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# MICROELEMENTS IN SOILS AND IN LEAVES OF SELECTED TREE SPECIES IN AN INDUSTRIAL URBAN AREA

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**Abstract**

Some adverse effects of human activities on the environment are observed with the development of civilization. Urban centers have a well-developed industrial infrastructure and transportation, hence the presence of numerous and diverse sources of environmental pollution.

The aim of the study was to determine the general content of Mn, Zn, Cu, Cr, and Ni in soils and in leaves of some tree species grown in Stalowa Wola, and to determine the trends in their spatial diversity.

Soil samples (from the layers 0-25 cm and 26-50 cm deep) were collected at sites located 0.5, 1, 2, 3, 4, 5 and 15 km (control) from the center point (the main gate of the Stalowa Wola Steelworks) to the east, west, north and south. Plant material (tree leaves) was collected from the vicinity of the soil sampling points.

The soils were characterized by strong acidity and the prevalence of the sand fraction: on average above 70% in both layers (0-25 cm and 26-50 cm). The content of microelements in soils from the town was within a wide range: 8÷1778 mg Mn $kg^{-1}$, 2.1÷1090 mg Zn $kg^{-1}$, 0.9÷61.5 mg Cu $kg^{-1}$, 3.8÷77.1 mg Cr $kg^{-1}$, 1.2÷56.5 mg Ni $kg^{-1}$. The arithmetic mean content of all the investigated metals in soils from Stalowa Wola was more than twice as high (more than 3-fold in the case of Cr and Ni) as the corresponding average values for the checkpoints. There were no clear patterns in the distribution of the analyzed elements depending on the depth. Except for one sample (the Zn content), no excess of heavy metals in the analyzed soils above the permissible levels was recorded. However, according to the IUNG criteria, only 50% of soil samples were characterized by the natural content of heavy metals (0 degree of contamination).

Leaves of some tree species were analyzed. The highest accumulation of manganese, an average of 640 mg $kg^{-1}$ DM, was found in oak leaves, while the lowest, an average of 4.3 mg $kg^{-1}$ DM, occurred in leaves of black locust. Linden leaves were distinguished by the tendency to accumulate chromium (mean 12.3 mg $kg^{-1}$), while ash leaves had a particularly high zinc content (mean 98.0 mg $kg^{-1}$). Concentrations of the analyzed elements in oak tree leaves from the north-south transect did not present any regular trend in the spatial differentiation.

**Key words:** microelements, environmental contamination, urban environment.

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**MIKROELEMENTY W GLEBACH I LIŚCIACH WYBRANYCH GATUNKÓW DRZEW Z TERENU MIEJSKO-PRZEMYSŁOWEGO**

**Abstrakt**

Wraz z rozwojem cywilizacji obserwuje się nasilenie negatywnego wpływu działalności człowieka na środowisko. Ośrodki miejskie charakteryzują się rozwiniętą infrastrukturą przemysłową i komunikacyjną, a więc występowaniem licznych i różnorodnych źródeł zanieczyszczeń środowiska. Celem badań było określenie ogólnej zawartości Mn, Zn, Cu, Cr i Ni w glebie i liściach wybranych gatunków drzew z terenu miasta Stalowa Wola i ustalenie tendencji w ich przestrzennym zróżnicowaniu.

Próby glebowe (z głębokości 0-25 cm i 26-50 cm) pobierano w miejscach zlokalizowanych w odległości 0,5; 1; 2; 3; 4; 5 i 15 km (kontrola) od punktu centralnego (rejonu bramy głównej Huty Stalowa Wola) w kierunku wschodnim, zachodnim, północnym i południowym. W okolicy punktów poboru prób glebowych pobierano także próby materiału roślinnego – liście drzew. Ogólną zawartość badanych metali oznaczono metodą płomieniową AAS po uprzedniej mineralizacji mikrofalowej próbek glebowych w mieszaninie stężonych kwasów HCl i $HNO_3$ (3:1), a materiału roślinnego – w stężonym $HNO_3$ z dodatkiem 30% $H_2O_2$.

Badane gleby charakteryzowały się silnym zakwaszeniem oraz zdecydowaną przewagą frakcji piasku, średnio w przypadku każdej z badanych warstw (0-25 cm i 26-50 cm) powyżej 70%. Stwierdzono, że zawartość mikroelementów mieściła się w szerokim zakresie: 8÷1778 mg Mn $kg^{-1}$, 2,1÷1090 mg Zn $kg^{-1}$, 0,9÷61,5 mg Cu $kg^{-1}$, 3,8÷77,1 mg Cr $kg^{-1}$, 1,2÷56,5 mg Ni $kg^{-1}$. Średnia arytmetyczna zawartość wszystkich badanych metali w glebach z terenu miasta Stalowa Wola była ponad 2-krotnie (w przypadku Cr i Ni ponad 3-krotnie) wyższa, w porównaniu z kontrolą. Nie stwierdzono wyraźnych prawidłowości w rozmieszczeniu badanych pierwiastków w zależności od głębokości. Nie stwierdzono przekroczenia dopuszczalnej zawartości analizowanych metali ciężkich w badanych glebach (z wyjątkiem Zn w 1 próbie glebowej). Jednakże uwzględniając kryteria IUNG, jedynie w 50% badanych prób glebowych stwierdzono ich naturalną zawartość (0 stopień zanieczyszczenia). Wykazano, że spośród badanych liści niektórych gatunków drzew, liście dębu akumulowały najwięcej manganu – średnio 640 mg $kg^{-1}$ s.m., najmniej – liście robinii akacjowej, średnio 4,3 mg $kg^{-1}$ s.m. Liście lipy miały tendencję do kumulacji chromu (średnio 12,3 mg $kg^{-1}$), a liście jesionu zawierały szczególnie dużo cynku (średnio 98,0 mg $kg^{-1}$). Analizując zawartość badanych pierwiastków w liściach dębu z transektu północ-południe, nie stwierdzono jednoznacznej tendencji w przestrzennym zróżnicowaniu wyników.

**Słowa kluczowe:** mikroelementy, zanieczyszczenie środowiska, środowisko miejskie.

# INTRODUCTION

Some adverse effects of human activities on the environment are observed together with the development of civilization (PACYNA, PACYNA 2001, NORRA, STÜBEN 2003, GAN-LIN et al. 2005, WÓJCIKOWSKA-KAPUSTA, MAKUCH 2007, SZYNKOWSKA et al. 2009). The civilization growth is intrinsically linked to growing human populations in urban agglomerations. So far, urban areas and populations have shown an upward trend. According to the data of the Central Statistical Office (GUS 2011), nearly 61% of the total Polish population in 2009 lived in 897 cities and towns, which covered just 1,572,402 hectares of land, i.e. about 5% of Poland. Urban centers are particularly vulnerable to environmental contamination. They are characterized by well-developed industrial infrastructure and transportation, hence the presence of numerous and diverse sources of environmental pollution. Particularly large contribution to the soil pollution is attributed to mining, metallurgy, metal industry, fuel combustion and transportation (Kabata-Pendias, Pendias 1993, Pacyna, Pacyna 2001, Salvagio Manta et al. 2002, Szerszeń et al. 2004, Szynkowska et al. 2009, Wei , Yang 2010). Different types of activities generate different emission of heavy metals into the environment, e.g. road transport emits mainly Pb, Cd, Ni, Cu, Zn, fuel combustion is the major source of V, Ni, Hg, Se, Sn, and metallurgy is responsible for remarkable emission of As, Cd, Cu, and Zn (Karczewska 2003, Maciejewska, Ociepa 2003). Green areas (parks, gardens, woodlands, allotments and gardens) are that part of an urban landscape which, among various functions, plays the role of natural filters of contaminants, able to accumulate significant amounts of metallic elements (Karczewska 2003, Maciejewska, Ociepa 2003, Piczak et al. 2003, Baran et al. 2007, Strzyszcz, Rachwał 2010). An elevated content of metallic elements, including Cu, Zn, Ni, and Cr, has been recorded in many urban soils worldwide (Koval`chuk et al. 2002, Salvagio Manta et al. 2002, Norra, Stüben 2003, Gan-Lin et al. 2005, Norra et al. 2006, Krmčowa et al. 2009, Wei , Yang 2010).

The Subcarpathian Province (*województwo podkarpackie*) is a typical agricultural region. Stalowa Wola is one of the major urban and industrial centers in this part of Poland. The aim of the study was to determine the general content of Mn, Zn, Cu, Cr, and Ni in soils and leaves of some tree species grown in Stalowa Wola, and to determine the trends in their spatial diversity.

## MATERIAL AND METHODS

The analyzed area lies in Stalowa Wola (Figure 1), a town located in the Sandomierz Basin, on the edge of Sandomierz Forest. It covers an area of 8240 hectares and has a population of over 70,000. Geologically, the area lies within the Carpathian Foredeep filled with sediments of the Miocene Sea. Stalowa Wola is a relatively young town. Plans to create the Central Industrial District were approved in 1937, and the construction of the Southern Works started in 1938, in a village called Pławo. Some of the factory buildings and a residential area named Stalowa Wola were founded before the outbreak of World War Two. In 1945, Stalowa Wola became a chartered town and in 1948 the Southern Works located in the southern part of the town were named Huta Stalowa Wola. The steel and defense industry continued to develop throughout the early 1990s. Today, after the restructuring, the former steelworks function as several companies, mainly representing the steel and metal industry. The second largest facility is the Stalowa Wola Power Plant, localized in the eastern part of the town. The total number of

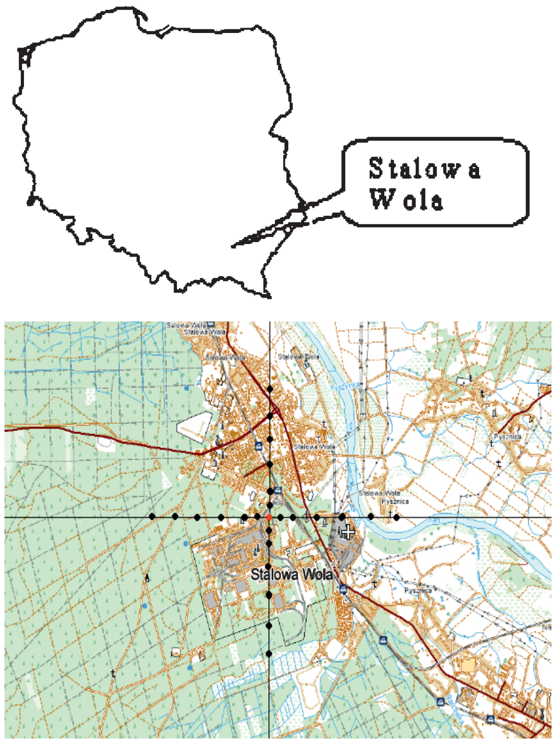


Fig. 1. Localization of the studied area (black dots indicate the sampling points)

business entities registered in the town is about 550. In the Subcarpathian Province, Stalowa Wola is a town with high emission of pollutants into the environment. Annual emissions of particulate pollutants in 2003-2005 was in the range of 523-714 million tons (*Strategy* ... 2007). In July 2009, soil samples were collected from the woodland area located at distances of 0.5, 1, 2, 3, 4, 5 km from the center point (the main gate of Huta Stalowa Wola) towards the east, west, north and south. Three soil samples were collected from each point (separately from the depth of 0-25 cm and 26-50 cm), which were subject to prepare a total of 50 average laboratory samples.

For comparison, soil samples were also collected at checkpoints (K) situated outside the town, in each of the geographical directions within 15 km from the center (8 samples).

Soil samples were air-dried, ground and passed through a sieve with 2 mm mesh. Tree leaf samples were air-dried and milled in a cutter mill. Analyses of soil material were carried out by means of the following methods (Ostrowska et al. 1991):

- grain size composition of soil – by the Bouyoucos-Casagrande aerometric method with modifications by Prószyński;

- soil reaction in 1 mol KCl dm$^{-3}$ solution ($pH_{KCl}$) – by potentiometry;
- hydrolytic acidity ($H_h$) – by the Kappen method;
- total exchangeable bases (TEB) and cation exchange capacity (CEC) – by the Kappen method;
- base saturation percentage (BS) – from the formula BS=TEB·100/CEC (%);
- organic carbon content in soil (Corg.) – by the Tiurin method;
- total contents of Mn, Zn, Cu, Cr, and Ni – by atomic absorption spectrophotometry (AAS, Hitachi Z-2000) in acetylene-air flame after microwaving the soil samples (Mars Xtraction, CEM) in a mixture of concentrated HCl and $HNO_3$ at the 3:1 ratio (Grzebisz et al. 2002).

The plant material (tree leaves) was collected within a radius of 100 m around the sampling points from the following tree species: maple (*Acer* sp.), oak (*Quercus* sp.), black locust (*Robinia pseudoacacia*), lofty ash (*Fraxinus excelsior*), and linden (*Tilia* sp.). About 1 kg FW was gathered. In order to determine the effect of winds on the pollution of the town with microelements, their content in oak leaves was analyzed along the north-south transect, chosen because of the prevailing southerly and west-southerly winds in the region. The content of microelements in the plant material was determined by the FAAS method after digestion in a microwave system in concentrated $HNO_3$ with 30% $H_2O_2$ (Buszewski et al. 2000).

The results were statistically processed applying the Excell and Statistica software. The means, medians and coefficients of variation were determined. Correlation analysis was performed for total trace elements and some properties of examined soil to determine the relationships between these parameters. Differences of the metal content in in soil between Stalowa Wola and the control area were demonstrated by Anova. The means for the different sites were separated by the Tukey`s test, using the significance level of $\alpha$=0,05.

## RESULTS AND DISCUSSION

Considering the particle size distribution, most of the soils were characterized by the predominant sand fraction: on average above 70% in each of the two layers. The average content of the clay fraction (below 0.002 mm) was 9%, in the 0-25 cm layer and 7% in the deeper layer. The soils contained an average of 18.2 g kg$^{-1}$ (0-25 cm layer) and 11.3 g kg$^{-1}$ (26-50 cm layer) of organic carbon. In terms of reaction, most of the soils were classified as acidic or very acidic (Table 1). They varied in the cation exchange capacity (5-48 cmol (+) kg$^{-1}$).

The arithmetic means of the content of the tested microelements in soils in Stalowa Wola can be put in the following order: Mn (283 mg kg$^{-1}$ from 0-25 cm depth and 305 mg kg$^{-1}$ from 26-50 cm depth), Zn (115.3 and 56.6 mg

Table1

General statistical parameters for properties of soil from Stalowa Wola

| Parameter | | $pH_{KCL}$ | $H_h$ | *TEB* | *CEC* | *BS* | Corg. | <0.002 mm |
|---|---|---|---|---|---|---|---|---|
| | | | (cmol(+) kg$^{-1}$) | | | | (g kg$^{-1}$) | (%) |
| City soils | | | | | | | | |
| Arithmetic mean | A | 5.20 | 3.77 | 18.5 | 22.3 | 81.0 | 18.2 | 9 |
| | B | 5.08 | 3.26 | 19.1 | 22.4 | 82.8 | 11.3 | 7 |
| Geometric mean | A | 5.06 | 2.58 | 14.4 | 19.4 | 74.1 | 13.7 | 5 |
| | B | 4.94 | 2.31 | 15.9 | 20.4 | 77.9 | 10.3 | 4 |
| Median | A | 5.30 | 2.00 | 15.8 | 17.6 | 84.5 | 17.5 | 5 |
| | B | 5.04 | 2.10 | 16.2 | 19.6 | 88.8 | 10.6 | 6 |
| Minimum | A | 2.89 | 0.50 | 0.5 | 5.0 | 4.3 | 0.5 | 1 |
| | B | 2.95 | 0.40 | 0.8 | 8.6 | 9.3 | 2.5 | 1 |
| Maximum | A | 7.59 | 11.20 | 42.5 | 48.0 | 97.4 | 36.3 | 30 |
| | B | 7.91 | 10.50 | 39.5 | 45.1 | 98.0 | 21.7 | 20 |
| Coefficient of variation (%) | *A* | 23.3 | 86.6 | 60.5 | 54.0 | 23.9 | 569.1 | 100.6 |
| | *B* | 24.4 | 79.1 | 52.8 | 45.6 | 22.9 | 395.6 | 73.7 |
| Control | | | | | | | | |
| Arithmetic mean | A | 4.00 | 4.45 | 21.8 | 26.2 | 82.1 | 18.4 | 10 |
| | B | 3.95 | 3.93 | 28.6 | 32.5 | 87.4 | 9.0 | 7 |
| Geometric mean | A | 3.99 | 4.41 | 20.9 | 25.5 | 82.0 | 16.8 | 9 |
| | B | 4.94 | 2.31 | 15.9 | 20.4 | 77.9 | 10.3 | 4 |
| Median | A | 4.02 | 4.15 | 18.6 | 23.5 | 80.9 | 14.3 | 10 |
| | B | 3.97 | 4.25 | 28.6 | 32.1 | 89.3 | 9.5 | 6 |
| Minimum | A | 3.78 | 4.00 | 16.8 | 20.8 | 77.4 | 11.9 | 4 |
| | B | 3.25 | 2.20 | 18.8 | 22.4 | 80.7 | 4.4 | 3 |
| Maximum | A | 4.17 | 5.50 | 33.1 | 37.1 | 89.2 | 33.2 | 16 |
| | B | 4.59 | 5.00 | 38.5 | 43.5 | 90.2 | 12.7 | 14 |
| Coefficient of variation (%) | *A* | 4.1 | 16.0 | 34.9 | 28.2 | 6.1 | 541.9 | 51.9 |
| | *B* | 14.0 | 31.1 | 36.9 | 34.5 | 5.2 | 382.7 | 66.0 |

A – soil from 0-25 cm depth
B – soil from 26-50 cm depth

kg$^{-1}$ respectively), Cr (27.6 and 24.8 mg kg$^{-1}$), Cu (15.7 and 16.2 mg kg$^{-1}$) , Ni (13.7 and 13.3 mg kg$^{-1}$). HAJDUK et al. (2012), when examining soils in the vicinity of the Stalowa Wola Power Plant, recorded slightly lower arithmetic means for Cu and Zn, but higher ones for chromium, which may indicate slightly different participation of emitters in the contamination of soils. The metal concentrations determined in the present study are much lower than those reported for the soils of the Upper and Lower Silesia (KARCZEWSKA

2003, Szerszeń et al. 2004, Baran et al. 2007, Strzyszcz, Rachwał 2010), and in some urban soils worldwide (Koval`chuk et al. 2002, Salvagio Manta et al. 2002, Burgos et al. 2008, Krmčowa et al. 2009).

The fact that the geometric means of the content of all the metals were significantly lower than the arithmetic mean values, and than the median values of Mn, Zn, and Cu seems to be very interesting (Table 2). This indicates an upward skew distribution of the results for elements in the

Table 2

General statistical parameters for microelement content in soils from Stalowa Wola (mg kg$^{-1}$)

| Parameter | | Mn | Zn | Cu | Cr | Ni |
|---|---|---|---|---|---|---|
| City soils (*n*=25) | | | | | | |
| Arithmetic mean | A | 283*a** | 115.3*c* | 15.7*e* | 27.6*g* | 13.7*i* |
| | B | 305*b* | 56.6*d* | 16.2*f* | 24.8*h* | 13.3*j* |
| Geometric mean | A | 179 | 59.0 | 10.5 | 20.9 | 9.4 |
| | B | 144 | 37.6 | 9.8 | 16.5 | 8.5 |
| Median | A | 221 | 64.1 | 12.6 | 20.3 | 9.1 |
| | B | 189 | 53.8 | 13.8 | 17.6 | 8.2 |
| Minimum | A | 25 | 2.1 | 0.9 | 6.2 | 1.5 |
| | B | 9 | 2.1 | 0.9 | 3.8 | 1.2 |
| Maximum | A | 1231 | 1091.2 | 46.8 | 77.1 | 42.1 |
| | B | 1778 | 189.7 | 61.5 | 74.7 | 56.5 |
| Coefficient of variation (%) | *A* | 98.3 | 183.2 | 82.1 | 80.2 | 82.5 |
| | *B* | 123.3 | 81.7 | 93.8 | 91.6 | 97.3 |
| Control (*n*=4) | | | | | | |
| Arithmetic mean | A | 126*a* | 33.1*c* | 7.9*e* | 9.0*g* | 3.8*i* |
| | B | 113*b* | 17.5*d* | 6.0*f* | 7.4*h* | 3.5*j* |
| Geometric mean | A | 117 | 26.1 | 6.0 | 8.5 | 3.5 |
| | B | 144 | 37.6 | 9.8 | 16.5 | 8.5 |
| Median | A | 116 | 24.0 | 4.4 | 8.4 | 3.1 |
| | B | 109 | 15.9 | 4.9 | 7.6 | 3.5 |
| Minimum | A | 73 | 12.6 | 3.5 | 5.3 | 2.4 |
| | B | 90 | 12.4 | 2.6 | 6.2 | 1.8 |
| Maximum | A | 198 | 71.8 | 19.1 | 14.1 | 6.8 |
| | B | 143 | 25.9 | 11.8 | 7.9 | 5.0 |
| Coefficient of variation (%) | *A* | 43.6 | 81.9 | 95.7 | 42.4 | 52.2 |
| | *B* | 19.9 | 33.4 | 67.2 | 10.8 | 43.6 |

A – soil from 0-25 cm depth
B – soil from 26-50 cm depth
* The same letters indicate arithmetic means not showing statistically significant differences according to Tukey's test ($\alpha$=0.05) (homogeneous groups).

soil, which in turn may suggest the presence of a number of points with abnormally high levels of pollutants (due to anthropogenic contamination). This is confirmed by the high values of variation coefficients (Table 2). The range of Zn, Cu, and Ni levels in the examined soils falls within the brackets expected for the humus layer of arable soils in the Subcarpathian Province (Terelak, Tujaka 2003), or in whole Poland (Oleszek et al. 2003). Similarly, the geometric mean values for these elements are higher than those reported by Oleszek et al. (2003), Terelak, Tujaka (2003).

Arithmetic means of all the tested metals in soils from Stalowa Wola were more than double (even over 3-fold higher for Cr and Ni) the corresponding averages for the control points, but the analysis of variance and the Tukey's test did not verify statistical significance of these differences (=0.05). This finding, as well as the variation coefficients significantly lower in soils from the checkpoints than from the whole study area, also implies that anthropogenic sources emitting these elements were present in Stalowa Wola.

In the light of the current legal regulations in Poland (*Regulation...* 2002), the permissible levels of heavy metals were not exceeded in soils of Stalowa Wola, except for the Zn content in a single sample. However, according to the criteria set by the IUNG (Kabata-Pendias et al. 1993), only 50% of the soil samples had the natural content of heavy metals (0 level of contamination), 31% showed an elevated content (I level), another 15.5% of soil samples had weak contamination (II level), and 1.7% represented moderate (III level) and strong pollution (IV level) – Figure 2.

The tendency to accumulate metallic elements in upper soil levels has been observed by many authors (Maciejewska, Ociepa 2003, Bieniek, Łachacz 2003, Burgos et al. 2008, Jaworska, Dąbkowska-Naskręt 2012, Medyńska-Juraszek, Kabała 2012, Lourenço et al. 2014). The studied microelements from the checkpoints localized south and (except for Mn) east of Stalowa

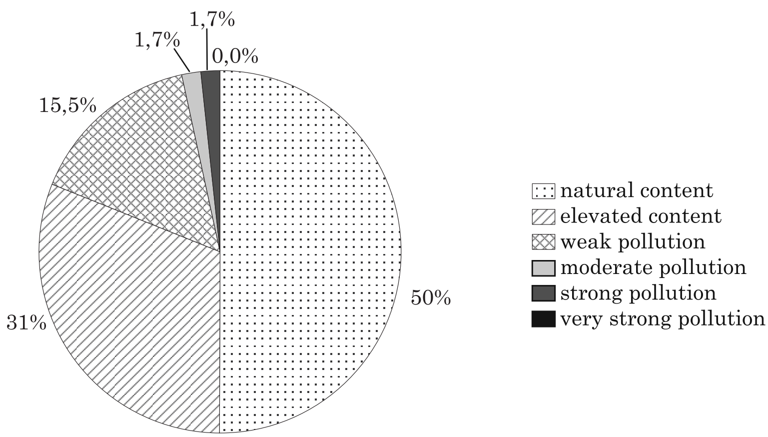


Fig. 2. Total percentage of soils in particular categories of copper, zinc, nickel, and chromium contamination according to the IUNG criteria (Kabata-Pendias et al. 1993)

Wola were usually subject to accumulation in the surface soil layer. Such trends were not observed at other points in the other directions. No regular distribution of the concentrations of the elements in the vertical pattern of urban soils was found, partly because of their specific characteristics such as mixing the layers or addition of sand and gravel during engineering works (Norra et al. 2006). Another reason could be the significant reduction in industrial emissions into the environment after 1990, which – combined with strong soil acidification and high mobility of metal compounds – could have led to their substantial transfer in the soil profile. Mercik et al. (2003) or Kiepul and Gediga (2009), based on their own and other authors' research, emphasized the increased solubility of microelements in acidic environment. Recently, these authors have stressed that in soil weakly contaminated with zinc, the metal accumulates in the surface soil layer and does not penetrate down the profile, although its transport depends on the flow of groundwater. It should be noted that the analyzed area is covered predominantly by sandy soils, through which water percolates easily. Furthermore, the presence of different man-made facilities, ongoing industrial activities, but also the share of green areas including forests, are likely to interfere with the direction of winds, causing variable immissions of dust settling on the soil surface. Especially tall trees in urban areas may stop falling dust particles containing heavy metals.

The results also indicate that the average content of Mn, Zn, Cu, Cr, and Ni was higher in soils from the north than from the south direction (Table 3). Also, the corresponding average values for soils from the eastern part of the city were higher than those from the western side (Table 3). It should be emphasized that southerly and south-westerly winds prevail in this part of Poland (Suchy 2008), and such a distribution of the analyzed metals in soils can be explained by the increased accumulation of contaminants due to large point sources of emissions in the town (the Stalowa Wola Steelworks, Stalowa Wola Power Plant) on the leeward side.

Taking into account the content of microelements in soils at different distances from the "central point" (the main gate of the Stalowa Wola Steelworks), quantities of all metals higher than average can be observed in points 3 and 4 km from the centre in the east-west transect. However, was observed a steady increase was observed along the perpendicular direction in the content of all elements in soils from of the southern outskirts of the town up to the central point of the transect, after which their concentrations significantly decreased in the northern direction, finally showing an upward tendency, peaking at 3 km from the center. Urban soils are typically characterized by a higher concentration of anthropogenic contaminants in the city centre (Alexandrovskaya, Alexandrovskiy 2000, Gąsiorek, Niemyska-Łukaszuk 2004, Bielińska et al. 2011) and that trend was noted in our study. Peng et al. (2013) examined soils of Beijing (China) and found that the content of heavy metals correlated not only with the distance from the center, but also

Table 3

The content of microelements in soils of Stalowa Wola at different distances from the central point – the main gate of the Stalowa Wola Steelwork

| Distance (km) | Mn | | Zn | | Cu | | Cr | | Ni | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B | A | B |
| 0 | 463 | 441 | 213.2 | 70.0 | 39.7 | 15.3 | 75.3 | 27.6 | 22.1 | 7.6 |
| East | | | | | | | | | | |
| 0.5 | 221 | 359 | 33.8 | 57.9 | 12.4 | 17.9 | 21.2 | 28.8 | 12.9 | 20.9 |
| 1 | 115 | 88 | 62.9 | 35.0 | 10.6 | 8.5 | 14.1 | 10.9 | 6.5 | 6.2 |
| 2 | 92 | 41 | 25.9 | 13.8 | 12.6 | 3.8 | 13.5 | 7.1 | 5.6 | 3.8 |
| 3 | 297 | 568 | 110.6 | 100.0 | 35.3 | 21.2 | 77.1 | 71.5 | 34.4 | 15.9 |
| 4 | 327 | 519 | 150.0 | 150.0 | 46.8 | 42.4 | 76.8 | 72.9 | 31.5 | 36.5 |
| 5 | 25 | 25 | 2.1 | 2.1 | 1.8 | 0.9 | 6.2 | 4.1 | 1.5 | 3.8 |
| 15 K | 198 | 113 | 71.8 | 25.9 | 19.1 | 5.9 | 14.1 | 7.6 | 6.8 | 1.8 |
| West | | | | | | | | | | |
| 0.5 | 403 | 83 | 62.9 | 57.4 | 14.4 | 8.5 | 25.0 | 15.0 | 17.6 | 7.4 |
| 1 | 45 | 16 | 70.9 | 21.8 | 2.9 | 1.5 | 10.0 | 6.2 | 2.9 | 2.1 |
| 2 | 59 | 122 | 25.3 | 37.1 | 5.0 | 8.5 | 9.7 | 10.0 | 4.7 | 3.8 |
| 3 | 728 | 635 | 68.5 | 70.6 | 23.5 | 24.4 | 34.7 | 38.5 | 24.7 | 24.7 |
| 4 | 72 | 246 | 22.4 | 189.7 | 4.1 | 28.8 | 8.8 | 62.6 | 4.4 | 21.2 |
| 5 | 469 | 476 | 55.6 | 53.8 | 16.2 | 15.3 | 26.2 | 25.6 | 22.1 | 20.9 |
| 15 K | 95 | 90 | 12.6 | 15.3 | 5.0 | 3.8 | 9.7 | 7.6 | 2.4 | 5.0 |
| North | | | | | | | | | | |
| 0.5 | 101 | 97 | 39.1 | 38.8 | 9.7 | 8.8 | 13.5 | 15.9 | 3.5 | 8.2 |
| 1 | 147 | 21 | 1091.2 | 10.9 | 19.7 | 61.5 | 20.3 | 3.8 | 11.8 | 3.8 |
| 2 | 482 | 500 | 65.9 | 59.4 | 21.2 | 21.5 | 33.5 | 34.1 | 22.9 | 24.1 |
| 3 | 1230 | 1780 | 105.9 | 132.4 | 38.2 | 46.8 | 53.2 | 74.7 | 42.1 | 56.5 |
| 4 | 403 | 462 | 32.4 | 42.6 | 7.9 | 11.5 | 12.9 | 19.7 | 6.2 | 10.3 |
| 5 | 601 | 593 | 65.6 | 54.4 | 17.9 | 17.9 | 37.6 | 29.7 | 21.8 | 20.0 |
| 15 K | 138 | 143 | 31.8 | 16.5 | 3.8 | 11.8 | 5.3 | 7.9 | 3.2 | 4.4 |
| South | | | | | | | | | | |
| 0.5 | 245 | 189 | 183.8 | 72.1 | 24.7 | 15.3 | 47.4 | 18.5 | 17.6 | 10.6 |
| 1 | 248 | 194 | 198.5 | 71.8 | 13.2 | 5.9 | 22.6 | 17.6 | 7.1 | 2.4 |
| 2 | 46 | 9 | 64.1 | 5.6 | 0.9 | 13.8 | 18.2 | 3.8 | 9.1 | 1.2 |
| 3 | 58 | 24 | 23.8 | 8.8 | 6.2 | 1.5 | 11.8 | 4.7 | 2.9 | 5.6 |
| 4 | 101 | 64 | 93.8 | 44.7 | 3.8 | 2.4 | 11.2 | 7.9 | 4.7 | 3.5 |
| 5 | 89 | 64 | 14.7 | 13.8 | 3.5 | 1.5 | 7.9 | 8.2 | 2.9 | 2.6 |
| 15 K | 73 | 104 | 16.2 | 12.4 | 3.5 | 2.6 | 7.1 | 6.2 | 2.8 | 2.6 |

K – control point
A – soil from 0-25 cm depth
B – soil from 26-50 cm depth

with the population density, density of the road grid and sometimes even the age of buildings. However, simple correlation coefficients between the distance from the central point and the content of microelements in soils calculated in the current study were statistically insignificant ($\alpha$=0.05).

The calculated simple correlation coefficients (Table 4) indicate the presence of statistically significant positive dependencies between the content of Mn, Cu, Cr, and Ni in the soil versus the content of <0.02 mm fraction and the amount of organic carbon. The content of Cr was also deoendent on soil $pH_{KCl}$. In contrast, the zinc content in the topsoil was not statistically associated with any of the analyzed soil characteristics, which may indicate its

Table 4

Simple correlation coefficients among microelements in soils of Stalowa Wola and soil properties (*n*=25)

| Parameter | | Mn | Zn | Cu | Cr | Ni |
|---|---|---|---|---|---|---|
| <0.02 mm | A | 0.8952*** | ns | 0.4480* | ns | 0.6807*** |
| | B | 0.8317*** | ns | 0.4104* | 0.5094** | 0.7875*** |
| <0.002 mm | A | 0.7375*** | ns | 0.4070* | ns | 0.5448** |
| | B | ns | ns | ns | ns | ns |
| $pH_{KCL}$ | A | ns | ns | ns | 0.4282* | ns |
| | B | ns | 0.4365* | ns | 0.4839* | ns |
| Hydrolytic acidity | A | ns | ns | ns | ns | ns |
| | B | ns | ns | ns | ns | ns |
| TEB | A | -0.6694*** | ns | -0.5538** | -0.4675* | -0.7004*** |
| | B | -0.5112** | ns | -0.4185* | -0.4288* | -0.5828** |
| CEC | A | -0.5413** | ns | -0.5333** | -0.4708* | -0.6560*** |
| | B | -0.4555* | ns | -0.4460* | -0.4629* | -0.5714** |
| BS | A | -0.8117*** | ns | ns | ns | -0.4798* |
| | B | -0.7000*** | ns | ns | ns | -0.5433** |
| Corg. | A | 0.4226* | ns | 0.5277** | 0.4770* | 0.4086* |
| | B | 0.5002* | ns | 0.4736* | ns | 0.4749* |
| Mn | A | | ns | 0.6282*** | 0.5346** | 0.8185*** |
| | B | | 0.5726** | 0.5307** | 0.7548*** | 0.9173*** |
| Zn | A | | | ns | ns | ns |
| | B | | | 0.5061** | 0.8984*** | 0.7211*** |
| Cu | A | | | | 0.9587*** | 0.8930*** |
| | B | | | | 0.5812** | 0.6281*** |
| Cr | A | | | | | 0.8585*** |
| | B | | | | | 0.8485*** |

* significant at $\alpha$=0.05, ** significant at $\alpha$=0.01, ***significant at $\alpha$=0.001

A – soil from 0-25 cm depth, B – soil from 26-50 cm depth, ns – insignificant correlation anthropogenic origin. Salvagio Manta et al. (2002) did not find statistically significant correlation coefficients between heavy metals and pH, CEC or organic matter in the soils of Palermo. These authors, after performing the hierarchical cluster analysis, distinguished two groups of metals: I – strongly correlating with the content of the alumino-silicate phase due to their natural content, and II – not having this characteristics, including metals from anthropogenic sources (Cu, Zn, Sb, Pb, Hg).

Plants have different adaptability to soil pollution with heavy metals (Zacarías et al. 2012). Among the examined tree species, oak leaves presented the highest accumulation of manganese (an average of 640 mg $kg^{-1}$ DM), while black locust leaves accumulated the least of this metal (an average of 4.3 mg $kg^{-1}$ DM) – Figure 3. Linden leaves tended to accumulate chromium (mean 12.3 mg $kg^{-1}$), whereas leaves of ash trees had a particularly high zinc content (mean 98.0 mg $kg^{-1}$). Average amounts of Cu and Ni determined in the plant material were similar, although ash leaves were characterized by the smallest quantities of these elements.

The arithmetic mean content of the microelements in the dry matter of oak

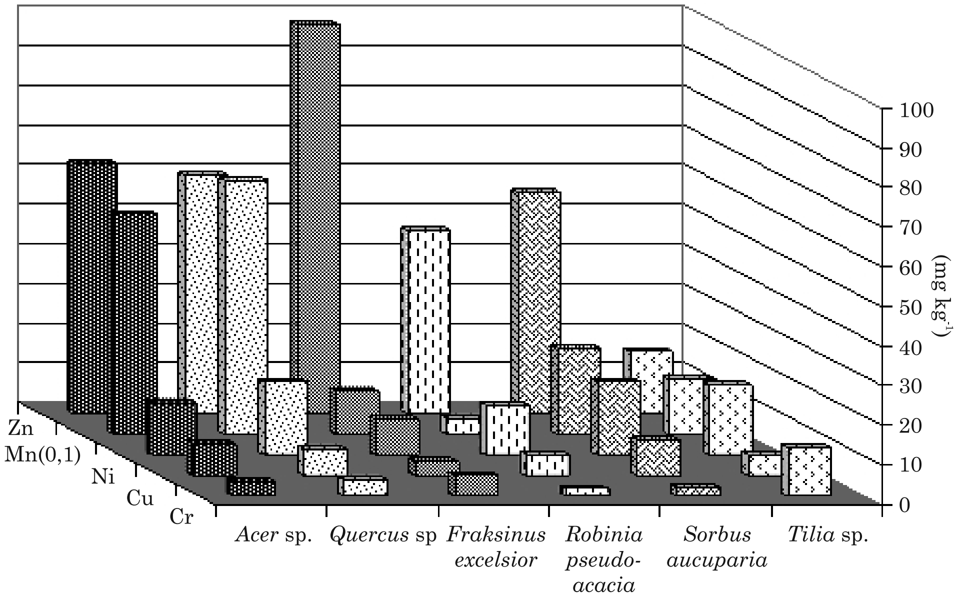


Fig. 3. Content of microelements in tree leaves from Stalowa Wola

leaves are following: Mn – 640, Zn – 60, Cu – 6.9, Cr – 4.3, Ni – 18.4 mg $kg^{-1}$ DM (Table 5). Variability coefficients for the manganese and chromium content were much larger than for the other elements. The medians of the Mn and Cr content were approximately 2-fold lower than the arithmetic average values. Analysis of the distribution of the analyzed elements in oak leaves from the north-south transect revealed that high levels of Ni were found in

Table 5

General statistical parameters for microelement content in oak leaves from Stalowa Wola ($mg\ kg^{-1}$ DM)

| Parameter | Mn | Zn | Cu | Cr | Ni |
|---|---|---|---|---|---|
| Arithmetic mean | 640 | 60 | 6.9 | 4.3 | 18 |
| Geometric mean | 410 | 58 | 6.6 | 2.3 | 17 |
| Median | 332 | 64 | 7.1 | 1.8 | 18 |
| Minimum | 62 | 30 | 3.6 | 0.8 | 5 |
| Maximum | 2145 | 98 | 10.6 | 19.6 | 32 |
| Coefficient of variable (%) | 104 | 26 | 33 | 129 | 35 |

samples collected from the surroundings of the main gate of Huta Stalowa Wola, and that leaves accumulated smaller amounts of this metal at a larger distance (Figure 4). This did not correspond with the content of Ni in soils of the northern part of the studied area (Table 3), where high amounts of Ni

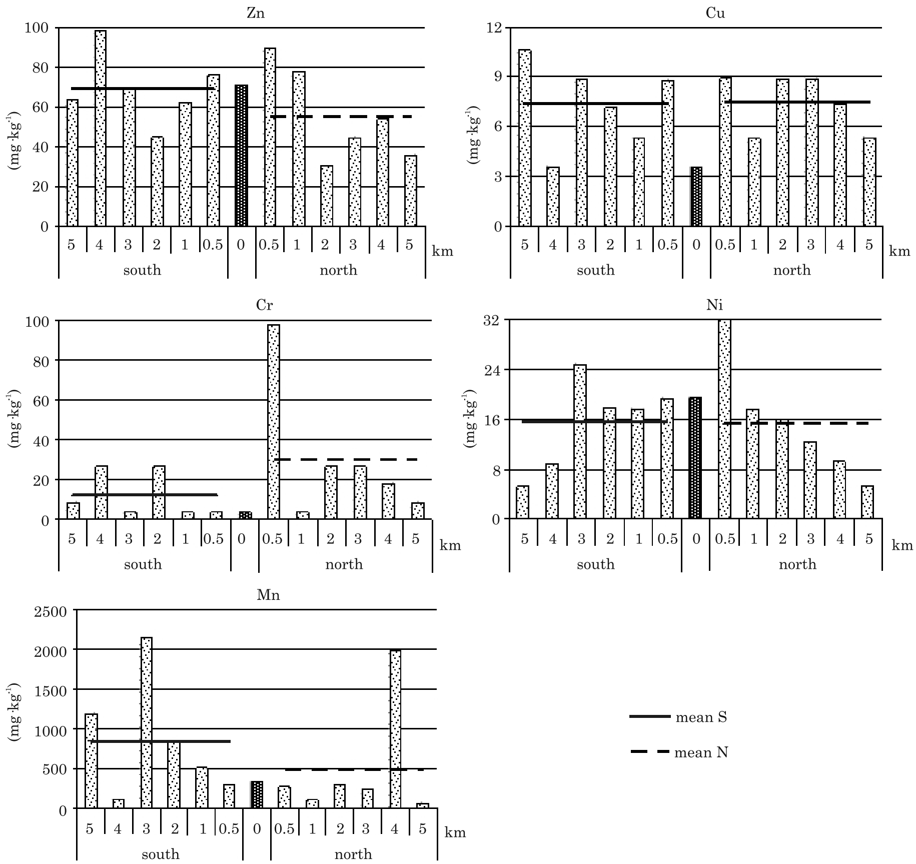


Fig. 4. Content of microelements in oak leaves from Stalowa Wola in the north-south transect at different distances from the central point

and other metals were observed in a 3 km zone. In general, higher amounts of Mn and Zn were observed in leaves from the southern part of the city. It was only chromium that was determined in higher amounts, in the northern part of the town, which was in accordance with the direction of prevailing winds. It can be assumed that the atmospheric pollution with microelements due to large sources emission (such as Huta Stalowa Wola) did not influence significantly the diversity of the content of elements in oak leaves, although it might have contributed in the past to their remarkable accumulation in soils of the northern part of the town. It should be emphasized that the emission of pollutants into the environment from industrial sources in Stalowa Wola was substantially reduced in the 1990s, but compared to other towns in the same region, high levels of dust and gas emissions into the atmosphere of the town continue to be recorded (*Strategy* ... 2007, Suchy 2008).

Tree leaves are often used to diagnose the environmental pollution (Sawidis et al. 2001, Piczak et al. 2003, Rosselli et al. 2003, Cicek, Koparal 2004, Madejòn et al. 2004, Aksoy, Demirezen 2006, Massadeh et al. 2009, Samecka-Cymerman et al. 2009). The chemical composition of leaves also indicates whether they can be composted. Madej et al. 2010). The averaged values of the Cu, Zn, Cr content in tree leaves from Warsaw reported by the above authors were similar to those obtained in the present study, although values for Ni were slightly lower. Hajduk et al. (2006) found significantly lower concentrations of nickel in leaves of trees located south of Rzeszów and in its surroundings, while noticing higher nickel amounts in the soil. Samecka-Cymerman et al. (2009), when examining the content of heavy metals in leaves of black locust from the Oleśnica environs, found zinc and copper levels similar to those obtained in the present studies, but a lower content of manganese, nickel, and chromium. Cicek, Koparal (2004) determined much higher amounts of Cr, Ni, Cu, and Zn in leaves of various tree species growing near a thermal power plant, but the soils were much more abundant of the analyzed elements. However, high content of microelements in soil does not always translate into their higer accumulation in tree leaves, for example Aksoy and Demirezen (2006) reported amounts of nickel and chromium in leaves of ash tree from Turkey similar to those found in leaves of trees from Stalowa Wola, with a much higher content of these metals in soils. It should be emphasized that the accumulation of metallic elements in plant tissues depends not only on the plant species, organ and plant growth phase, but also on their content in soils (in particular available forms), on soil properties (including pH, redox potential, organic matter content, and other elements contents), and on air pollution (Kabata-Pendias, Pendias 1993, Sawidis et al. 2001, Karczewska 2003, Kabata-Pendias 2004, Madejòn et al. 2004, Massadeh et al. 2009, Madej et al. 2010). The low pH of the soils in the studied area is worth mentioning, as it means better bioavailability of the analyzed micronutrients. However, except for Mn, there was no statistically significant correlation between the content of microelements in tree leaves and the pH or acidity of soils. The content of all the analyzed elements in tree leaves was not statistically significantly ($\alpha$=0.05) related to their content in the soil, soil texture, total exchangeable bases, cation exchange capacity, or (except for Zn in the 26-50 cm layer) the organic carbon content.

Absence of any statistically significant relationship between the content of the metals in leaves of trees and their content in soil, as well as the soil's physicochemical properties in part may be due to the existence of active barriers protecting plants against the uptake of toxic quantities of various substances from soil (Rascio, Navari-Izzo 2011), but it can also be directly caused by the leaf uptake of elements from atmospheric dust settling on their surface. This seems to be particularly important in the case of nickel and chromium, as the levels of these two metals in leaves of the tree species exceeded values reported by Kabata-Pendias and Pendias (1993) as normal (physiological) for plants with moderate sensitivity (Ni 5 mg kg$^{-1}$ , 0.5 mg Cr kg$^{-1}$). Furthermore, 30% of leaf samples contained more than 300 mg Mn kg$^{-1}$, which is the upper limit given by those authors as typical for plants.

It should be emphasized that Ni, Cr, and Mn were classified by Kabata-Pendias and Pendias (1993) as elements with a low degree of accumulation at plants, for which the accumulation index, calculated from the ratio of the content of these elements in the plant to their concentrations in the soil, is in the range of 0.01-0.1. In contrast, calculations made on the basis of our results indicate that the plant-soil accumulation ratios exceeded the upper limit of the range in over 90% of cases for Mn and Ni and about 60% for Cr. In general, the highest values of these coefficients were recorded in the southern part of Stalowa Wola, where industrial facilities, including Huta Stalowa Wola, are located. It can be concluded that although the permisible thresholds of heavy metals in soil were not exceeded, there is a risk of environmental pollution (especially with nickel, chromium, and manganese) as a result of particulate emissions, rich in these elements, from a large number of industrial facilities in the southern part of the town (including the steel industry and metallurgy). These dusts are largely retained by woody vegetation, and some microelements are accumulated in leaves.

## CONCLUSIONS

1. Light soils prevailed in the area of Stalowa Wola city, with an average content of the fraction < 0.002 mm: 9% in the 0-25 cm layer and 7% in 26-50 cm layer. They were usually strongly acidic soils with varied cation exchange capacity (5-48 cmol(+) kg$^{-1}$).

2. The content of microelements in the urban soils was in a wide range: 8 to 1778 mg Mn kg$^{-1}$, 2.1÷1090 mg Zn kg$^{-1}$, 0.9÷61.5 mg Cu kg$^{-1}$, 3, 8÷77.1 mg Cr kg$^{-1}$, 1.2÷56.5 mg Ni kg$^{-1}$. The arithmetic means of the content of all the investigated metals in soils from Stalowa Wola were over two-fold (more than 3-fold for Cr and Ni) higher than the corresponding average values for

the control points, which may indicate a large impact of anthropogenic factors on soil contamination. There were no clear patterns in the distribution of the analyzed elements depending on the depth.

3. The levels of the analyzed heavy metals in the soils did not exceed the legal norms in Poland (except for Zn in one soil sample). However, according to the IUNG criteria, only 50% of soil samples were characterized by the natural content of heavy metals (0 degree of contamination).

4. Most Mn, Zn, Cu, and Ni were found in soils in the northern part of the town (Cr in the eastern part). The lowest average content of these elements was in the western and southern parts of the town. Such a distribution of elements in urban soils may be the result of atmospheric transport of pollutants by the southerly and south-westerly winds, prevailing in this region.

5. The zinc content in the topsoil was not correlated with any of the analyzed soil characteristics. Some positive correlations were recorded between concentrations of Mn, Cu, Cr, and Ni in the soil and the content of <0.02 mm fraction and the amount of organic carbon; statistically significant albeit negative correlation coefficients were obtained between the soil content of the analyzed elements and the total exchangeable bases and cation exchange capacity.

6. It was found that oak leaves showed the highest manganese accumulation (average 640 mg $kg^{-1}$ DM) while the least manganese accumulated in leaves of black locust (average 4.3 mg $kg^{-1}$ DM). Linden leaves tended to accumulate chromium (mean 12.3 mg $kg^{-1}$), while leaves of ash had a particularly high content of zinc (average 98.0 mg $kg^{-1}$). When analyzing the content of the elements in oak leaves from the north-south transect, no regular trends in the spatial differentiation of the results were observed.

7. Numerous cases of exceeding the natural concentration limits for Cr, Ni, and Mn in leaves of the tree species and high values of the soil-plant accumulation coefficients indicate the risk of pollution by these metals as a result of particulate pollutant emissions from industrial plants localized in the southern part of the town.

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