawa.
- MORAWSKI W., 1980 Objaśnienia do Szczegółowej Mapy Geologicznej Polski 1:50 000, ark. Warszawa Zachód (523). Inst. Geol., Warszawa.
- MORAWSKI W., 2008 Objaśnienia do Mapy Geologicznej Polski 1:200 000, ark. Warszawa Zachód. Państw. Inst. Geol., Warszawa.
- MORAWSKI W., 2011 Objaśnienia do Mapy Geologicznej Polski 1:200 000, ark. Warszawa Wschód. PIG-PIB, Warszawa.
- MORAWSKI W., NOWACKA M., 2007 Mapa Geologiczna Polski 1:200 000, ark. Warszawa Zachód. Państw. Inst. Geol., Warszawa.
- MORAWSKI W., PIELACH M., 2011 Mapa Geologiczna Polski 1:200 000, ark. Warszawa Wschód. PIG-PIB, Warszawa.
- MORILLO E., ROMERO A.S., MAQUEDA C., MADRID L., AJMONE-MARSAN F., GRCMAN H.C., DAVIDSON M.C., HURSTHOUSE A.H., VILLAVERDE J., 2007 Soil pollution by PAHs in urban soils: a comparison of three European cities. *J. Environ. Monit.*, **9**, 9: 1001–1008.
- NIEDZIELSKI P., SIEPAK M., SIEPAK J., 2015 Występowanie i zawartości arsenu, antymonu i selenu w wodach i innych elementach środowiska. Internet: http://old.ros.edu.pl/text/pp_2000_015.pdf.
- NOWAKOWSKI W., 2004 Metale ciężkie w środowisku przyrodniczym Warszawy w pracach profesor Krystyny Czarnowskiej. *Ochr. Środ. Zas. Nat.*, **27**: 71–85.
- OROS D.R., SIMONEIT B.R.T., 2001 Identification and emission factor of molecular tracers in organic aerosols from biomass burning. Part 2. Deciduous trees. *Appl. Geochem.*, **16**, 13: 1545.

- PANORAMA dzielnic Warszawy w 2013 roku. Urząd Statystyczny, 2014. Internet: http://warszawa.stat.gov.pl/publikacje-i-foldery/inne-opracowania/panorama-dzielnic-warszawy-w-2013r-,5,14.html
- PASIECZNA A., 2003 Atlas zanieczyszczeń gleb miejskich w Polsce. Państw. Inst. Geol., Warszawa.
- PASIECZNA A. (red.), 2010a Szczegółowa Mapa Górnego Śląska 1:25 000, ark. Imielin. Państw. Inst. Geol. PASIECZNA A. (red.), 2010b Szczegółowa Mapa Górnego Śląska 1:25 000, ark. Katowice. Państw. Inst.
- Geol., Warszawa.
- PASIECZNA A. (red.), 2010c Szczegółowa Mapa Górnego Śląska 1:25 000., ark. Mysłowice. Państw. Inst. Geol., Warszawa.
- PASIECZNA A., 2014 Ocena wpływu działalności przemysłowej na chemizm gleb w rejonie Jaworzna. *W*: Geochemia i geologia środowiska terenów uprzemysłowionych: 125–137. Gliwice.
- PATHAK H., BHATNAGAR K., JAROLI D.P., 2011 Physico-chemical properties of petroleum polluted soil collected from transport Nagar (Jaipur). *Indian J. Fundamemnt. Appl. Life Sci.*, **1**, 3: 84–89.
- PLACHÁ D., RACLAVSKÁ H., MATÝSEK D., RÜMMELI M.H., 2009 The polycyclic aromatic hydrocarbon concentrations in soils in the Region of Valasske Mezirici, the Czech Republic. *Geochem. Transactions*, 10: 12, doi:10.1186/1467-4866-10-12.
- PLAN gospodarkiodpadami dla m.st. Warszawy na lata 2008–2011 z uwzględnieniem lat 2012–2015. Warszawa, 2008.
- PORTAL informacyjny warszawskiej Pragi, 2015a Internet: http://www.twojapraga.pl/praga/fabryki/2425.html
- PORTAL informacyjny warszawskiej Pragi, 2015b Internet: http://www.twojapraga.pl/praga/fabryki/2955.html
- PRUSINKIEWICZ Z., KONYS L., KWIATKOWSKA A., 1994 Klasyfikacja uziarnienia gleb i problemy z nią związane. *Rocz. Glebozn.*, **45**, 3–4: 5–20.
- PRZEGLĄD Statystyczny Warszawy. Rok XXIV, nr 2. Urząd Statystyczny w Warszawie, Warszawa 2015. Internet: http://warszawa.stat.gov.pl/opracowania-biezace/komunikaty-i-biuletyny/inneopracowania/przeglad-statystyczny-warszawy-ii-kwartal-2015-r-,5,18.html
- RAMAMOORTHY S., RAMAMOORTHY S., 1997 Chlorinated organic compounds in the Environment: 125–233. Lewis Publishers: Boca Raton New York.
- RIFFALDI R., LEVI-MINZI R., CARDELLI R., PALUMBO S., SAVIOZZI A., 2006 Soil biological activities in monitoring the bioremediation of diesel oil-contaminated soil. *Water, Air, Soil Poll.*, **170**: 3–15.
- RAPORT Stan zanieczyszczenia osadów dennych rzek i jezior w 2013 roku. Etap II. Monitoring osadów dennych rzek i jezior w latach 2013–2015. PIG-PIB, Warszawa, 2014.
- ROCZNA ocena jakości powietrza w województwie mazowieckim. Raport za rok 2014. WIOŚ Warszawa 2015. I n t e r n e t : http://www.wios.warszawa.pl/pl/publikacje-wios/publikacje/1065,Roczna-Ocena-Jakosci-Powietrza-w-wojewodztwie-mazowieckim-Raport-za-rok-2014.html
- ROZPORZĄDZENIE Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi. Dz.U. 2002, nr 165, poz. 1359.
- ROZPORZĄDZENIE Ministra Środowiska z dnia 9 listopada 2011 r. w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych. Dz.U. 2011, nr 257, poz. 1545.
- ROZPORZĄDZENIE Ministra Środowiska z dnia 22 października 2014 r. w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych. Dz.U. 2014, poz. 1482.
- ROZPORZĄDZENIE Ministra Zdrowia z dnia 20 kwietnia 2010 r. zmieniające rozporządzenie w sprawie jakości wody przeznaczonej do spożycia przez ludzi. Dz.U. nr 72, poz. 466.
- RÓŻKOWSKA A., PTAK B., 1995a Bar w węglach kamiennych Górnego Śląska. Prz. Geol., 43, 3: 223–226.
- RÓŻKOWSKA A., PTAK B., 1995b Atlas geochemiczny złóż węgla kamiennego Górnośląskiego Zagłębia Węglowego. Państw. Inst. Geol., Warszawa.
- RUTKOWSKA-GURAK A., 2000 Miejski obszar przemysłowy jako środowisko lokalizacji firm (na przykładzie Służewca Przemysłowego). *W*: Monografie i opracowania, 472. Warszawa.
- SALMINEN R. (red.), 2005 Geochemical atlas of Europe. Part 1. Geological Survey of Finland, Espoo.
- SARNACKA Z., 1980a Szczegółowa Mapa Geologiczna Polski 1:50 000, ark. Warszawa Wschód (524). Inst. Geol. Warszawa.
- SARNACKA Z., 1980b Objaśnienia do Szczegółowej Mapy Geologicznej Polski 1:50 000, ark. Warszawa Wschód (524). Inst. Geol., Warszawa.

- SARNACKA Z., 1992 Stratygrafia osadów czwartorzędowych Warszawy i okolic. Pr. Państw. Inst. Geol., 138: 29s.
- SIVEY J.D., LEE C.M., 2009 Polychlorinated biphenyl contamination trends in Lake Hartwell, South Carolina (USA): sediment recovery profiles spanning two decades. *Chemosphere*, **66**, 10: 1821–1828.
- STAN środowiska w województwie mazowieckim w 2013 roku. WIOŚ Warszawa, 2014. Internet: http://www.wios.warszawa.pl/pl/publikacje-wios/publikacje/1033,Stan-srodowiska-w-wojewodztwie-mazowieckim-w-2013-roku.html
- SZUFLICKI M., MALON A., TYMIŃSKI M. (red.), 2014 Bilans zasobów złóż kopalin w Polsce wg stanu na 31 XII 2013 r. PIG-PIB, Warszawa.
- SUNITHA S., KRISHNAMURTHY V., MAHMOOD R., 2011 Analysis of Endosulfan residues in cultivated soils in Southern India. International Conference on Biotechnology and Environment Management IPCBEE 18: 110–114.
- TA 3001, 2012 Utkast til Bakgrunnsdokument for utarbeidelse av miljøkvalitetsstandarder og klassifisering av miljøgifter i vann, sediment og biota.
- TARGÓWEK FABRYCZNY, UTRATA Spacer śladami przemysłu i usług, 2015. Internet: http://warszawazacisze.blox.pl/2015/05/Targowek-Fabryczny-Utrata-spacer-sladami.html
- TOMASSI-MORAWIEC H., WOŁKOWICZ S., DOBEK P., DUSZA A., MARKOWSKI M., KOŁECKI T., 2007 — Wykonanie planu batymetrycznego, mapy miąższości osadów dennych oraz oceny stanu jakości wód i osadów dennych Potoku Służewieckiego i Jeziorka Wilanowskiego. NAG PIG-PIB, Warszawa.
- VANE CH., MA Y-J., CHEN S-J., MAI B-X., 2010 Increasing polybrominated diphenyl ether (PBDE) contamination in sediment cores from the inner Clyde Estuary, UK. *Environ. Geochem. Health*, **32**: 13–21.
- VANE C.H., KIM A.W., BERIRO D.J., CAVE M.R., KNIGHTS K., MOSS-HAYES V., NATHANAIL P.C., 2014 — Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. *Appl. Geochem.*, **51**: 303–314.
- WCISŁO E., 1998 Soil contamination with polycyclic aromatic hydrocarbons (PAHs) in Poland a review. *Pol. J. Environ. Stud.*, 7, 5: 267–272.
- WIŁKOMIRSKI B., GALERA H., SUDNIK-WÓJCIKOWSKA B., STASZEWSKI T., MALAWSKA M., 2012
 Railway tracks habitat conditions, contamination, floristic settlement. A review. *Environ. Nat. Resour. Res.*, 2, 1: 86–95.
- WITCZAK S., ADAMCZYK A., 1994 Katalog wybranych fizycznych i chemicznych wskaźników zanieczyszczeń wód podziemnych i metod ich oznaczania. T. 1. Bibl. Monit. Środ., Warszawa.
- YANG L., XIA X., LIU S., BU Q., 2010 Distribution and sources of DDTs in urban soils with six types of land use in Beijing, China. J. Hazard Mater., **174**, 1/3: 100–107.