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# ASSESSMENT OF SOIL CONTAMINATION BY ROOF RUNOFF. A CASE STUDY FROM WROCŁAW, POLAND

The study focused on the determination of heavy metals originating from anthropogenic sources to assess the environmental and health risks to city residents. The single pollution indices showed the key pollutants in soils such as Zn, Cd, and Pb. Contamination level assessment and the toxicity of pollutants were done by the multi-elemental pollution indices. They showed heavy pollution of tested soils with high ecological risk. The correlation analysis and the principal component analysis model were utilized to identify the relative contribution of metals to soil pollution and provide information about the potential sources of metals. The most important for elemental composition in soils in Wrocław are three emission sources: leaching of pollutants from the materials used in the roof coverings and guttering, domestic heating with fossil fuel combustion and other solid materials, leaching of the air pollution including of the road traffic. The health risk analysis shows that ingestion and then dermal contact are the greatest exposure pathways for humans. The health risk was low, although children have greater risks than adults.

## 1. INTRODUCTION

Current environmental changes are mainly manifested by the increase in temperature and the extension of periods without precipitation, as well as the more frequent occurrence of heavy rain. Despite the maintenance of the average annual rainfall sum, which is close to the multi-year average, the distribution of rainfall intensity is noticeably changing. Intense and short-term rainfall causes flooding but does not replenish groundwater resources. This results in a decrease in the level of groundwater and, consequently, in the shrinking of water resources, which shortly may lead to a shortage of

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drinking water. With limited groundwater resources, it is therefore rational to manage rainwater, especially in highly urbanized areas with a large share of paved surfaces. Collecting and storing rainwater in the city is beneficial because it reduces the effects of heavy rains and periodic droughts. Artificial water reservoirs for collecting rainwater can also be valuable natural habitats that will increase the biodiversity of urban ecosystems. Unfortunately, in many places, rainwater management is problematic due to the lack of appropriate reservoirs or accompanying infrastructure that would make it possible to collect and use rainwater. Usually, cities do not have available areas for infiltration and water retention in the ground.

In 2021, Poland recorded an increase in copper and lead emissions of 20 Mg (6%) and 9 Mg (3%), respectively. Road transport is a significant source of copper emissions (69%) due to tribological processes. Compared to 1990, there was a 77% increase in Cu emissions in the road transport sector due to the increased number of road vehicles and their transport work (increased mileage). In consequence, there was an increase in the consumption of fuel, vehicle consumable parts, and road infrastructure. Transport in agglomerations is characterized by a specific traffic model. Vehicles emit significantly larger amounts of pollutants due to slowing down traffic in traffic jams, at intersections, in front of traffic lights, roundabouts, entrances, and exits from main roads. On the other hand, a 12% increase in mercury emissions is related to the increase in the consumption of solid fuels in the energy sector. This sector is also responsible for the largest emissions of nickel (43%), arsenic (35%), and zinc (19%) [1]. The problem of soil contamination with heavy metals from linear emissions near communication roads is widely discussed by researchers [2–4].

According to the regulations in force in Poland, rainwater and meltwater are not treated as sewage and cannot be discharged into the sanitary sewage system [5]. However, it is worth using rainwater for your own needs, such as sanitary purposes, washing properties, watering lawns, ornamental plants, or growing vegetables in the garden. This requires determining the suitability of rainwater for economic and living purposes in terms of contamination, most often the content of heavy metals, PAHs, or microbiological contamination, especially when it is intended for animal watering [6]. The chemical composition of rainwater depends on the type of roof covering, the corrosion state of the run-off surface, the pH of the water, climatic conditions, and air pollution throughout the hydrological year [7–10].

In Wrocław, the main sources of air pollution are the municipal-residential sector and transport. Moreover, due to the industrial structure of the considered agglomeration, activities related to the machine-metal, food, electrical, metal, clothing, and chemical industries are distinguished. Air monitoring in Wrocław in the years 2013–2022 shows a gradual improvement in air quality in terms of the level of dust pollution (PM10 and PM2.5) and heavy metals determined in PM10. To protect human health, the content of heavy metals in PM10 is assessed concerning lead (0.5 mg Pb/m$^3$ is the average annual permissible level), nickel (20 ng/m$^3$), cadmium (5 ng/m$^3$), and arsenic (6 ng/m$^3$). The concentrations of the above pollutants recorded in 2022 were lower than the permissible levels and amounted to 0.01 mg $Pb/m^3$ (2% of the permissible level), 1.5 ng $Ni/m^3$ (8%), 0.2 ng $Cd/m^3$ (4%), and 1.7 ng $As/m^3$ (29%), respectively. In the years 2013–2022, the annual concentrations of lead, nickel, and cadmium were at a similar level, and in the case of arsenic, a clear reduction in concentration has been noticeable since 2018 [11].

Water flowing from roof surfaces covered with various materials contains more heavy metals than rainwater, as shown by Sikora et al. [12]. The first reason for the anthropogenic enrichment of rainwater with trace elements is the degree of corrosion of the contact surface and the leaching of coating components. The second reason is the leaching of dust contaminants deposited on the contact surface, namely mineral dust, road dust, and products of incomplete combustion of solid fuels. In water flowing from roofs covered with copper sheets, the permissible copper content for sewage discharged into water or soil was exceeded 5 times. However, water flowing from roofs covered with galvanized sheets exceeded the critical concentration of zinc in sewage discharged into surface waters or the ground by three times. The average iron enrichment factor of water after flowing from a roof covered with galvanized sheet metal was over 8. Compared to rainwater, the average amount of zinc was 40 times higher in rainwater from a galvanized roof, and there was 13 times more manganese. In the case of roofs covered with ceramic and cement roof tiles, the smallest changes in the content of heavy metals in rainwater were found after flowing from the contact surface. In addition, the pH values of water flowing from cement roof tiles, corrugated asbestos cement, and copper sheets were higher by 1–1.8 units compared to rainwater.

In the case of watering ornamental plants, the content of carcinogenic pollutants in rainwater has a negligible effect on human health and life. The situation is different in the case of watering plants intended for food. Providing plants with polluted water can lead to the incorporation of harmful substances into their structure and, after consumption by humans, to an increase in their levels in the body. Potentially toxic metals, such as lead, cadmium, nickel, or chromium, are harmful elements even in trace amounts, which, accumulating in the body gradually over time, can lead to chronic health problems and impairment of various physiological functions [6, 13].

The study aimed to assess the content of metals in soil successively saturated with rainwater from roofs in Wrocław. The studies were conducted in winter in Wrocław in places with significant air pollution with suspended dust and fuel combustion products in local boiler rooms and individual central heating furnaces. It should be emphasized that the tested samples are not an equivalent of momentary rainwater pollution, but correspond to the long-term accumulation of pollutants.

## 2. MATERIALS AND METHODS

*Sampling location.* The research was conducted in Wrocław, Poland, a city with a population of 893 506 according to estimates by the Wrocław City Hall as of December 31, 2022 [14]. The locations of measurement points were selected in places with high building density. The Small Ring Road or the the Large Ring Road are near the sampling points. The traffic intensity in both directions on the Small Ring Road is, on average, 1010 vehicles per hour during the morning and afternoon rush hours (7–8 AM and 4–5 PM). During this time, an average of 1700 vehicles per hour pass through the Large Ring Road [15] throughout the year. Individual heating using solid fuels in Wrocław has a major impact on the emission of pollutants into the environment. Therefore, as part of the KAWKA and KAWKAplus subsidy programs in Wrocław, activities related to co-financing the replacement of solid fuel heating with low-emission heating for single-family houses and residential premises in multifamily buildings are being carried out. In the period from 2014 to the end of 2023, 15 542 individual solid fuel heaters were removed [16].


Fig. 1. Google map with a monitored area

The locations of the sampling points are shown in Fig. 1. Concentric sampling of soil was forced by the city's urban layout. In total, there were taken 120 soil samples at 40 locations, with 72 soil samples taken along the the Large Ring (24 locations) and 48 soil samples taken along the Small Ring (16 locations) surrounding the Old Town of Wrocław with the oldest buildings. The age of the buildings at the Large Ring is at least 50 years, and for the buildings at the Small Ring, approximately 100 years and more. The Large Ring area includes approximately 350 000 inhabitants, and the Small Ring area contains 60 000 inhabitants. The ellipse diameters of the the Large Ring are 7200 and 5800 m, and those of the Small Ring are 3200 m and 2400 m, respectively. Samples were taken at least 30 m from the main streets or the yard side to avoid the direct influence of traffic pollution.

*Laboratory analysis.* The soil sampling took place at the end of February 2023, after several days of no rainfall, no snow cover, and during the heating season. Samples were taken from green areas where rainwater was directly drained from roofs via downpipes. The research material was collected from the top layer of soil to a deep of 2–5 cm. Three measurement points (3 independent samples) were designated at each location. To ensure the representativeness of the samples, at each measurement point, a maximum of

4 subsamples were collected in one container at a distance of 1 m from the outlet of the downpipe with rainwater. The distance between subsamples was about 0.3 m in an area of 1 $m^2$. The research material was air-dried, crushed, sifted through a 1 mm sieve, and placed in closed containers. After homogenization about 150 g of soil was obtained.

About 0.2 g of each sample was weighed for the microwave digestion process using the START D device from Milestone to then determine the total content of selected metals in the obtained solutions. The digestion of the collected materials was carried out with 65% nitric acid from Sigma-Aldrich. The obtained mineralizates were filtrated into 50 $cm^3$ volumetric flasks, filling them with deionized water to the full volume. Microwave digestion of soils in acid was performed twice. The contents of Cu, Zn, Pb, Cr, Cd, Ni, and Fe were measured using the flame atomic absorption method (FAAS) on a Thermo Solaar iCE 3500 device from Thermo Scientific according to PN-ISO 11047: 2001 [17]. All measurements were carried out three times. The instrument readings were checked using the reagent blank samples. The limits of detection were estimated based on three times the standard deviation for digestion blanks. The accuracy of the determination was controlled using the standard addition method, and the recovery percentage was 94–98%. For the calibration curve method, the validation of analytical methods and the standard addition method were used with the CRM's solutions of metals from Sigma-Aldrich.

The FAAS results were checked through the standard deviation, the coefficient of variation within 10%, and the confidence interval with the *p*-value being 0.05 for the *t*-Student test. Chemical analyses were carried out in the certified Laboratory of Environmental Research in the Faculty of Environmental Engineering at the Wrocław University of Science and Technology [18]. To evaluate the content of soluble metal fractions, soil extracts were prepared in the stoichiometric system 1:2.5 (m:v). pH was measured in solutions with 1 M KCl according to PN-ISO 10390:1997 [19] and the soil salinity in distilled water.

*Computational procedure.* Statistical analysis was performed using the Statistica program. Metal content in soil was calculated as the mean value with standard deviation for three independent samples from one sampling site. The hierarchical cluster analysis (HCA) was performed using Ward's algorithm and the squared Euclidean distance for the mean values of the *PI* index at a given location. The data were checked for a normal distribution using the Shapiro–Wilk *W*-test. Significance tests were performed at a 95% confidence level. The Mann–Whitney *U*-test was used for data that did not show a normal distribution. The Spearman rank correlation coefficients were calculated for the concentration of heavy metals in all samples. Correlations were considered strong above 0.6, and moderate between 0.4–0.6 for the *p*-value equal to 0.05. The Pearson correlation coefficient ($p < 0.05$) was used to examine the relationship between the total trace element contents. The principal component analysis (PCA) was used to identify the principal sources of soil pollution in the selected area. The loadings were considered significant for values of 0.7 or greater [20].

The soil quality monitoring was performed using pollution indices that allowed for the assessment of the effect of single trace element concentration, as well as the indices that enabled the integration of the heavy metal group [21]. The group of single-element indices is represented by the enrichment factor (*EF*), the pollution index (*PI*), and the geoaccumulation index ($I_{\text{geo}}$). The group of multi-element indices is represented by the pollution load index (*PLI*), the Nemerow pollution index ($PI_{\text{Nem}}$), and the potential ecological risk index (*RI*). There were also used the indices that allowed for the assessment of health risks estimated concerning exposure to heavy metals entering the human body unintentionally through ingestion, inhalation, and dermal routes, and the hazard index (*HI*).

The reference environment adopted by us was the average concentrations of elements in the Earth's crust (the UCC background) by Rudnick and Gao [22]. The reference UCC background values in mg/kg for determined chemical metals are the following: 28 (Cu), 67 (Zn), 17 (Pb), 47 (Ni), 92 (Cr), 0.09 (Cd), and 39 000 (Fe).

Enrichment factor (*EF*) is based on the standardization of the element being tested relative to a reference element, in this case, iron. The reference element is characterized by low variability of occurrence, and it is most often iron, aluminum, calcium, titanium, scandium, or manganese. The *EF* index is described by the following formula [21]

$$EF = \frac{\dfrac{C_n}{C_{\text{ref}}}}{\dfrac{B_n}{B_{\text{ref}}}} \tag{1}$$

where: $C_n$, $C_{\text{ref}}$ are the concentrations of the tested and reference (namely Fe) elements in the soil sample, mg/kg, $B_n$ and $B_{\text{ref}}$ are the concentrations of the tested and the reference (namely Fe) elements, respectively, in the reference environment such as the UCC background, mg/kg.

The *EF* values can be divided into five categories: < 2 deficiency to minimal enrichment (1st class), 2–5 moderate enrichment (2nd class), 5–20 significant enrichment (3rd class), 20–40 very high enrichment (4th class), > 40 exceptionally high enrichment (5th class) [21].

Geoaccumulation index ($I_{\text{geo}}$) is calculated based on the equation by Müller [21]

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5B_n} \tag{2}$$

with six classes of its values: <0 unpolluted (0 class), 0–1 unpolluted to moderately polluted (1st class), 1–2 moderately polluted (2nd class), 2–3 moderately to highly polluted (3rd class), 3–4 highly polluted (4th class), 4–5 highly to extremely polluted (5th class), >5 extremely highly polluted (6th class).

Single pollution index (*PI*) [21]

$$PI = \frac{C_n}{B_n} \tag{3}$$

Classification of pollution considering the *PI* values: <1 unpolluted (1st class), 1–2 low (2nd class), 2–3 moderate (3rd class), 3–5 strong (4th class), >5 very strong (5th class).

Pollution load index (*PLI*) integrates single pollution indices (*PI*) for heavy metals [21]

$$PLI = \left(PI_1 PI_2 \ldots PI_n\right)^{1/n} \tag{4}$$

where $n$ is the number of trace elements studied ($n = 6$).

Three levels of contamination of the tested material are distinguished by comprehensive index values (*PLI*): < 1 perfect quality (1st class), 1 baseline level of pollution (2nd class), > 1 deterioration of quality (3rd class).

Nemerow pollution index ($PI_{\text{Nem}}$) combines the values of *PI* indices for heavy metals

$$PI_{\text{Nem}} = \left(\frac{PI_{\text{avg}}^2 + PI_{\text{max}}^2}{2}\right)^{1/2} \tag{5}$$

where

$$PI_{\text{avg}} = \frac{PI_{\text{sum}}}{n}, \qquad PI_{\text{sum}} = \sum_{i=1}^{n} PI_i$$

The assessment criteria according to the $PI_{\text{Nem}}$ index include five pollution classes: <0.7 clean (1st class), 0.7–1 warning limit (2nd class), 1–2 slight pollution (3rd class), 2–3 moderate pollution (4th class), >3 heavy pollution (5th class).

Potential ecological risk (*RI*) is the sum of the ecological risk factors ($E_{\text{r}i}$) determined for all tested metals in the sample [21]

$$RI = \sum_{i=1}^{n} E_{\text{r}i} \tag{6}$$

There are five classes of pollution for the *RI* index: <90 low (1st class), 90–180 moderate (2nd class), 180–360 strong (3rd class), 360–720 very strong (4th class), >720 highly strong (5th class).

The ecological risk factor ($E_r$) is calculated for each metal separately as follows

$$E_r = T_r PI \tag{7}$$

The values of the biological toxic-response factor for a single metal ($T_r$) are: Cu, Pb, and Ni 5, Cr 2, Zn 1, Cd 30 [23].

Probability of toxicity (*MERMQ*) is

$$MERMQ = \frac{\sum_{i=1}^{n} \frac{C_i}{ERM}}{n} \tag{8}$$

The *MERMQ* index is based on four risk levels: <0.1 means the probability of toxicity with a low (9%) risk level (1st class), 0.1–0.5 medium risk level of 21% (2nd class), 0.5–1.5 a high risk level of 49% (3rd class), >1.5 a very high risk level of 76% (4th class). The effect range median (*ERM*) is as follows: 34/270 (Cu), 150/410 (Zn), 46.7/218 (Pb), 20.9/51.6 (Ni), 81/370 (Cr), 1.2./9.6 (Cd).

The estimation of the risk to human health caused by the presence of heavy metals in the topsoil is widely used in the process of determining the carcinogenic and non-carcinogenic risks. Heavy metals enter the human body through air, contaminated water, and contaminated food products [24, 25]. The average daily doses (*ADD*) of individual metals, unintentionally entering the body via the three routes of ingestion, inhalation, and dermal contact, can be calculated as follows [26].

Ingestion dose

$$ADD_{\text{ing}} = C_n \frac{EF\,ED\,Ing\,R}{BW\,AT} \tag{9}$$

Inhalation dose

$$ADD_{\text{inh}} = 10^6 C_n \frac{EF\,ED\,Inh\,R}{PEF\,RW\,AT} \tag{10}$$

Dermal dose

$$ADD_{\text{derm}} = C_n \frac{SL\,SA\,ABS\,EF\,ED}{BW\,AT} \tag{11}$$

*ADD* – the average daily dose (ingestion, inhalation, or dermal dose), ng/(kg·day),
$C_n$ – the average concentration of the tested element in the soil sample, mg/kg,
*IngR* – the value of daily intake, mg/day (200 adults, 100 children),
*InhR* – daily lung ventilation, $m^3$/day (20 adults, 7.6 children),

*EF* – contact frequency, day/year (180 adults, 180 children),
*ED* – duration of contact, years (70 adults, 6 children),
*BW* – average body weight, kg (70 adults, 15 children),
*AT* – averaging period, days (70 × 365 adults, 6 × 365 children),
*PEF* – particle emission factor, $m^3/kg$ ($1.39 \cdot 10^9$ adults, $1.39 \cdot 10^9$ children),
*SL* – coefficient of adherence to the skin, $mg/(cm^2 \cdot day)$, (0.7 adults, 0.2 children),
*SA* – exposed skin area, $cm^2$ (5700 adults, 2800 children),
*ABS* – percutaneous absorption coefficient, (0.001 adults, 0.001 children).

The hazard quotient (*HQ*) defines health risk as a function of human exposure to toxic substances. The value of *HQ* above 1 means a possibility of negative health effects as a result of long-term exposure to a specific toxic substance.

$$HQ = \frac{ADD}{RfD} \tag{12}$$

where *RfD* is the reference dose from the Integrated Information Risk System (IRIS), ng/(kg·day). $RfD_{\text{ing}}$ are: $4 \cdot 10^4$ (Cu), $3 \cdot 10^5$ (Zn), $3.5 \cdot 10^3$ (Pb), $2 \cdot 10^4$ (Ni), $3 \cdot 10^3$ (Cr), $1 \cdot 10^3$ (Cd); $RfD_{\text{inh}}$: $4 \cdot 10^4$ (Cu), $3 \cdot 10^5$ (Zn), $3.5 \cdot 10^3$ (Pb), $2 \cdot 10^4$ (Ni), $2.86 \cdot 10^1$ (Cr), $1 \cdot 10^3$ (Cd); $RfD_{\text{derm}}$: $1.2 \cdot 10^4$ (Cu), $6 \cdot 10^4$ (Zn), $5.25 \cdot 10^2$ (Pb), $5.4 \cdot 10^2$ (Ni), $6 \cdot 10^1$ (Cr), $1 \cdot 10^1$ (Cd).

Hazard index (*HI*) is estimated as the total effect resulting from a resident's exposure to a single heavy metal entering the body through all exposure routes at the same time. The value of *HI* below one means the probability of a chronic threat occurring in a given location is negligible

$$HI = HQ_{\text{ing}} + HQ_{\text{inh}} + HQ_{\text{derm}} \tag{13}$$

The hazard index (*HQ*) is calculated as a resident's health exposure after the intake of all heavy metals but only through a single exposure route.

$$HI_{\text{Me}} = \sum_{i=1}^{n} HQ_i \tag{14}$$

## 3. RESULTS AND DISCUSSION

### 3.1. ELEMENTAL CONCENTRATIONS

Selected metals in soils after penetration of rainwater from roofs can be arranged in the following order with the median values in mg/kg for the Large Ring and the Small Ring, respectively: Zn (1190/1220) > Pb (94/72) > Cu (56/49) or Cr (35/52) > Ni (22/28) > Cd (1.4/1.0). The orders of maximum levels in mg/kg for both rings are almost the same: Zn (6950/5065) > Pb (1300/514) > Cu (1226/139) > Cr (95/115) > Ni (79/102) >

Cd (4.2/2.9). The same amount of zinc was recorded in the Large Ring as in the Small Ring. Similar observations were made for copper, which indicates that these metals originate from the materials used for roofing, gutters, and downpipes. On the Large Ring, Pb and Cd levels are 1.3 and 1.4 times higher, respectively, due to the shifting of transit outside the city center. On the other hand, The Small Ring has higher levels of Cr and Ni of 1.5 and 1.3 times, respectively, which may be related to the road's age.

Very strong variability (*CV* above 100%) was recorded for Cu at the Large Ring and for Pb on both rings. For other metals, a strong spatial variability (*CV* above 45%) in trace metal contents in soils was found. It means a high concentration heterogeneity in soils. Point accumulation of metals may be related to corrosion of the surfaces of roofing, the leaching of coating components and dust contaminants, and also products of the combustion of solid fuels [12]. The lack of spatial homogeneity is also confirmed by the *p*-value below 0.05 of Shapiro–Wilk's *W*-test. Furthermore, the frequency histograms of the studied metals indicate a deviation from the Gaussian curve. The kurtosis is positive, indicating a concentration of scores around the mean value and the presence of a few outliers. The positive skewness values indicate that the mean values are higher than the median values.

The concentrations of cadmium, nickel, and lead in the studied samples do not exceed the permissible metal contents for group I of soils, in mg/kg: 2 (Cd), 150 (Ni), and 200 (Cu, Pb, and Cr), which are accepted at service development areas, residential and recreational, following the Polish Regulation [27]. The limit value of 500 mg Zn/kg was exceeded in 23% of the locations, including 6 locations on the Large Ring (Nos. 11, 13, 14, 16, 17, 22) and 3 locations on the Small Ring (Nos. 4A, 14A, 16A).

Table 1

Correlation analysis

| | Metal | Cu | Pb | Cr | Ni | Cd |
|---|---|---|---|---|---|---|
| Large Ring | Zn | 0.43 | 0.60 | 0.46 | 0.46 | 0.60 |
| | Cu | | 0.72 | 0.65 | 0.71 | 0.59 |
| | Pb | | | 0.75 | 0.65 | 0.70 |
| | Cr | | | | 0.89 | 0.68 |
| | Ni | | | | | 0.58 |
| Small Ring | | Cu | Pb | Cr | Ni | Cd |
| | Zn | 0.69 | 0.60 | 0.60 | 0.52 | 0.47 |
| | Cu | | 0.74 | 0.84 | 0.80 | 0.48 |
| | Pb | | | 0.85 | 0.51 | 0.67 |
| | Cr | | | | 0.67 | 0.45 |
| | Ni | | | | | 0.49 |

Strong relationships between all pairs of metals confirm the findings of the Spearman's correlations analysis (Table 1). Due to the classification, from 60 to 67% strong correlations were identified for the Large Ring and the Small Ring, respectively. The remaining correlations between metals are moderate, such as the correlations of Zn with

Cu, Cr, and Ni on the Large Ring, or the correlations of Cd with other metals on the Small Ring, except lead.

The result of PCA on the elemental composition of soils is shown in Table 2. According to the adopted criterion, the first two components present in the Large Ring are statistically significant and account for 86% of the total variance in the data. The first component (PC1) explains 68% of the total variance and shows that the concentrations of Cu, Pb, Cr, Ni, and Cd in soils are strongly associated. These elements can suggest an anthropogenic enrichment due to the combustion of fossil fuels and solid materials in individual central heating systems and emissions from the road traffic in the Wrocław agglomeration. The second component (PC2) explains 18% of the total variance and is associated only with the content of Zn in soils. An important contribution of Zn to the PC2 shows that it is most likely related to the corrosion and leaching of the roof and guttering materials.

Table 2

Matrix of loads for statistically significant principal components

| Component | Large Ring | | Small Ring | | |
|---|---|---|---|---|---|
| | PC1 | PC2 | PC1 | PC2 | PC3 |
| Cu | –**0.81** | 0.46 | –**0.86** | –0.21 | –0.03 |
| Zn | –0.42 | –**0.86** | –**0.74** | 0.46 | –0.35 |
| Pb | –**0.88** | 0.28 | –0.60 | 0.10 | **0.74** |
| Cr | –**0.90** | -0.15 | –**0.81** | –0.41 | 0.28 |
| Ni | –**0.93** | 0.03 | –0.48 | –0.61 | –0.51 |
| Cd | –**0.89** | -0.16 | –0.67 | 0.59 | –0.21 |
| Total variance, % | 68 | 86 | 50 | 68 | 87 |

The PCA analysis for the Small Ring shows three main components, which contribute 87% of the total variance in environmental characteristics. The PC1 describes 50% of the total variance and shows a strong influence of Cu, Zn, and Cr concentrations in soils. The total variances of PC2 and PC3 have similar percentage shares of 18% and 19%, respectively. The PC2 does not show statistically significant principal components according to the criterion used. Pb has a significant contribution to PC3. The shares of Ni and Cd in different components are similar and considered not statistically significant. It is not possible to precisely indicate the sources of the contribution of both metals in studied soils. In general, the greatest probability of heavy metal emissions in the Small Ring can be seen in the degradation of roofing materials and rainwater drainage systems, as well as in the linear emission of traffic pollutants. Almost half of street dust can be resuspended in the air with the wind, and about 10% of street dust enters the respiratory system [28].

### 3.2. POLLUTION ASSESSMENT

The analysis of single pollution indices confirms the heterogeneous distribution of metals in the studied soils (Fig. 2). Considering the geochemical reference background (the UCC), the median values of single indices change position compared to the trend observed for concentrations of metals in studied soils. They are respectively ranked for *PI*, $I_{geo}$, and *EF* indices as follows: Zn > Cd > Pb > Cu > Ni > Cr. Median values for *PI*, $I_{geo}$ and *EF* indices are respectively: 17.75/3.57/32.76 (Zn), 15.96/3.41/29.06 (Cd), 5.54/1.88/10.55 (Pb), 2.00/0.41/3.86 (Cu), 0.48/–1.66/0.89 (Ni), 0.38/–2.00/0.75 (Cr) on the Large Ring, and 18.22/3.60/32.64 (Zn), 11.37/2.92/24.93 (Cd), 4.29/1.51/7.49 (Pb), 1.76/0.22/2.84 (Cu), 0.59/–1.34/1.05 (Ni), 0.56/–1.41/0.81 (Cr) on the Small Ring. The maximum values indicate the change in the position of Pb, Cd, and Cu compared to the median values of the pollution indices. Maximum values for *PI*, $I_{geo}$ and *EF* indices are properly: 103.71/6.11/222.33 (Zn), 46.65/4.96/96.41 (Cd), 76.57/5.67/48.60 (Pb), 43.80/4.87/54.68 (Cu), 1.68/0.17/1.67 (Ni), 1.03/–0.54/1.36 (Cr) on the Large Ring, and 75.61/5.66/68.53 (Zn), 32.46/4.44/41.11 (Cd), 30.21/4.33/56.71 (Pb), 4.95 /1.72/6.20 (Cu), 2.16/0.53/4.08 (Ni), 1.26/–0.26/1.98 (Cr) on the Small Ring.

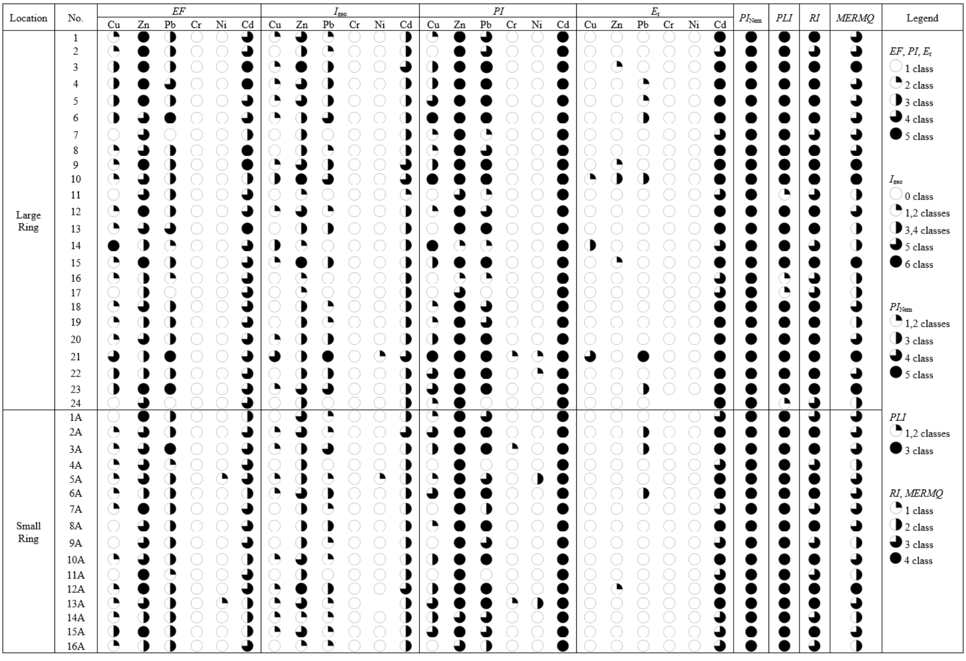


Fig. 2. Pollution assessment of soils based on single- and multi-elemental pollution indices in 40 sampling sites

The assessment of the degree of pollution of soils with Zn, Cd, and, Pb, after penetration by roof runoff indicates strong or very strong contamination. The *PI* median values show very strong pollution of Zn and Cd on both rings (the 5th class), and very strong or strong pollution of Pb (the 5th to 4th class) at the Large Ring and the Small Ring, respectively. Contamination of soils with the same elements is confirmed by the

$I_{geo}$ index (the 4th to 3rd class). The *EF* index classifies a high enrichment of soils by Zn and Cd to the 4th class, and in the case of Pb to the 3rd class. Tested soils are only moderately contaminated with copper, whereas Ni and Cr do not contaminate them at all. The maximum UCC background exceedance was 104 times higher for Zn, 77 times higher for Pb, 47 times higher for Cd, and 44 times higher for Cu.

The presence of cadmium causes high and very high ecological risk in the studied soils, due to the high toxic-response factor ($E_r$) above the value of 175 for this element. Additionally, in some samples a high value of $E_r$ index for Pb and Cu was noted, such as in the location No. 21 on the Large Ring (Fig. 2). The $E_r$ index confirms the indications of the previously discussed single pollution indices by excluding the ecological risk posed by Cr and Ni in the tested soils.

The integrated pollution indices of $PI_{Nem}$, *PLI*, and *RI* classify all soils as heavily contaminated with metals regardless of the amount of the UCC background value exceedance (Fig. 2). The median values of the $PI_{Nem}$, *PLI* and *RI* indices are, respectively: 15.59/2.98/553.93 for the Large Ring, and 16.91/3.14/405.22 for the Small Ring. Similarly, the maximum values are as follows: 75.98/12.95/2029.09 for the Large Ring and 55.26/6.03/1101.16 for the Small Ring. Calculated the *MERMQ* index shows a medium, high or very high risk level for samples from Wrocław, with a 21%, 49% or 76% probability of toxicity for tested soils.

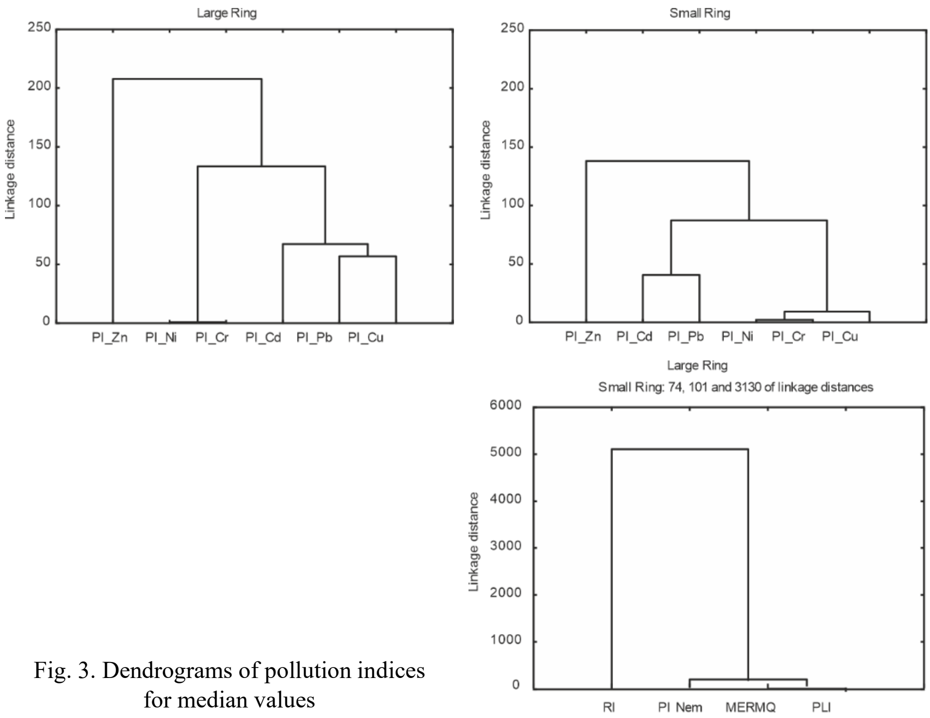


Fig. 3. Dendrograms of pollution indices for median values

Identification of trace element clusters using the HCA method shows a strong aggregation for copper and lead, which is further associated with cadmium in the Large Ring (Fig. 3). In the Small Ring, copper is also associated with lead and cadmium, which this time forms a separate group. The binding distances of the above metal subgroups are comparable for both rings. It is worth noting that zinc occurs separately, which is the result of its highest content in all samples, originating from roofing and gutter materials.

Dendrograms for multi-elemental indices (Fig. 3) are based on median values and show close integration of the $PI_{\text{Nem}}$ index with a separated group of *MERMQ* and *PLI* indices on both rings. The *RI* index cannot be compared with other integrated pollution indices. Its separation in the dendrogram from other multi-elemental pollution indices is caused by very high values, which result from its calculation formula, and more precisely, very high toxic response factors to the tested metals. On the other hand, the *RI* index assesses the potential ecological risk very well.

## 4. HEALTH HAZARD

Human health risk indices can be used to assess the level of urbanization better. It allows for much more precise planning of activities related to setting directions for improving the environmental condition in cities.

According to our estimation, the largest doses of metals are ingested by adults through the oral route ($ADD_{\text{ing}}$), and they are suitable for the Small Ring and the Large Ring, respectively: 82–185 (Cu), 2180–2430 (Zn), 183–185 (Pb), 70–58 (Cr), 49–36 (Ni), and 1.7–2.2 (Cd) ng/kg·day. A significantly smaller amount of metals is absorbed through the dermal route in a range of $ADD_{\text{dem}}$ values: 1.6–3.7 (Cu), 44–48 (Zn), 3.6–5.1 (Pb), 1.4–1.2 (Cr), 1.0–0.7 (Ni), and 0.03–0.04 (Cd) ng/kg·day. Doses of heavy metals entering the human body through the inhalation route ($ADD_{\text{inh}}$) are the following: $6.0\cdot10^{-3}$–$1.0\cdot10^{-3}$ (Cu), $1.6\cdot10^{-1}$–$1.8\cdot10^{-1}$ (Zn), $1.0\cdot10^{-3}$–$2.0\cdot10^{-3}$ (Pb), $5.0\cdot10^{-3}$–$4.0\cdot10^{-3}$ (Cr), $4.0\cdot10^{-3}$–$3.0\cdot10^{-3}$ (Ni), and $1.0\cdot10^{-4}$–$2.0\cdot10^{-4}$ (Cd) ng/kg·day.

Children are a group with a higher health risk in the considered population. The doses of metals consumed by children are more than 2.3 times higher for the oral route, and over 1.7 times higher for the inhalation route compared to adults. The opposite is observed for the dermal route, where adults receive, on average, 50–60% higher doses of metals.

It is worth noting that for each of the three considered exposure routes, the calculated values of the hazard quotients (*HQ*) were below one. These results indicate a lack of significant non-carcinogenic risk levels resulting from exposure to heavy metals present in soils. The obtained *HQ* values indicate a dependence on the route of entry of metals into the human body and are the results of the exposure dose. The hazard quotient values decrease as follows: $HQ_{\text{ing}} > HQ_{\text{derm}} > HQ_{\text{inh}}$ both for adults and children.

The overall hazard (*HI*) indices for each single heavy metal through taking multiple exposure routes together, and the $HI_{\mathrm{Me}}$ indices for all heavy metals taken through a single exposure route were below one. These results indicate a low harmfulness of metals to human health in Wrocław. The health risk for children from lead ($1.8–1.3\cdot10^{-1}$), copper ($0.5–1.1\cdot10^{-2}$), and zinc ($1.8–1.9\cdot10^{-2}$) is more than twice as high as for adults. Health exposure determined by the $HI_{\mathrm{Me\_ing}}$ index shows 2.3 times greater risks for children compared to adults. The $HI_{\mathrm{Me\_inh}}$ value is 1.8 times greater in children for the inhalation route. By the dermal route ($HI_{\mathrm{Me\_derm}}$) 1.6 times higher exposure for adults was reported.

## 5. CONCLUSIONS

The present study shows the presence of selected elements of Cu, Zn, Pb, Cr, Ni, and Cd in soils after penetration of rainwater from roofs. All investigated sites are strongly polluted with Cd, Zn, and Pb, and, to a lesser extent, with Cu, according to *PI* and $I_{\mathrm{geo}}$ indices. Soils assessed were very highly to extremely highly enriched with these three main pollutants and minimally to highly enriched with Cu. Chromium and nickel do not contaminate the studied soils. The *EF* factor for Wrocław agglomeration confirmed the assessment using *PI* and $I_{\mathrm{geo}}$ indices and an anthropogenic origin of the studied metals. Multi-elemental pollution indices also show deterioration of soil quality and high pollution. According to all pollution indices, Zn, as the primary pollution element, probably originated from materials used for roofing and gutters, as well as road traffic and coal combustion. Fuel combustion, traffic activities, and domestic heating can also be sources of emissions of Cu and Cd. Pb may be in soil due to long-term deposition before the withdrawal of leaded gasoline.

Additionally, the principal component analysis and correlation analysis confirm information about three main emission sources of metals: leaching of components from roofing and guttering materials, road traffic (both exhaust and non-exhaust), and domestic combustion of fossil fuels.

Health risk analysis shows the main route of exposure is absorption of contamination by oral route for children and adults in both rings, followed by dermal contact. The inhalation route posed the least danger. However, the overall hazard index is low, suggesting a low risk for human health.

Future studies should focus on long-term monitoring of soil quality to assess changes in metal contamination levels over time and minimize health risk from uncontrolled use of contaminated rainwater for irrigation of food crops.

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