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Primary Soil Contaminants and Their Risks, and Their Relationship to Myocardial Infarction Susceptibility in Urban Krakow (Poland)

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Abstract

We recorded the concentrations, distributions and sources of 16 polycyclic aromatic hydrocarbons (PAHs), along with zinc (Zn), lead (Pb) and cadmium (Cd), in soils from different areas of Krakow—the city-centre, industrial and residential zones—and from outside the city. Their relationships to the soil properties were examined, and associations were established between the soil pollution in the different areas and myocardial infarction (MI) incidences in 5054 hospitalised patients who had lived in Krakow for more than 30 years. The PAH and Cd concentrations exceeded threshold-effect levels in the city-centre and industrial zones, while Zn, Pb and phenanthrene exceeded probable-effect levels. Industrial incineration processes, coal combustion and petrol-powered vehicles are the main sources of the PAHs, Zn and Cd, while the Pb originates mainly from historical accumulation and the use of Pb-enriched petrol. The mean number of MI incidences in Krakow equated to 0.72% of the residents, while in the city-centre and industrial zones it was ~ 2.8 and 1.2%, respectively. In the residential zone, the mean number of MI incidences was < 0.5% of the residents. These results may suggest that differences in MI incidence in Krakow residents is, at least in part, linked to chronic PAH and heavy-metal exposure.

Keywords Polycyclic hydrocarbons · Heavy metals · Long-term soil pollution · Hospitalised patients · Cardiovascular disease

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) are abundant pollutants in the environment due to their persistence, and their resistance to microbial and chemical degradation (Hiller et al. 2015; Wang et al. 2015, 2020). Increased emissions of these contaminants, which emanate from industry, traffic and indoor heating, are especially observed in urban areas due to dense population, and high energy consumption and exhaust production (Stogiannidis and Laane 2015).

The PAHs and HMs released into the atmosphere as a result of anthropogenic activities are eventually precipitated out, being deposited on soils, making them both a major reservoir for, and a potential source of, pollutants (Jiang et al. 2016). While PAHs are somewhat soluble, being readily adsorbed by soil particles, the mobility of HMs is controlled by alkaline reactions that favour their binding to soil organic matter, especially in urban soils (Ciarkowska and Gambus 2020; Wang et al. 2015). Therefore, the accumulation of PAHs and HMs in urban soils reflects centuries of habitation and/or the legacy of industrial activity (Peng et al. 2013).

A potential route from these soil pollutants to humans is via direct contact with contaminated soils through inhalation, dermal exposure and/or oral ingestion in both occupational and non-occupational settings (Kulawik et al. 2018). Certain experimental and epidemiological studies have indicated that chronic human exposure to PAHs results in the development and progression of atherosclerosis, arterial

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hypertension and some complications, such as myocardial infarction (MI) and stroke (Asweto 2018; Holme et al. 2019).

The effects of exposure to HMs on coronary artery disease (CAD) and the risk of MI are less evident. Most existing studies have serious limitations, including insufficient statistical power, lack of a comprehensive assessment of the exposure, and their cross-sectional design (Yang et al. 2020). However, a few studies have reported significant associations between cardiovascular disease (CVD) and exposure to HMs, especially lead (Pb) and cadmium (Cd) (Lamas et al. 2016; Solenkova et al. 2014).

Lead exposure has also been associated with an increased incidence in clinical cardiovascular endpoints, such CAD, stroke and peripheral arterial disease, as well as with other cardiovascular-function abnormalities, such as left ventricular hypertrophy and alterations in cardiac rhythm (Navas-Acien et al. 2007). The impact of zinc (Zn) on the incidence of MI is not unambiguous, with some authors having postulated that higher concentrations of Zn considerably increase the chances of having MI (Nowicki et al. 2021), while others have not established any link between MI risk and Zn concentration (Martin-Moreno et al. 2003).

In order to assess PAH- and HM-related risks, a clarification of the sources of these pollutants in urban areas is needed. One of the methods that allows for the differentiation of PAH contamination sources is the use of diagnostic ratios based on differences in thermodynamic stability (Katsoyiannis et al. 2011; Santos et al. 2017). Diagnostic ratios are widely used to distinguish between petrogenic (i.e. originating from petroleum) and pyrogenic (i.e. deriving from combustion) PAHs (Peng et al. 2013; Yunker et al. 2002), while an effective assessment of soil contaminated with HMs may be performed using pollution indices (Ciarkowska 2018). Mapping of the spatial distribution of pollutants and their toxicity threshold effects, as suggested in the Sediment Quality Guidelines (SQGs 2020), is a useful tool for assessing the human and ecological risks, and assists in the development of strategies aimed at protecting humans against harmful, long-term contaminant accumulation (Chagas et al. 2016; Ciarkowska and Gambus 2020).

The soil quality in urban environments is of vital importance to the residents because it can affect human health and ecosystems in many ways (Jiang et al. 2016). Consequently, in recent years, much attention has been paid to urban soils polluted with PAHs (Jiang et al. 2016; Wang et al. 2015), HMs (Ciarkowska and Gambus 2020; Solek-Podwika et al. 2016) and their combined effects (Ciarkowska et al. 2019; Peng et al. 2013; Wang et al. 2020).

However, up-to-date contaminant levels from PAHs and HMs, their risk indices and historical associations, including their possible relationships with MI occurrence, based on data from hospitalised residents from the studied areas, are still missing. To address this, we: (i) assessed PAH and HM soil contamination in relation to the functionality and population density in different parts of the city of Krakow; (ii) indicated the possible sources of contamination; (iii) evaluated the relationships between soil properties and the contaminants; and (iv) compared the soil pollution in different functional areas of Krakow with MI incidence in hospitalised residents.

This study adds to the knowledge base on how to assess the pollution status of soils in urban areas and their risks to the residents, and the results may guide actions that can be taken to reduce the incidence of CVDs in the local inhabitants.

Materials and Methods

Study Area and Sampling

The study was carried out in Krakow (50.0304100 N, 19.5601800E), which for years has been classified by the European Environment Agency (EEA) as one of the cities with the highest number of days per year in which permissible amounts of falling dust are exceeded in Europe (EEA 2021). Soil samples for testing were taken from sodded areas at 25 locations in Krakow: (i) the historical city centre, dominated by compact buildings, and where, until recently, the only source of heat has been coal-fired stoves; (ii) residential districts with various building types, generally supplied with heat from the central power plant of the city; and (iii) the industrial eastern part of the city, where a large ironworks, a cement plant and power plant have been operating for almost 80 years. For comparison, three reference soil samples were collected from non-cultivated, sodded grounds in the area of the Jurassic Landscape Parks Complex near Ojcow, ~25 km north of Krakow (Fig. 1S).

Each soil sample weighed ~1 kg, and consisted of 10 subsamples taken from the 0–10-cm layer over an area of ~3×3 m (the locations are indicated in Fig. 1S). Prior to analysis, the samples were dried at room temperature and sieved through a 2-mm-mesh sieve.

Laboratory Analyses

Basic Soil Analysis

The particle size distribution in the samples was established using the densimetric-sieve method, with the amount of clay being presented as a percentage. The pH values were determined potentiometrically in a suspension of soil with deionised water at a ratio of 1:2.5 (Tan 2005). The total carbon (TC) and nitrogen concentrations were determined using an automatic CNS analyser (Elementar Vario MAX CUBE), with detection limits of 0.001% for all elements determined.

The cation exchange capacity (CEC) was determined as the sum of the calcium, magnesium, sodium and potassium cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and hydrogen ions (H^+) forming the soil hydrolytic acidity (HA) associated with the soil sorption complex. The basic cations were removed from the sorption complex using ammonium acetate, and H^+ using calcium acetate (Tan 2005). The available phosphorous (P_{av}) and potassium (K_{av}) contents in the soil were determined using the Egner method, after they were moved into solution using a calcium lactate solution acidified with hydrochloric acid to pH = 3.55 (Tan 2005).

Determination of HM and PAH Concentrations

The concentrations of Cd, Pb and Zn and 16 PAHs were determined from sample fractions obtained after grinding and sieving through a 100-mesh sieve. The HMs were measured following digestion of the sample in a mixture (1:3 v/v) of concentrated acids ($HClO_4$ and HNO_3) using an atomic-emission spectrometer (PerkinElmer ICP-OES Optima 7300 DV). The PAH contents, including naphthalene (Naf), acenaphthylene (Anaf), acenaphthene (Acnaft), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Py), chrysene (Chr), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3,cd)pyrene (Inp), dibenzo(ah)anthracene (DibA) and benzo(ghi)perylene (BeghiPe), were analysed after extraction of the sample with 2-propanol and determination using a gas chromatograph (Varian GC/MS/MS 4000) equipped with a FactorFour VF-17MS capillary column.

These methods, as well as analysis quality-control procedures, have been described in detail in our previous publications (Ciarkowska and Gambus 2020; Ciarkowska et al. 2019) and are also included in the Supplementary Materials.

Patients

The data used came from a cross-sectional, retrospective cohort study. From a database of the John Paul II Hospital (which treats patients with acute coronary syndromes from all districts of the city of Krakow, Poland), 7789 patients, hospitalised between December 2012 and December 2017, and with a final diagnosis of MI at discharge, were selected. Patients with MI who died during hospitalisation were included, but participants with unstable angina and MI in the absence of obstructive CAD were excluded from the study. Only inhabitants who had lived in Krakow for at least 30 years, and who resided there at the time of the onset of their MI, were included in the study. The clinical diagnoses of MI were performed by cardiologists and were based on the presence of clinical symptoms and elevated troponin or creatine kinase–MB concentrations, as well as electrocardiograph analysis. In all the study patients, a coronary angiography was performed to confirm the CAD. The final study sample included 5054 participants.

Ethics

A retrospective study protocol was approved by the ethics committee of the Jagiellonian University, Krakow (KBET 1072.61.20.283, obtained by EK). The study protocol also complied with the Declaration of Helsinki.

Data Processing and Calculations

The soil descriptive statistics calculated included the mean, median, standard deviation, and minimum, maximum and coefficient of variation (CV). The Bonferroni correction was applied post hoc (at $\alpha \leq 0.05$), in order to estimate the least significant differences between the mean values of homogeneous groups. The sources of the PAHs and HMs, and their relationships, were investigated by factor analysis using the varimax rotation method. Principal component analysis (PCA) was performed in order to demonstrate relationships among the examined variables (soil parameters) and the soils from different sites. To meet the requirements for an analysis of variance (additivity, homogeneity of variance and normality of distribution), the data were subjected to logarithmic transformation prior to PCA. All continuous variables (regarding the patients) were expressed as the mean standard deviation (SD), with categorical variables being expressed as percentages. The Mann–Whitney U test was used to compare both normally and non-normally distributed continuous variables. The chi-square test was applied to evaluate the differences in categorical variables between the respective study groups. All the statistical tests were two-sided. The relationships between the data were assessed by Spearman's rank correlation coefficient. Statistical significance was accepted at $\alpha \leq 0.05$.

All statistical analyses were conducted using Statistica PL v.13 software (2019, StatSoft Inc., Poland) and Canoco 5 (ter Braak and Smilauer 2012).

Kriging-method maps of the studied area, showing the soil sampling locations and the spatial distributions of Cd, Pb, Zn and PAHs in the soils, were created using Surfer 19.0 software.

The toxicity equivalency factor (TEF) was estimated based on the relative toxicity of a PAH compared to a reference chemical. For the PAHs, the reference chemical was BaP. The reference compound was assigned a TEF of 1, whilst the other seven most toxic PAHs ($_{tox}$PAHs) among the 16 (i.e. BaP, BaA, BbF, BkF, Inp + DibA and Chr) were assigned TEFs that were order-of-magnitude estimates of their potency. To assess the risk from a mixture of $_{tox}$PAHs (i.e. to estimate the BaP-equivalent concentration, BaP_{eq}),

the concentration of the individual chemical (Ch) was multiplied by its TEF value (Bull and Collins 2013; Jiang et al. 2016; Santos et al. 2017):

$$BaP_{eq} = \Sigma(Ch \times TEF) \tag{1}$$

Potential ecological risk (RI) is an indicator used to assess the degree of environmental risk caused by the concentration of HMs in a soil:

$$RI = \sum_{(i=1)}^{m} Er^i \tag{2}$$

$$Er^i = Tr^i \times Pi \tag{3}$$

where Er is a single index of the ecological risk factor, m is the number of studied HMs, Tr^i is the toxicity response coefficient of the HMs (Håkanson 1980), and Pi is the pollution index of a single HM. The potential ecological risk classes are (according to Håkanson 1980): ≤ 90, low; 90–180, moderate; 180–360, strong; 360–720, very strong; and > 720, highly strong.

Results

Basic Soil Properties

The descriptive statistics of the site-related grouped soil properties are presented in Table 1S. Generally, the soils had similar properties, in terms of the amount of clay, TC, N, K_{av} and CEC values. Statistically significant differences were noted only in pH, HA value and amount of P_{av}. The reference soils from outside of Krakow were slightly acidic, while the mean pH value for all the urban soils was 7.0. Thus, the HA of the reference soils was higher than for the soils from Krakow. In the city-centre soils, there were greater mean amounts of P_{av} (265.7 mg/kg) than in the industrial zone soils, where this value was 126.4 mg/kg, while in the reference and residential-zone soils, P_{av} was the lowest (79.18 and 66.7 mg/kg, respectively).

PAH Concentration and Distribution

In the city-centre and industrial zones of Krakow, the concentrations of individual PAHs were higher than the threshold-effect levels (TELs) for these and, in some cases (e.g. Phe in both areas and Ant in the industrial zone), they exceeded the probable-effect levels (PELs) established by the SQGs. In the city centre, Chr, BaA, BkF, BbF and BaP, and all the PAHs in the industrial zone, exceeded the permissible values established by Polish national regulations (Ministry Directive 2016). In the residential zone, only Phe exceeded its TEL, whilst in the reference areas, the PAH

concentrations were much lower than all of the permissible values (Table 1). The sums of the 16 PAHs from the city-centre and industrial zones were similar, and exceeded 5000 μg/kg. These amounts were higher than the low-effect-range values (ERL). In the residential zone, the sum of the PAHs was about 10 times lower than in the city-centre and industrial zones, but still higher than the no-effect level (NEC). Safe total amounts of PAHs of 58.8 μg/kg were determined only in the reference area located outside Krakow (Table 1).

The concentrations of PAHs in the studied zones have been illustrated in maps of the spatial distributions of the sums of the PAHs, and of the seven most toxic PAHs—BaA, Chr, BkF, BaP, BbF, Inp and DibA—and BaP, individually (Fig. 1A–C). The maps show three zones with high concentrations of the 16 PAHs, toxic PAHs and BaP—the city centre and two industrial zones (Nova Huta, with its large metallurgical complex, and Łęg, where a heat and power plant is located). Much lower concentrations of the PAHs were recorded in the residential areas (Mistrzejowice, Bronowice and Dębniki).

The concentrations of individual PAHs grouped by site indicate the similarity between the soils in the city-centre and industrial zones. The amounts of all the PAHs were significantly higher in the city-centre and industrial zones than in the residential zone and reference areas (Fig. 2).

Zn, Pb and Cd Concentrations and Distribution

The mean amounts of three of the HMs (Cd, Pb and Zn) established in the soils of the city-centre and industrial zones were significantly higher than in the residential zone and reference locations. Concentrations of Zn in the city-centre and industrial-zone soils amounted to 662.2 and 846.2 mg/kg, respectively, with Pb being 142.3 and 118.6 mg/kg, respectively. The amounts of Zn were significantly higher in the industrial- than in the city-centre-zone soils, contrary to the Pb level, which was highest in the city-centre soils (Table 1). The levels of both Zn and Pb determined in those zones exceeded the PELs established by the SQGs. Zinc was also higher than the permissible values established by Polish regulations in the soils of the industrial zone (Table 1). The mean Zn (299.8 mg/kg) and Pb (47.6 mg/kg) concentrations in the residential zone exceeded their TEL values, with Pb being higher than its TEL value even in the reference soils. The concentrations of Cd in the city-centre and industrial zones, which amounted to 1.5 and 1.6 mg/kg, respectively, both exceeded the TEL values (Table 1). The distributions of Zn, Pb and Cd (Fig. 1D–F) indicated increased accumulations of these HMs in soils in the same areas as the PAHs—that is, in the city centre, and around the power and heat plant in Łęg and the Nowa Huta smelting complex, both in the industrial zone. This accumulation of HMs suggests

Table 1 Comparisons of PAHs and HMs in analysed areas with background, Polish legislation and Sediment Quality Guidelines[2] values

Pollutant	Mean amounts				Background	Polish regulation	NEC[3]	TEL[4]	ERL[5]	PEL[6]
	Cen	Ind	Res	Ref						
Naf	58.2	94.0	15.16	4.47	n.d[7]	100		30	160	390
Anaf	40.7	59.1	5.62	0.95	n.d	–		10	20	90
Acnaft	83.4	115.2	10.44	3.26	n.d	–		10	40	130
Flu	102.3	123.1	17.47	5.89	6.0	–		20	20	140
Phe	764.1	791.8	103.1	11.89	1.5	–		90	240	540
Ant	206.4	240.0	21.34	1.12	1.2	200		50	260	240
Fla	1003.2	997.1	107.1	6.91	8.9	–		110	600	1490
Py	789.6	865.7	86.03	4.92	4.9	–		150	660	1400
Chr	381.0	383.0	40.18	3.69	6.5	200		110	380	850
BaA	340.9	328.3	31.33	2.28	5.1	100		70	260	690
BkF	277.5	269.4	22.26	2.39	4.4	100		60	280	610
BbF	356.6	322.7	30.10	4.98	8.9	100		70	320	710
BaP	502.3	596.6	56.47	4.10	2.9	100		90	430	760
Inp + DibA	75.0	60.9	7.55	0.79	17.0	100		–	–	135
BeghiPe	69.9	60.1	8.98	1.16	14.0	200		–	–	–
Sum PAHs	5051.1	5307.0	563.1	58.8	n.d	–	190	870	3500	8040
Zn	626.2	846.2	299.8	90.2	150	500		123	120	315
Pb	142.3	118.6	47.6	38.72	20	200		35	35	91.3
Cd	1.5	1.6	0.9	0.8	0.7	2		0.6	5	3.53

PAHs in µg kg^{-1}, HMs in mg kg^{-1}, [1]Regulation…2016, [2] Sediment Quality Guidelines. A review and their use in practice, [3]no effect conc. [4]treshold effect level, [5]effect range low, [6]probable effect level, [7]not detected,

similar sources for both the organic and inorganic pollutants. Similarly to the individual PAH concentrations, the amounts of Zn, Pb and Cd were significantly higher in the city-centre and industrial zones than in the residential zone and reference areas (Fig. 3).

Demographic Characteristics of the Functional City Areas and the Incidence of MI

The demographic and clinical data of Krakow inhabitants with significant CAD, who were hospitalised due to MI between December 2012 and December 2017, are presented in Table 2. The patients with MI were a well characterised group, in terms of risk factors other than pollutants, with atherosclerosis (including ageing, hypertension, diabetes, lipids disturbances, obesity) as a confounder, so they represented a perfect control group within themselves. In the group, there were no significant differences between the age and concomitant cardiovascular risk factors among the patients with MI who were inhabitants of different residential areas in Krakow. However, there was a positive correlation between the mean concentrations of seven toxic PAHs (BaP, BbF, BaA, BkF, Inp + Diba, Chr) ($r = 0.35$, $p \leq 0.002$) and between the mean concentrations of the HMs—Zn ($r = 0.70$, $p \leq 0.009$), Pb ($r = 0.36$, $p \leq 0.040$) and Cd ($r = 0.82$, $p \leq 0.001$)—and the rate of MI in the most polluted zones in Krakow. The results

were insignificant in the zones with the lowest concentrations of pollutants.

Table 3 shows the number of MI incidences in the patients in each of the studied zones in the given period of time. The number of patients with MI was compiled alongside the population density in each given area in order to obtain the share of residents in each area with MI, as well as the mean share of patients who had had heart attacks out of the total number of residents in the studied zones. The highest percentage of residents suffering from MI (2.77%) lived in the city centre, with those in the industrial zone representing 1.15% and in the residential zone 0.49%, out of the whole population of the given area. The mean percentage of residents in all the zones with a MI diagnosis was 0.72%, indicating a strong skew towards the city-centre and industrial zones.

Discussion

PAH- and HM-Related Sources of Soil Contamination

In the soils of all the studied locations, Phe, Fla, Py and BaP dominated among the 16 assessed PAHs, their presence primarily attributable to incineration processes, coal combustion and petrol-powered vehicles (Banger et al. 2010; Jiang et al. 2016; Wang et al. 2015), with Py also considered to be the most dominant PAH component emanating from tyre

Fig. 1 Spatial distribution of sum of 16-th PAHs **A**, 7-th toxic PAHs ((BaP, BbF, BaA, BkF, Inp + Diba, Chr) **B**, benzo(a) pyrene -BaP **C**, zinc-Zn **D**, lead-Pb **E** and cadmium-Cd **F** contents in soils of studied areas
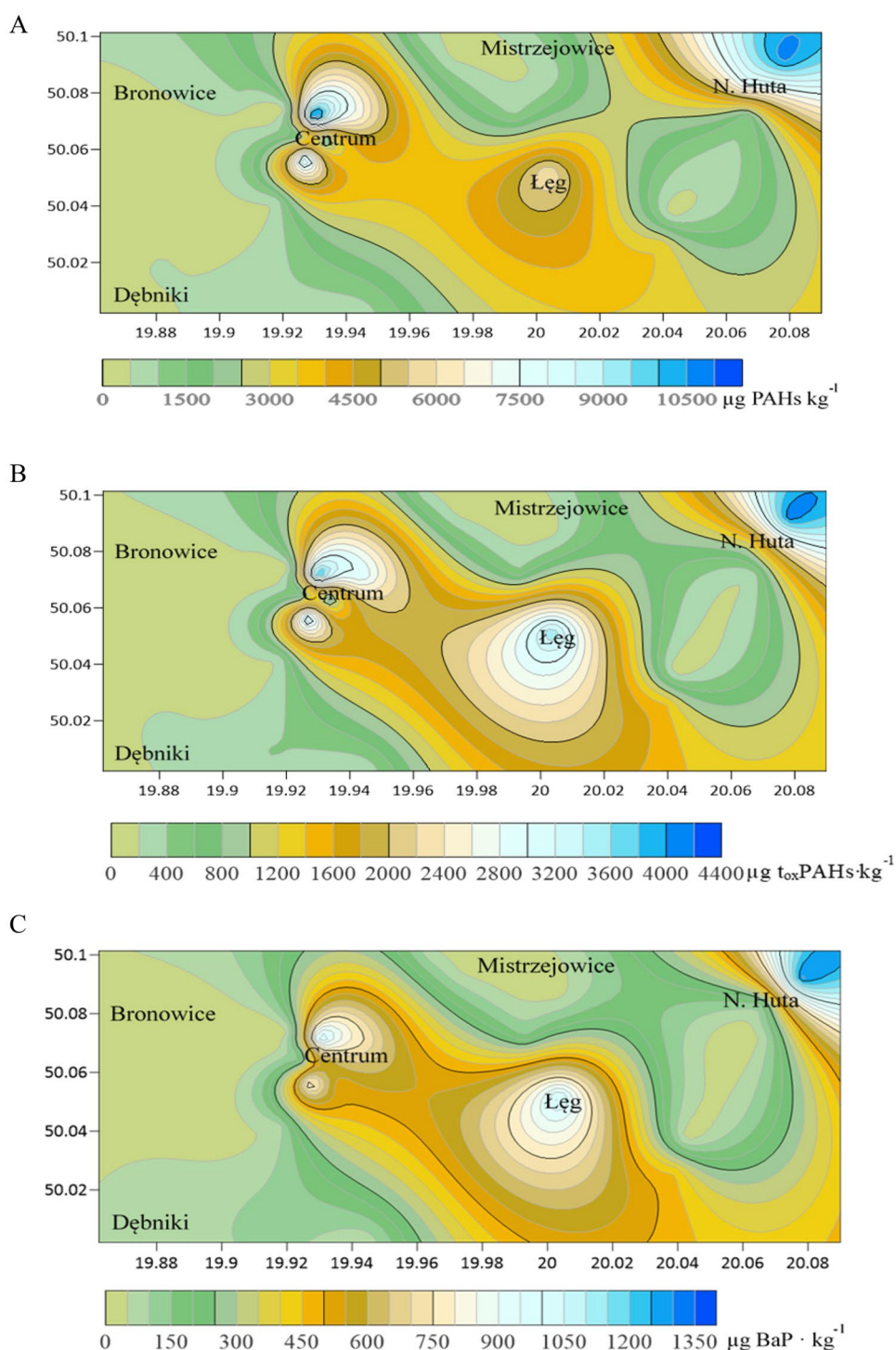
abrasion and tailpipe soot (Hiller et al. 2015). To further distinguish the possible sources of the PAHs, individual PAH ratios were calculated (Table 3). The ratio of low-molecular-weight (LMW) to high-molecular-weight (HMW) PAHs and their individual ratios indicated petrogenic sources for the Phe:Ant PAHs in the reference soils, and a pyrogenic (mainly from coal combustion) source for the soils in the other areas (Hiller et al. 2015; Peng et al. 2013). Moreover, a lower share of LMW PAHs in the city-centre- and industrial-zone soils, compared to the residential-zone and especially reference-area soils, can be explained by the LMW PAHs deriving mostly from natural sources, such as biological processes, which are much less important in urban areas than anthropogenic sources (Hiller et al. 2015). Greater

Fig. 1 (continued)
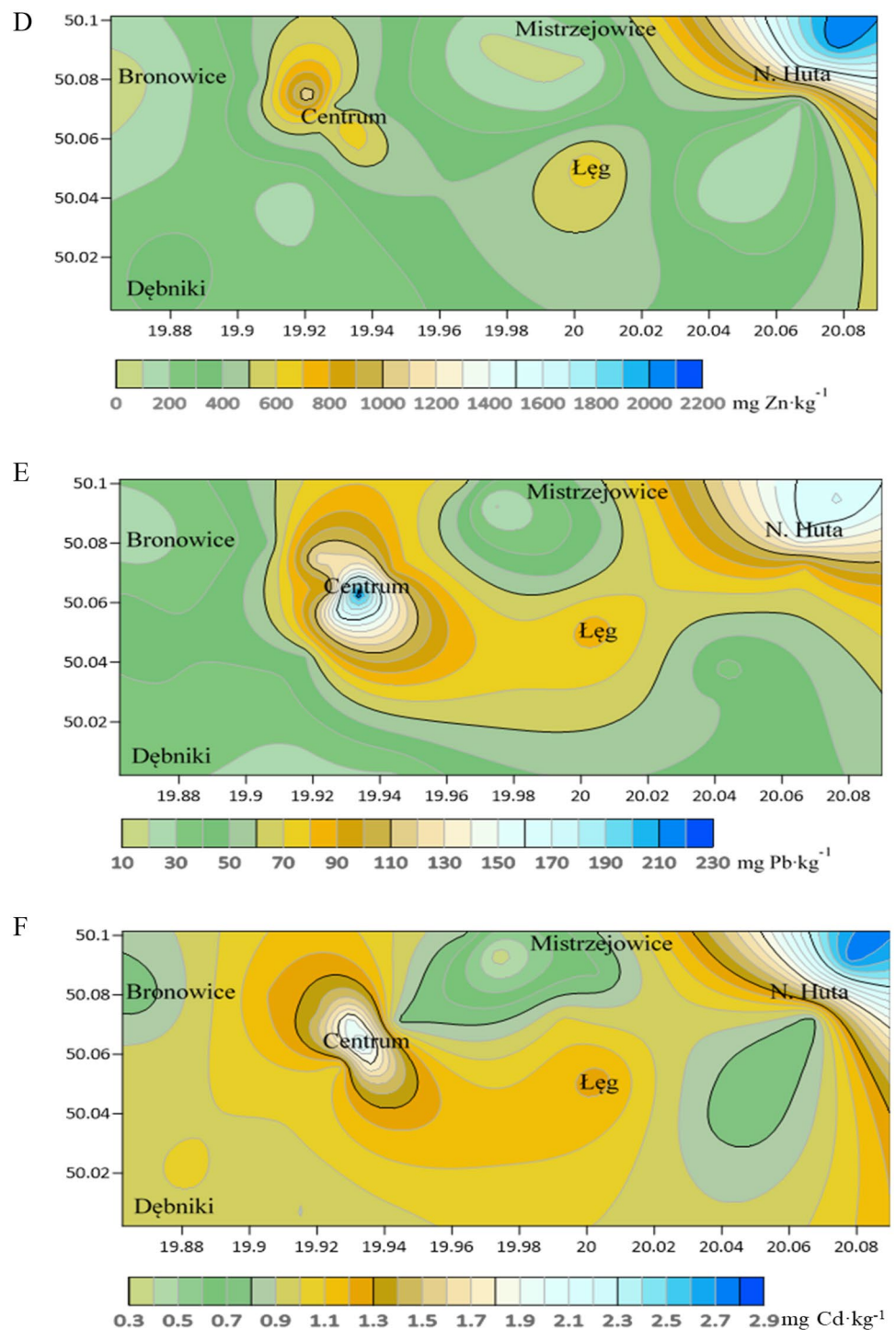
amounts of LMW PAHs in the residential zone than in the other urban areas reflects their spatial dispersion, this phenomenon being related to the progression of urbanisation, as observed by Peng et al. (2013) in urban and suburban locations. They can also indicate recent pollution, since LMW PAHs are more biodegradable and less lipophilic, and so are not expected to persist or be sorbed as strongly as HMW PAHs (Jiang et al. 2016). The different sources of the PAHs in the reference soils compared to the urban soils is emphasised by the Flu:Py and Flu:Flu + Py ratios, which indicate gasoline emissions in the urban soils and diesel emissions and/or wood combustion in the reference soils (Peng et al. 2013). However, there were also ratios (BaP:BeghiPe and Fla:Fla + Py) that suggested that a share of the PAHs came from the same sources in all the studied areas, such as from traffic and coal combustion.
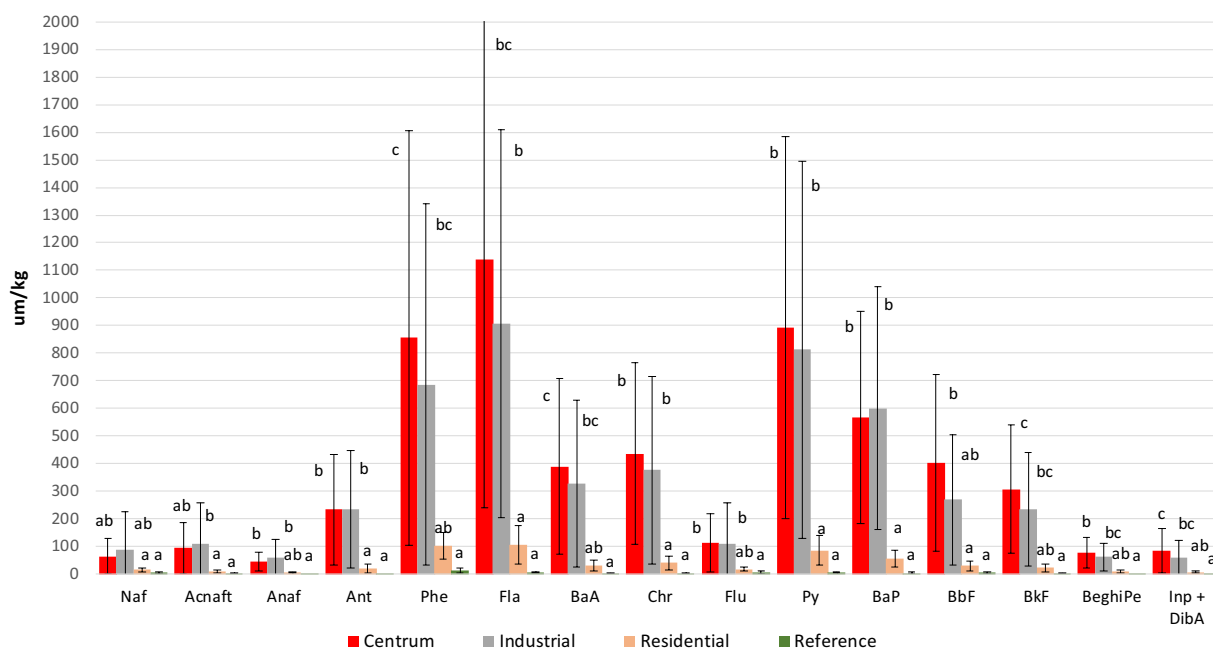
Fig. 2 Distribution of individual PAH contents grouped site related: naphthalene (Naf), acenaphthene (Acnaft), acenaphthylene (Anaf), anthracene (Ant), phenanthrene (Phe), fluoranthene (Fla), benzo(a) anthracene (BaA), chrysene (Chr), fluorene (Flu), pyrene (Py), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(ghi)perylene (BeghiPe), indeno(1,2,3,cd)pyrene (Inp) and dibenzo(ah)anthracene (DibA)
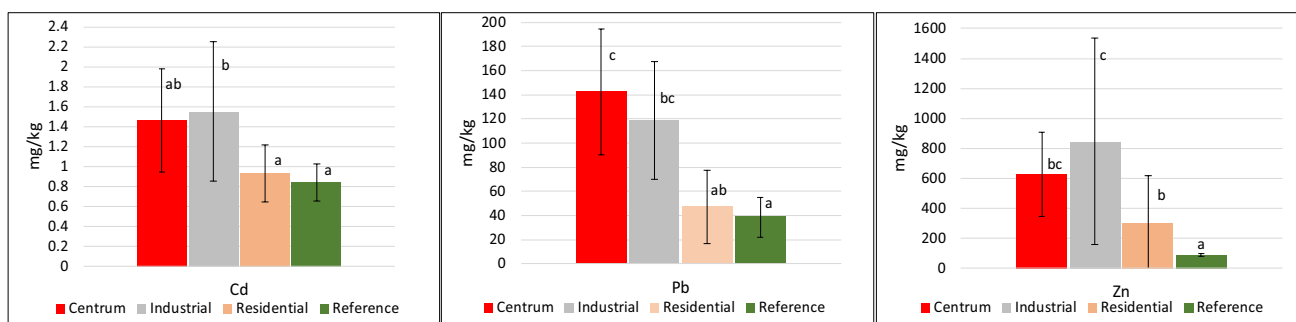
Fig. 3 Zn, Pb and Cd contents grouped site related

The individual ratios of the PAHs tentatively identified traffic and coal combustion as sources for the Krakow PAH and HM soil contamination. In order to refine the sources of the contaminants, and to understand the relationship between the accumulation of PAHs and Zn, Pb and Cd in the soils, a factor analysis was performed (Fig. 4). The first factor explained a total variance of 63.8% in the data. This factor was determined by BaA, BaP, BbF, BkF, BeghiPe, Inp + DibA, Fla, Chr and Py, with all of them being strongly correlated. These are predominantly HMW PAHs with four to six rings, and are the most toxic. They are known to derive from the incomplete combustion and pyrolysis of hydrocarbon-based fuel. Inp and BkF have been found in

gasoline-based vehicle soot, and both gas and diesel engine emissions (Santos et al. 2017; Wang et al. 2015). High concentrations of BeghiPe and BaP in road dust from urban areas and traffic tunnels suggest that these are tracers of auto emissions (Stogiannidis and Laane 2015). The abundance of these compounds has been considered as an index for the determination of auto exhaust from gasoline engines. Therefore, this factor was selected to represent a combustion source for the PAHs. Several studies have identified Py, BaA, Chr and Fla as markers of coal combustion because these individual PAHs are dominant in coal-combustion profiles (Banger et al. 2010; Stogiannidis and Laane 2015). In Krakow, coal is the main energy source, and is also widely

Table 2 Demographic and clinical characteristics of the study population (N = 5 054)

Parameter	Value
Age, y, mean (SD)	73.3 (12.5)
Male sex, *n* (%)	3437 (68)
Arterial hypertension, *n* (%)	4397 (87)
Diabetes, *n* (%)	3386 (67)
Obesity, *n* (%)	3487 (69)
Hyperlipidemia, *n* (%)	3437 (68)
Smoking, *n* (%)	1415 (28)
Infections before hospital admission, *n* (%)	101 (2)
Primary PCI, *n* (%)	4902 (97)
Primary CABG, *n* (%)	126 (2.5)
Only pharmacological treatment, *n* (%)	25 (0.5)
Previous MI, *n* (%)	1263 (25)
Heart failure, *n* (%)	708 (14)
In-hospital deaths, *n* (%)	303 (6)

MI myocardial infarction, *PCI* percutaneous coronary intervention, *CABG* coronary arteries bypass grafting

used for industrial and domestic purposes, such as house heating. During indoor coal burning, particulate matter is emitted that is mostly soot coated with a mixture of various toxic chemicals, including PAHs (Liu et al. 2008). Therefore, it is reasonable to assign these PAHs to coal-combustion and traffic-related sources, which, considering the large share of these PAHs, can be considered to be the primary sources of these pollutants.

The second factor, responsible for 12.7% of the total variance, was related to Acnaft, Naf, Flu and Phe. Apart from Flu, these are LMW PAHs, which originate from petrogenic sources. Their concentrations in the soils may have resulted from oil spills, biomass and wood combustion, and incineration processes, with Naf also likely forming during biological processes (Ciarkowska et al. 2019; Peng et al. 2013).
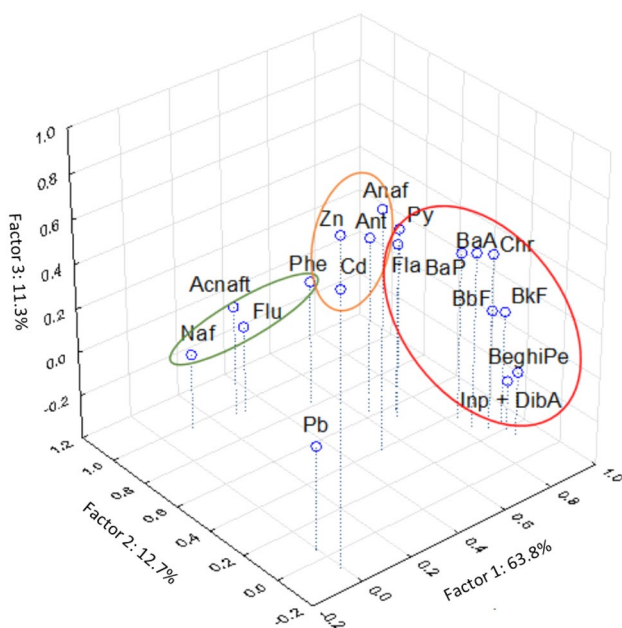
The third factor explained 11.2% of the total variance, and was composed of Zn, Cd and Anaf. These pollutants likely originate from industrial sources, such as coking and smelting processes (Jiang et al. 2016). Contamination with HMs from metallurgical activities has already been determined in soils located near steel plants in Poland (Nowa Huta, Krakow) (Ciarkowska and Gambus 2020), Madrid, Spain (Garcia-Guinea et al. 2010) and Iraq (Khudhur et al. 2018), as well as around Zn/Pb metallurgical plants in Poland (Ciarkowska and Gambus 2005), and in heavily-industrialised regions in China (Jiang et al. 2016; Li et al. 2015; Yang et al. 2018) and the United Kingdom (Zahid et al. 2017), raising concerns about inhabitant health risks. According to Wang et al. (2020), environmental Zn and Cd levels are directly related to industrial sources, whereas Pb levels are typically influenced by traffic activities. In fact, Pb was the only HM explained by the fourth factor, constituting 5.8% of the variance, and probably represents historical accumulation connected to many years of using petrol enriched with Pb.
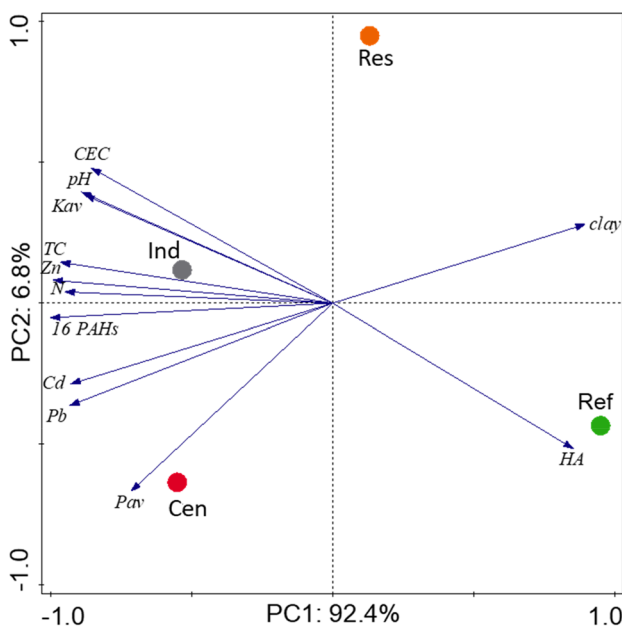
Relationship Between Soil Properties and Contaminants

A PCA was performed to reveal relationships between the soil properties, such as pH, TC and N content, CEC, K_{av} and P_{av}, and the Zn, Pb, Cd and 16 PAH contents in the soils of the given functional zones (Fig. 5). The graph shows strong correlations between CEC, pH, K_{av}, P_{av}, TC, Zn, N, the 16 PAHs, Cd and Pb, with high values being characteristic of soils from the city-centre and industrial areas, and much smaller values being related to the residential and especially reference soils. Gradual changes in

Table 3 Functional areas characteristics and MI incidence

Sources indicators	Scales	References	Centrum	Industrial area	Residential area	Reference area
∑LMW/∑HMW	<1 = pyrogenic >1 = petrogenic	Banger et al. (2010)	0.75	0.75	0.91	1.04
Phe/Ant	>10 = petrogenic <10 = pyrogenic coal/wood combustion	Yunker et al. (2002)	3.67	2.93	4.83	10.62
Flu/Py	<1.0 = gasoline 1.0–1.4 = biomass, coal combustion		0.13	0.14	0.20	1.20
BaP/BeghiPe	<0.6 = non-traffic >0.6 = traffic	Katsoyiannis et al. (2011)	7.40	9.66	6.29	3.54
Flu/Flu + Py	<0.5 = petrol emission >0.5 Diesel emissions		0.11	0.12	0.17	0.54
Fla/Fla + Py	<0.4 = petrogenic 0.4–0.5 = fossil fuel >0.5 wood/coal combustion		0.56	0.53	0.55	0.58

Fig. 4 Loading plot of factor analysis for PAHs and HMs

these soil properties occurred according to the first axis, which formed the first principal factor. It explained 92.4% of the variability, and may be associated with an anthropogenic effect on the soil properties. It reflects an influence of the intensity and length of time during which the studied areas were submitted to certain human activities, from the soils most affected by humans in the city centre, to a little less affected in the industrial zone, followed by much less affected in the residential zone and, ultimately, little affected in the reference areas. The soils of the oldest historical area (Krakow Centrum), which has been inhabited since medieval times, are characterised by high amounts of P and Pb, both immobile elements. The enrichment in P is likely connected to past human activities, when garbage was simply dumped on the ground, along with human waste (especially residues from human and animal bones), as explained by Kowalska et al. (2016), who examined the soils from under the Main Market in Krakow. A high P content, and traces of anthropogenic additions of this element, is also typical of convent garden soil in Krakow (Halecki and Gasiorek 2015).

The high accumulations of Pb in the soils of the city centre originate from two sources. One is connected to olden times, when the city was a centre of the Pb metal trade, with processing being located close to Pb mining activities, as noted by Kowalska et al. (2016). The other is connected to heavy traffic, and the use of petrol containing Pb in the twentieth century. This Pb enrichment in the soil can still be found in other towns in Poland, even non-industrialised ones, such as Zakopane, as automobiles were one of the major sources of Pb emitted into the environment up to 2001 (Ciarkowska 2018). The Pb content was correlated with Cd, these two HMs often occurring together with Zn, with Cd and Zn being emitted as a result of tire abrasion. These are the reasons for their accumulation in soils in the oldest part of Krakow.

The industrial zones are mainly characterised by high accumulations of Zn and PAHs, as well as the highest TC, N and K contents. These areas are located in the eastern part of the city, where a large industrial complex—including steel, cement and coke plants—is situated, as well as a heat and power plant that uses coal. These plant activities have produced high emissions of Zn and PAHs, but have also increased the soil pH values and K contents. In addition to the HMs, the cement plant located close to the steel smelter emits alkaline dust, with the carbonates (from limestone) contributing K during steel production (Ciarkowska and Solek-Podwika 2012; Ciarkowska et al. 2019). Anthropogenic HMs are preferentially associated with carbonate minerals because they have similar ionic radii and can substitute for the cations in carbonate compounds (Li et al. 2015). For this reason, the Zn was positively correlated with K_2O, and the pH increased as a result of the alkaline dust emissions.

Fig. 5 Principal component analysis (PCA) showing the relationship between the examined variables (selected soil parameters) and soils of different functional areas. In PCA following soil parameters were included: pH, clay, cation exchange capacity (CEC), hydrolytic acidity (HA), total carbon (TC), total N (N), available P (P_{av}), K (K_{av}), total Cd, Pb, Zn and sum of 16th PAH contents. Sampling areas: Cen—central areas of Krakow; Ind—Krakow industrial areas; Res—Krakow residential areas and Ref—reference areas located outside Krakow

Soils from the residential zone were much less affected by human activity than those of the city-centre and industrial zones. The residential areas have been built up relatively recently, with dispersed buildings, new heating technologies (gas or electrical) and wide streets free of traffic congestion, and so there is a much shorter history of human activity in these areas. The factor of length of human occupation seems to be quite important, considering that the strong negative influence of the large industrial complex in the industrial zone, resulting in highly polluted soils in the area, is comparable to the effect of the less intense, but more long-lasting, influence of human activity in the centre of the city. The effect of the age of urban areas on PAH concentrations in soils has also been documented in other cities, such as Bergen, Norway (Haugland et al. 2008), Beijing, China (Liu et al. 2010) and Bratislava, Slovakia (Hiller et al. 2015), where urban soils in the oldest parts of the cities were found to have much higher PAH concentrations than soils in the outer and younger parts.

The variability in the reference soils can be explained by their having the highest HA values and the lowest pollution indicators. These soils, from outside the city (about 30 km away), were the most natural. Their low pH values are typical of soil in the humid climate of Poland. The PC2 factor, which explained only 6.8% of the variance in these soils, is probably connected to their natural variability.
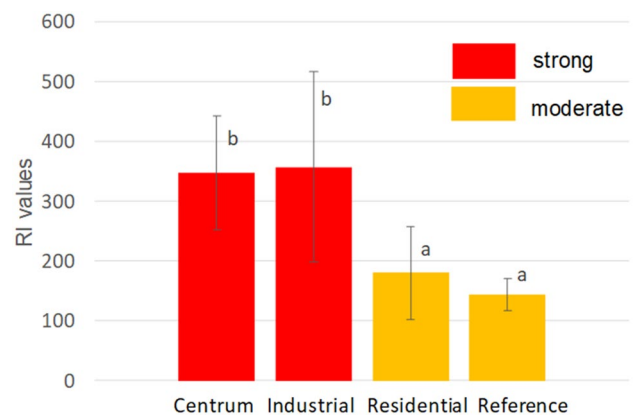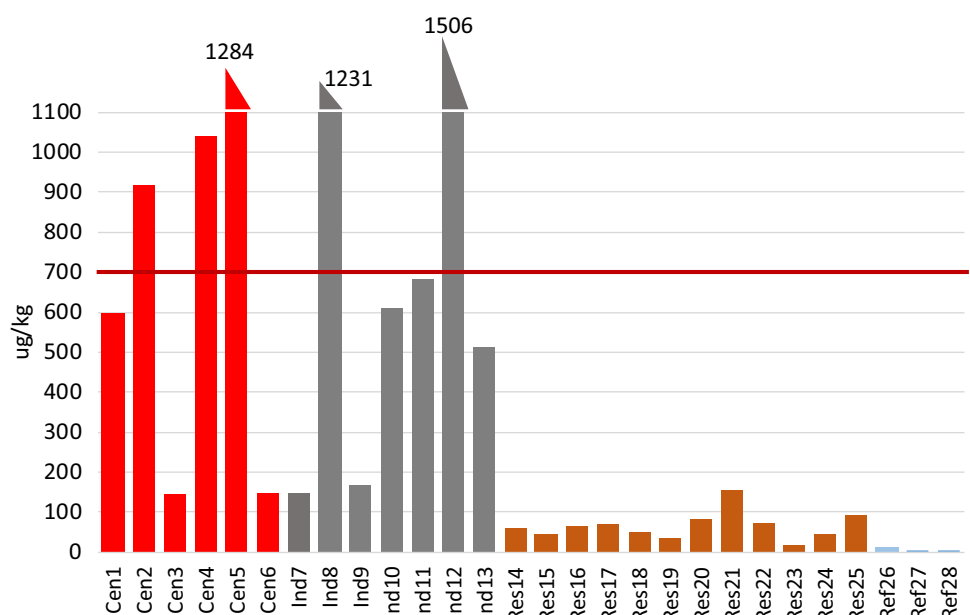
PAH and HM Toxicity and Related Risks

Health risk assessments associated with PAH uptake are often estimated on the basis of BaP concentrations, with BaP being considered the most toxic PAH in almost every study (e.g. Bull and Collins 2013; Wang et al. 2015, 2020).

The toxicity of the $_{tox}$PAHs was determined as the sum of BaP_{eq} (Eq. 1) for each studied zone (Fig. 6). Among the soils of the studied locations, three out of six in the city centre and two out of seven in the industrial zone had concentrations above safe values (700 μg/kg BaP_{eq}), as established by the Canadian SQGs for the protection of environmental and human health (CCME 2015; Liu et al. 2010). All the BaP_{eq} concentrations in the residential and reference soils were at safe levels.

The potential ecological risk values for the soils of the city-centre and industrial zones were significantly higher than for the soils in the residential and reference locations (Fig. 7). These high values in the former locations indicate a strong potential ecological risk in these areas, according to Håkanson (1980), while the soils in the latter areas have moderate ecological risk.

Fig. 7 Potential ecological risk index (RI) values

Fig. 6 Sum of toxic equivalent concentrations (BaP_{eq}) in soils of each studied area

Myocardial infarction—one of the complications of atherosclerosis—is caused by unstable atherosclerotic plaques causing the sudden thrombotic occlusion of a coronary artery. However, the aetiology of atherosclerosis and MI is known to be multifactorial, and different environmental factors should always be assessed as additional risk factors for atherosclerosis and MI. Short-term and chronic exposure to different environmental chemicals are taken into consideration as additional factors that can modulate the development and progression of different cardiovascular disorders (Alhamdow et al. 2019; Cosselman et al. 2015; Konduracka et al. 2019; Tellez-Plaza et al. 2008).

Our study indicates a relationship between the frequency of MI incidences among the citizens of Krakow, who are well characterised in terms of CAD risk factors, and their residential zones, which differ in the degree of PAH and HM contamination. The number of patients hospitalised in Krakow with MI who lived in locations where the soils were the most PAH- and HM-polluted (i.e. in the city centre) was about four times higher than the overall average number of patients hospitalised for this reason ($n=5054$), and about six times higher than the MI patients from residential locations with the lowest PAH and HM soil contamination (Table 4).

Our findings are consistent with epidemiological and toxicological evidence that environmental PAH exposure is a risk factor for CVD, including CAD (Alhamdow et al. 2019; Asweto 2018; Burstyn et al. 2005). Holme et al. (2019) indicated a monotonic, but non-significant, trend between chronic occupational exposure to BaP and acute MI in a cohort of 12,367 male asphalt workers from various nations. Similarly, the association between HMs, including Pb and Cd, and CVDs has already been reported (Lamas et al. 2016), with Pb and Cd being ranked second and seventh, respectively, in terms of environmental chemicals of concern by the Agency for Toxic Substances and Disease Registry (2019). Cosselman et al. (2015) indicated that residing in areas highly polluted with HMs is strongly associated with high levels of cardiovascular risk, but that adverse effects on cardiovascular health may occur at exposure levels below the current regulatory standards. The findings of a meta-analysis that used 871 references limited to clinical CVD (Tellez-Plaza et al. 2008) indicated a statistically significantly higher risk with higher Cd levels for all clinical cardiovascular endpoints, except for stroke. Overall, this is supportive evidence for Cd being a cardiovascular risk factor. In addition to clinical cardiovascular outcomes, chronic exposure to Cd has also been associated with CVD risk factors and with subclinical endpoints. A systematic review performed by Navas-Acien et al. (2007) provided sufficient evidence to infer a causal relationship between Pb exposure and elevated blood pressure, although this was not sufficient enough to infer a causal relationship between Pb and clinical cardiovascular outcomes or cardiovascular function tests. Indeed, no lower threshold has been established for any Pb/cardiovascular association. Because our study was aimed at finding possible relationships between the low quality of the Krakow urban environment and the MI incidences of its residents, we are not able to specify any strict dependence between the incidence of MI and the pollution of soil with Zn, Pb, Cd and PAHs. We are aware that the present study only found an association between PAH/HM exposure and CAD risk, whilst not proving that PAH and HM exposure actually causes CAD and MI. It should be emphasised that the classical risk factors of atherosclerosis (ageing, hypertension, diabetes, lipid disorders, etc.) are very important confounders in correlating between pollutants and MI occurrence, and are alternative variables to the contaminants associated with MI occurrence. Also, it is not possible to determine the percentage of pollutants involved in the incidence of MI. However, our findings suggest that these pollutants are neglected risk factors in MI prevention and mitigation, hence the need to address them. In addition, we acknowledge that it was not possible to analyse certain other confounders, such as individual susceptibility and occupational exposure, or they were not evaluated in this study. Heavy metals and PAHs may penetrate from the soil into plants, which may be eaten by humans and herbivores. The consumption of contaminated plants and animal products is an additional way for humans to be exposed to these contaminants.

Considering our increasingly greater exposure to HMs and PAHs in the environment, this study identified numerous implications for public health. The recognition of environmental factors, such as increased concentrations of PAHs and HMs, as additional priorities in considering the eradication of CVD can attract social and political support for targeted legislation, and the proposal of strategies and

Table 4 Site related diagnostic ratios of PAH sources in soils of Krakow and reference area

Area	Districts of Krakow	Surface km^2	Residents/km^2	Residents No	Hospitalized after MI Number	Hospitalized after MI % residents
Cen	I	5.57	5775	32 169	890	2.77
Res	II-XII, XV, XVI	194.1	2748	533 490	2 595	0.49
Ind	XIII, XIV, XVII, XVIII	127.1	1075	136 630	1 569	1.15
Together	I-XVIII	326.9	2149	702 289	5 054	0.72

Data on the population and area of districts for January 6, 2018 (Central Statistical Office, 2019)

preventive standards that can eliminate those environmental factors that significantly affect the health of residents. Some initiatives to reduce pollution in Krakow have already been undertaken, including a prohibition on heating homes with solid fuels and the expansion of zones that exclude vehicular traffic.

Conclusions

To conclude, our study has illustrated the diversity of soil contamination by Zn, Pb, Cd and PAHs related to the functional areas of the city of Krakow. Soils from the old and densely inhabited city-centre and industrial zones were found to be significantly more polluted than soils from the residential zone and locations outside Krakow. Some sites in the central and industrial zones that were characterised by toxicity indices, based on BaP toxicity, exceeded safe values, and the amounts of Zn, Pb and Cd in the soils in these areas showed a strong ecological risk.

In areas with higher concentrations of PAHs and HMs, more frequent incidences of MI were found among the residents, strongly suggesting that long-term PAH and HM exposure may be a risk factor for developing MI and CAD. Considering the chronic exposure of residents to PAHs and HMs in the environment, this study has important implications for the health of city inhabitants, and points to a need to take action to reduce pollutant emissions. A sequel investigation to establish the nature of the relationship between the exposure of the inhabitants to contaminants and MI incidences must be performed.

Declarations

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