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Deposited Particulate Matter Enrichment in Heavy Metals and Related Health Risk: A Case Study of Krakow, Poland †

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Abstract: The aim of these investigations was to determine the impact of heavy metals bound with deposited particulate matter (PM) on contamination degree and related toxicological effects by calculating enrichment indices, namely, the geo-accumulation index (I_{geo}), contamination factor (CF), and enrichment factor (EF), as well as the ecological risk index (ERI) and modified hazard quotient (mHQ). Calculations were made based on the selected element concentrations determined in deposited PM samples in Krakow. The results of the investigations revealed that deposited PM was enriched in heavy metals. As I_{geo} provides information on the level of metal accumulation, it was found that deposited PM was practically uncontaminated with Be, Cd, and Tl (class 0) but heavily to extremely contaminated (class 5) with Co and Sn and extremely contaminated (class 6) with As, Ba, Cr, Cu, Li, Mn, Ni, Pb, Sr, Ti, V, and Zn. On the other hand, the calculated values of CF revealed very high contamination of deposited PM with Cd and Zn, considerable contamination with Sn, Pb, and As, and moderate contamination with Cu and Li. Values of calculated EF revealed that among the investigated elements, only Zn originated from anthropogenic sources. For Cd, a small influence of anthropogenic sources was observed. For Pb and Sn, non-crustal sources of emission were expected. The calculated ERI values indicated potential ecological risk levels that were very high for Cd and considerable for Zn, as well as low potential ecological risk for As, Co, Cr, Cu, Ni, Pb, and Tl. Moreover, the calculated mHQ values of severity of contamination were extreme for Zn, considerable for Cr, and moderate for As, Cu, and Pb. The analysis revealed that the impact of atmospheric and re-suspended PM on inhabitants constitutes a complex effect of a mixture of heavy metals simultaneously affecting human health.

Keywords: air quality; particulate matter; heavy metals; contamination factors; health risk

1. Introduction

The air quality is of utmost importance due to its direct effect on human health. For many years, Krakow has been an example of a city with constant poor or even very poor air quality [1]. Analyzing the results of the ambient air quality monitoring network in Krakow, operated by the Regional Environmental Protection Inspectorate in Krakow (WIOŚ), it was observed that particulate matter (PM) is the key air pollutant [2–4]. Moreover, PM particles bind other contaminants, especially heavy metals, that, alongside PM, cause negative health effects after entering the body through inhalation, digestion, or dermal contact. Heavy metals cause many negative health effects associated with renal, cardiovascular, blood, nervous, or bone systems [5]. The enrichment indices are widely used to

provide information on element contamination in the investigated component in relation to an uncontaminated medium, i.e., Earth's crust or uncontaminated/natural soils. These indices have recently been used in air pollution research, and permissible contents of heavy metals have been established for just a few of them. Taking the above under consideration, the aim of the investigations presented herein was to determine the impact of heavy metals bound with deposited PM on contamination degree and related toxicological effects by calculating enrichment indices, namely, the geo-accumulation index (I_{geo}), contamination factor (CF), and enrichment factor (EF), as well as the ecological risk index (ERI) and modified hazard quotient (mHQ).

2. Material and Methods

Deposited PM samples were investigated from 2014 to 2016 as described in detail in Gruszecka-Kosowska and Wdowin [6]. Heavy metal concentrations were analyzed using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) after digestion of samples in *aqua regia* and mineralization for 2 h in 130 °C in an SCP Science DigiPREP HT High Temperature Digestion System (SCP Science, Quebec, Canada) according to the USEPA 3050B extraction method [7]. As element contents in PM for the calculation of enrichment indices, mean values of heavy metal concentrations in deposited PM from the investigations of Gruszecka-Kosowska and Wdowin [6] were taken (Table 1).

Table 1. Heavy metal concentrations in deposited particulate matter (PM) samples in Krakow (modified from [6]).

Element	Mean value (mg/kg)
As	14.7
Ba	111.5
Be	0.54
Cd	1.2
Co	2.35
Cr	90
Cu	74.5
Li	21.1
Mn	623.5
Ni	24.5
Pb	85.5
Sn	12.5
Sr	140.5
Ti	223
Tl	0.26
V	30
Zn	5820

A detailed description of the calculated enrichment indices in this study is given in Table 2. The geo-accumulation index (I_{geo}) provides information on the accumulation of heavy metals in relation to the background value. Contamination factor (CF) determines the contamination of heavy metals in reference to the background value as well. As the background values for calculating I_{geo} and CF values, local geochemical values [8] were taken. Enrichment factor (EF) describes enrichment with heavy metals in relation to elements with a low variability of occurrence; here, Fe was chosen, and as background values both concentrations from the upper continental crust [9] and local geochemical values [8] were used. For determination of ecological risk, the ecological risk index (ERI) and modified hazard quotient (MHQ) were used, which enabled the assessment of contamination by comparing the metal concentration with the synoptic adverse ecological effect distributions for slightly differing threshold levels [10].

3. Results and Discussion

The calculated values of the enrichment indices used and the corresponding classes are presented in Table 3. The results of the investigations revealed that deposited PM was enriched in heavy metals. Based on the calculated I_{geo} values, in the investigated deposited PM samples, accumulation of the analyzed heavy metals was the highest for As, Ba, Cr, Cu, Li, Mn, Ni, Pb, Sr, Ti, V, and Zn (class 6), as well as for Co and Sn (class 5). Instead, for Be, Cd, and Tl, the calculated I_{geo} values indicated no accumulation (class 0). On the other hand, the calculated CF values revealed very high contamination of the analyzed deposited PM samples with Cd and Zn, considerable contamination with As, Pb, and Sn, and moderate contamination with Cu and Li. For the other investigated elements, CF values indicated low contamination. Also, the EF values (presented here as the mean values of EF calculated for different background values as described above) indicated that the analyzed deposited PM samples were extremely severely enriched with Zn, moderately severely enriched with Sn, and severely enriched with Cd. Minor enrichment of PM was observed for Cu. For the other investigated elements, EF values indicated no enrichment. The calculated EF values indicated anthropogenic sources (EF > 30) of elements only in the case of Zn. For Cd, a small proportion of anthropogenic sources was determined. For Pb and Sn, non-crustal sources of elements were revealed. Crustal sources of elements were defined for As, Ba, Be, Co, Cr, Cu, Li, Mn, Ni, Sr, Ti, Tl, and V.

The calculated values of ERI indicated very high ecological risk of the analyzed deposited PM samples only in the case of Cd and considerable ecological risk for Zn. For As, Co, Cr, Cu, Ni, Pb, and Tl, low ecological risk was determined. For Ba, Be, Li, Mn, Sn, Sr, Ti, and V, ecological risk values were not defined due to the lack of adverse ecological effect values. Ecological risk defined based on the mHQ index revealed extreme severity of contamination of the deposited PM samples with Zn and considerable severity of contamination with Cr. For As, Cu, and Pb, moderate-severity contamination was indicated, while for Cd and Ni, low-severity contamination was indicated. Values of mHQ were not defined for Ba, Be, Co, Li, Mn, Sn, Sr, Ti, Tl, and V due to the lack of adverse ecological effect values.

Table 2. Description of the enrichment indices used in the study.

Enrichment factor	Formulas	Explanation	Limit values	Classification	References
Geo-accumulation index I_{geo}	$I_{geo} = \log_2(C_i/1.5*B_n)$	C_i—content of element in PM; B_n—background value; 1.5—constant	$I_{geo} \leq 0$	Class 0—practically uncontaminated	[11,12]
			$0 \leq I_{geo} < 1$	Class 1—uncontaminated to moderately contaminated	
			$1 \leq I_{geo} < 2$	Class 2—moderately contaminated	
			$2 \leq I_{geo} < 3$	Class 3—moderately to heavily contaminated	
			$3 \leq I_{geo} < 4$	Class 4—heavily contaminated	
			$4 \leq I_{geo} < 5$	Class 5—heavily to extremely contaminated	
			$5 \leq I_{geo}$	Class 6—extremely contaminated	
Contamination factor CF	$CF = Cm_i/C_{ref}$	Cm_i—mean element concentration in PM; C_{ref}—reference value of element	$CF < 1$	low contamination	[13,14]
			$1 \leq CF < 3$	moderate contamination	
			$3 \leq CF < 6$	considerable contamination	
			$6 \leq CF$	very high contamination	
Enrichment factor EF	$EF = (C_i/C_{ref})/(B_i/B_{ref})$	C_i—content of element in PM; C_{ref}—content of Fe in sample; B_i—reference content of single element; B_{ref}—reference content of Fe	$EF \leq 1$	no enrichment	[15,16]
			$1 < EF \leq 3$	minor enrichment	
			$3 < EF \leq 5$	moderate enrichment	
			$5 < EF \leq 10$	moderately severe enrichment	
			$10 < EF \leq 25$	severe enrichment	
			$25 < EF \leq 50$	very severe enrichment	
			$EF > 50$	extremely severe enrichment	
Ecological risk index ERI	$ERI = Tr_i \times CF_i$	Tr—toxicity response coefficient of single element; CF_i—contamination factor of single element	$ERI < 40$	low potential ecological risk	[13,17–20]
			$40 \leq ERI < 80$	moderate potential ecological risk	
			$80 \leq ERI < 160$	considerable potential ecological risk	
			$160 \leq ERI < 320$	high potential ecological risk	
			$320 \leq ERI$	very high potential ecological risk	
Modified hazard quotient mHQ	$mHQ = \left[Ci\left(\frac{1}{TELi} + \frac{1}{PELi} + \frac{1}{SELi}\right)\right]^2$	Ci—concentration of element in PM; TEL—threshold effect level; PEL—probable effect level; SEL—severe effect level for single element	$mHQ < 0.5$	nil to very low severity of contamination	[10,21]
			$0.5 < mHQ < 1.0$	very low severity of contamination	
			$1.0 < mHQ < 1.5$	low severity of contamination	
			$1.5 < mHQ < 2.0$	moderate severity of contamination	
			$2.0 < mHQ < 2.5$	considerable severity of contamination	
			$2.5 < mHQ < 3.0$	high severity of contamination	
			$3.0 < mHQ < 3.5$	very high severity of contamination	
			$mHQ > 3.5$	extreme severity of contamination	

Table 3. Enrichment index classes for deposited PM in Krakow.

Element	I_{geo}		CF		EF (mean)		ERI		mHQ	
	value	class	value	class	value	class	value	class	value	class
As	5.6	6	3.06	considerable	2.63	minor	30.6	low	1.90	moderate severity
Ba	15.5	6	0.18	low	0.15	no	-	-	-	-
Be	−0.4	0	0.26	low	0.22	no	-	-	-	-
Cd	−3.8	0	13.3	very high	11.44	severe	400	very high	1.24	low severity
Co	4.8	5	0.14	low	0.12	no	0.7	low	-	-
Cr	12.4	6	0.98	low	0.84	no	2.0	low	2.12	considerable severity
Cu	10.4	6	2.66	moderate	2.28	minor	13.3	low	1.57	moderate severity
Li	8.2	6	1.00	moderate	0.86	no	-	-	-	-
Mn	18.3	6	0.81	low	0.69	no	-	-	-	-
Ni	9.6	6	0.52	low	0.45	no	2.6	low	1.18	low severity
Pb	9.9	6	5.03	considerable	4.32	moderate	25.1	low	1.86	moderate severity
Sn	4.1	5	5.95	considerable	5.11	moderately severe	-	-	-	-
Sr	14.9	6	0.44	low	0.38	no	-	-	-	-
Ti	19.6	6	0.04	low	0.03	no	-	-	-	-
Tl	−2.7	0	0.29	low	0.25	no	2.9	low	-	-
V	10.9	6	0.31	low	0.27	no	-	-	-	-
Zn	18.0	6	86.87	very high	74.56	extremely severe	86.9	considerable	36.45	extreme severity

- not applicable.

4. Conclusions

The studies revealed enrichment of the analyzed deposited PM samples with heavy metals. Extreme contamination (class 6) was observed for As, Ba, Cr, Cu, Li, Mn, Ni, Pb, Sr, Ti, V, and Zn, as well as heavy to extreme contamination (class 5) for Co and Sn according to the I_{geo} index. Very high contamination of deposited PM with Cd and Zn, considerable contamination with Sn, Pb, and As, and moderate contamination with Cu and Li were indicated according to the CF values. The EF values indicated extremely severe enrichment with Zn, moderately severe enrichment with Sn, severe enrichment with Cd, and minor enrichment with Cu. The calculated values of EF revealed that among the investigated elements, only Zn originated from anthropogenic sources. For Cd, a small influence of anthropogenic sources was observed. For Pb and Sn, non-crustal sources of emission were expected. The potential ecological risk was determined as very high for Cd, considerable for Zn, and low for As, Co, Cr, Cu, Ni, Pb, and Tl according to the calculated ERI values. Moreover, the severity of contamination as indicated by calculated mHQ values was extreme for Zn, considerable for Cr, and moderate for As, Cu, and Pb. The analysis confirmed that atmospheric and re-suspended PM has a comprehensive health impact.

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