proceedings

MDPI

Proceedings

Deposited particulate matter enrichment in heavy metals and related health risk: A case study of Krakow, Poland†

Agnieszka Gruszecka-Kosowska [1,*]

[1] AGH University of Science and Technology, Faculty of Geology, Geophysics, and Environmental Protection, Department of Environmental Protection, Al. Mickiewicza 30, 30-059 Kraków, Poland; agnieszka.gruszecka@agh.edu.pl
ORCID 0000-0002-4988-173X

* Correspondence: agnieszka.gruszecka@agh.edu.pl (A.G-K.)

† Presented at the 2nd International Electronic Conference on Environmental Health Sciences, 4–29 November 2019.

Received: date; Accepted: date; Published: date

Abstract: The aim of the investigations was to determine an impact of heavy metals bound with deposited PM on contamination degree and related toxicological effects by calculating enrichment indices, namely: geo-accumulation index (I_{geo}), contamination factor (CF), enrichment factor (EF), as well as ecological risk index (ERI) and modified hazard quotient (mHQ). Calculations were 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} index provides information of the level of metal accumulation it was stated 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, 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 from investigated elements only Zn originated from anthropogenic sources. For Cd small influence of anthropogenic sources was observed. For Pb and Sn non-crustal sources of emission were expected. Calculated ERI values indicated very high for Cd and considerable for Zn potential ecological risk, as well as low potential ecological risk for As, Co, Cr, Cu, Ni, Pb and Tl. Moreover, calculated mHQ values indicated extreme for Zn, considerable for Cr, and moderate for As, Cu and Pb severity of contamination. The analysis revealed that the impact of atmospheric and re-suspended PM on inhabitants constitutes the complex effect of mixture of heavy metals affecting simultaneously the human health.

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

1. Introduction

The air quality is of most importance due to its direct effect on human health. From many years Krakow is the example of the city of 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 the particulate matter (PM) is the key air pollutant [2-4]. Moreover, PM particles bound other contaminants, especially heavy metals, that alongside with 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

uncontaminated medium i.e. Earth's crust or uncontaminated/natural soils. These indices are lately used in air pollution research as well as permissible contents of heavy metals are established for just a few of them. Taking above under consideration the aim the investigations was to determine impact of heavy metals bound with deposited PM on contamination degree and related toxicological effects by calculating enrichment indices, namely: geo-accumulation index (I_{geo}), contamination factor (CF), enrichment factor (EF), as well as 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 metals concentrations were analyzed using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) after digestion of samples in *aqua regia* and mineralization for 2h in 130°C in the SCP Science DigiPREP HT High Temperature Digestion System (SCP Science, Quebec, Canada) according to the USEPA 3050B extraction method [7]. As element content in PM for calculation of enrichment indices mean values of heavy metal concentrations in deposited PM from investigations of Gruszecka-Kosowska and Wdowin [6] were taken (**Table 1**).

Table 1. Heavy metal concentration in deposited PM samples in Krakow (modified form [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

The detailed description of calculated enrichment indices in this study is given in **Table 2**. The geoaccumulation index (Igeo) provides information on accumulation of heavy metals in relation to background value. Contamination factor (CF) determines the contamination with heavy metals in reference to background value as well. As background values for calculating I_{geo} and CF values the local geochemical values [20] were taken. Enrichment factor (EF) describes enrichment with heavy metals in accordance to element with a low variability of occurrence, here Fe was chosen and as background values both concentrations from upper continental crust [21] and local geochemical values [20] were used. For determination of ecological risk the ecological risk index (ERI) and modified hazard quotient (MHQ) were used, which enable the assessment of contamination by comparing metal concentration with the synoptic adverse ecological effect distributions for slightly differing threshold levels [18].

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	[8,9]
			$0 \leq I_{geo} < 1$	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	[10,11]
			1≤ CF <3	moderate contamination	
			3≤ CF <6	considerable contamination	
			6 ≤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 ≤1	no enrichment	[12,13]
			1< EF ≤3	minor enrichment	
			3< EF ≤5	moderate enrichment	
			5< EF ≤10	moderately severe enrichment	
			10< EF ≤25	severe enrichment	
			25< EF ≤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 40≤ ERI <80 80 ≤ERI <160 160≤ ERI <320 320≤ ERI	low potential ecological risk moderate potential ecological risk considerable potential ecological risk high potential ecological risk very high potential ecological risk	[10,14-17]
Modified hazard quotient mHQ	$mHQ = [Ci\ (\frac{1}{TELi} + \frac{1}{PELi} + \frac{1}{SELi})]^2$	Ci – concentration of element in PM; TEL – threshold effect level; PEL – probable effect level; SEL – severe effect level for single element	mHQ <0.5 0.5< mHQ <1.0 1.0< mHQ <1.5 1.5< mHQ <2.0 2.0< mHQ <2.5 2.5< mHQ <3.0 3.0< mHQ <3.5 mHQ >3.5	nil to very low severity of contamination very low severity of contamination low severity of contamination moderate severity of contamination considerable severity of contamination high severity of contamination very high severity of contamination extreme severity of contamination	[18,19]

Table 3. Enrichment indices 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

3. Results and discussion

The calculated values of used enrichment indices and corresponding classes are presented in **Table 3**. The results of the investigations revealed that deposited PM was enriched in heavy metals. Basing on the calculated I_{geo} values it was stated that in investigated deposited PM samples accumulation of 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 calculated I_{geo} values indicated no accumulation (class 0). On the other hand, calculated CF values revealed very high contamination of analyzed deposited PM samples with Cd and Zn, considerable contamination with As, Pb, and Sn and moderate contamination with Cu and Li. For other investigated elements CF values indicated low contamination. Also EF values (present here as the mean values of EF calculated for different background values as described above) indicated that analyzed deposited PM samples were extremely severe enriched with Zn, moderately severe enriched with Sn, and severe enriched with Cd. Minor enrichment of PM was stated for Cu. For other investigated elements EF values indicated no enrichment. Calculated EF values indicated anthropogenic sources (EF >30) of elements only in the case of Zn. For Cd small proportion of anthropogenic sources was stated. 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.

Calculated values of ERI indicated very high ecological risk of 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 stated. 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 deposited PM samples with Zn and considerable severity of contamination with Cr. For As, Cu, and Pb moderate severity of contamination, while for Cd and Ni low severity of contamination were stated. 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.

4. Conclusions

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

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

References

1. European Environment Agency. *Air Quality in Europe—2018 Report*; EEA Report No 12/2018; Publications Office of the European Union: Luxembourg, 2018.
2. Bokwa, A. Environmental impact of long-term air pollution changes in Krakow, Poland. *Polish J of Environ Stud* **2008**, *5*, 673–686.
3. Choi. H.; Melly, S.; Spengler, J. Intraurban and Longitudinal Variability of Classical Pollutants in Kraków, Poland, 2000–2010. *Int. J. Environ. Res. Public Health* **2015**, *12*, 4967–4991.
4. Gruszecka-Kosowska, A. Assessment of the Krakow inhabitants' health risk caused by the exposure to inhalation of outdoor air contaminants. *Stoch Environ Res Risk Assess* **2018**, *32*, 485–499.
5. Bini, C., Bech, J. *PHEs, environment and human health. Potentially harmful elements in the environment and the impact on human health*, Springer, 2014.
6. Gruszecka-Kosowska, A.; Wdowin, M. 2016. The mineralogy, geochemistry and health risk assessment of deposited particulate matter (PM) in Krakow, Poland. *Geology, Geophysics & Environment* **2016**, *42(4)*, 429–441.
7. *Method 3050B: Acid Digestion of Sediments, Sludges, and Soils. Revision 2*. US Environmental Protection Agency, Washington, DC, USA, 1996.
8. Müller, G. Index of geoaccumulation in sediments of the Rhine River, *GeoJournal* **1969**, *2(3)*, 108–118.
9. Kowalska, J.B.; Mazurek, R.; Gąsiorek, M.; Zaleski, T. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination. *Environ Geochem Hlth* **2018**, *40*, 2395–2420.
10. Håkanson, L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res* **1980**, *14*, 975–1001.
11. Loska, K.; Wiechuła, D.; Korus, I. Metal contamination of farming soils affected by industry. *Environ Int* **2004**, *30*, 159–165.
12. Sutherland, R.A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ Geol* **2000**, *39(6)*, 611–627.
13. Ho, H.H.; Swennen, R.; Van Damme, A. Distribution and contamination status of heavy metals in estuarine sediments near Cua Ong Harbo, Ha Long Bay, Vietnam. *Geol Belg* **2010**, *13(1-2)*, 37–47.
14. Gong, Q.; Deng, J. Calculating pollution indices by heavy metals in ecological geochemistry assessment and as case study in parks of Beijing. *J China Univ Geosci* **2008**, *19(3)*, 230–241.
15. Chai, L.; Li, H.; Yang, Z.; Min, X.; Liao, Q.; Liu, Y.; Men, S.; Yan, Y.; Xu, J. Heavy metals and metalloids in the surface sediments of the Xiangjiang River, Hunan, China: distribution, contamination, and ecological risk assessment. *Environ Sci Pollut Res* **2017**, *24*, 874–885.
16. Liu, Y., Wang, Q., Zhuang, W., Yuan, Y., Jiao, K., Wang, M., & Chen, Q. (2018). Calculation of thallium's toxicity coefficient in the evaluation of potential ecological risk index: a case study. *Chemosphere*, 194, 562–569.
17. Wang, N., Wang, A., Kong, L., & He, M. (2018). Calculation and application of Sb toxicity coefficient for potential ecological risk assessment. *Science of the Total Environment*, 610–611, 167–174.
18. Benson, N.U.; Adedapo, A.E.; Omowunmi, H.F.A.; Williams, A.B.; Udosen, E.D.; Ayejuyo, O.O.; Olajire, A.A. New ecological risk indices for evaluating heavy metals contamination in aquatic sediment: A case study of the Gulf of Guinea. *Regional Studies in Marine Science* **2018**, *18*, 44–56.
19. MacDonald, D.D.; Ingersoll, C.G.; Berger, T.A. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Con Tox* **2000**, *39*, 20–31.
20. Kabata-Pendias, A. *Trace elements in soils and plants (4th ed.)*. Boca Raton: CRC Press, Taylor &Francis Group, 2011.
21. Rudnick, R.L.; Gao, S. Composition of the continental crust. *Treatise on Geochemistry (Second Edition)* **2014**, *4*, 1–51.