E3S Web of Conferences **17**, 00071 (2017) DOI: 10.1051/e3sconf/20171700071
EKO-DOK 2017

Exposure of urban agglomeration population to the selected components of PM_1 emitted from low emission sources

Łukasz Pachurka[1,*], *Wioletta* Rogula-Kozłowska[2,3], *Anna* Chlebowska-Styś[1], *Alicja* Nych[1], and *Anna* Zwoździak[1]

[1]Wroclaw University of Science and Technology, Faculty of Environmental Engineering, Unit of Ecologistics and Environmental Risk Management, Wybrzeże Wyspiańskiego 27 St., 50-370, Wroclaw, Poland
[2]Institute of Environmental Engineering, Polish Academy of Sciences, M. Skłodowskiej-Curie 34 St., 41-819, Zabrze, Poland
[3]The Main School of Fire Service, Faculty of Fire Safety Engineering, Słowackiego 52/54 St., 01-629 Warsaw, Poland

Abstract. The sources of gaseous and particulate (PM) pollutants in Polish cities are mainly: municipal sector, industry, emissions from the road transport and the upstream emission (pollution "flowing" to the cities, derived from emission sources located outside of cities). The residents of the cities are mainly exposed to air pollutants from low-emission sources (i.e. municipal sector and road traffic). In the paper, the results of the study from field campaign, conducted in January of 2016 in Wroclaw will be presented. During the field campaign the 24-h concentrations of submicron particulate matter (PM_1) and 24-h concentrations of selected PM_1-bound heavy metals were determined. The cancer risk associated with inhalation exposure to arsenic, nickel, and cadmium to the city's residents, based on the US Environmental Protection Agency (US EPA) standards methodology including the so-called lifelong chronic exposure of adult and child, was calculated. Measurements results showed that in Wroclaw during the winter season in 2016 the 24-h concentrations of PM_1-bound arsenic, nickel and cadmium ranged from 0.51 to 4.26 ng/m^3, 0.21-52.89 ng/m^3 and 0.08-1.01 ng/m^3, respectively. Obtained calculations results of cancer risk values for inhalation exposure to arsenic were: for men: $6.11\cdot10^{-6}$, women: $7.30\cdot10^{-6}$, children: $14.90\cdot10^{-6}$, to nickel: for men: $1.91\cdot10^{-6}$, women: $2.29\cdot10^{-6}$, children: $4.67\cdot10^{-6}$, to cadmium: for men: $0.37\cdot10^{-6}$, women: $0.44\cdot10^{-6}$, children: $0.91\cdot10^{-6}$. The values obtained for inhalation exposure among children indicated the high potential risk of cancer, mainly for arsenic exposure.

[*] Corresponding author: lukasz.pachurka@pwr.edu.pl

1 Introduction

Air pollution contributes to the deterioration of the environment through the introduction of gaseous, liquid and solid substances into the atmosphere [1, 2]. Cardiovascular disease is considered to be the main cause of death in the European Union, accounting for about 40% of all deaths. In terms of a number of inhabitants, it constitutes about 2 million people per year [3]. In Poland, the premature death caused by the cardiovascular disease is twice as high compared to other Western European countries [4]. The most often cardiovascular disease that occurs in society is hypertension. Beyond the incorrect lifestyle, the factor responsible for the occurrence of cardiovascular disease is air pollution caused by particulate matter, $PM_{2.5}$ (fine particulate matter; a fraction of atmospheric particles with aerodynamic diameter Dp not greater than 2.5 microns) and PM_{10} (Dp $\leq$ 10 microns) [5]. The emissions data from 2013 show that combustion processes outside the industry (51%), road transport (13%), combustion processes in the transformation of energy (10%), combustion processes in industry (7%), other vehicles and equipment (7%), waste management (5%), production processes (5%,) distribution of fossil fuels and their distribution (1%), the use of solvents and other products (1%) and agriculture (0.2%) are mainly responsible for the emission of $PM_{2.5}$ [6].

The conducted worldwide studies have shown an association between increased hospitalization due to cardiovascular disease and the number of daily deaths from cardiovascular and respiratory diseases due to environmental exposure to a fine fraction of particulate matter, $PM_{2.5}$ [5].

Heavy metals such as nickel and cadmium cause a threat to human health and life, due to their good absorption through the respiratory system. Formation of complexes with proteins causes depositing cadmium in the liver and kidney. The toxic effects of cadmium deposition are hypertensive disease, impaired reproductive function, kidney disorder, cancer (kidney, prostate) [7].

Inhalation exposure to nickel contributes to allergic reactions and damage to mucous membranes. Other disorders related to long-term exposure to metal include malignancy, bone marrow changes and chromosomes disturbances in the metabolism of plasma proteins [7]. Exposure to arsenic presence contributes to the incidence of lung cancer [8, 9].

The aim of the study was to analyse the variability of 24-h concentrations of PM_1 (Dp $\leq$1 microns) and PM_1-bound heavy metals, i.e. cadmium, arsenic and nickel and assessment of inhalation exposure of the residents of the selected area of the city of Wroclaw associated with the presence of the above heavy metals in PM_1.

2 Materials and methods

The 24-h concentrations of PM_1 in the selected measuring site (Biskupin - Kosiby St.) were determined in the study carried out during a two-week campaign in the heating (winter) and non-heating (spring) season in 2016 in Wroclaw. The measuring site was located in the area covering both high and low buildings.

The sampling and weighing of PM_1 were performed according to the methods described in [10, 11]. The arsenic (As), cadmium (Cd) and nickel (Ni) concentrations were identified in all 24-h samples of PM_1. Metals quantitative analysis was preceded by the samples mineralization in a mixture of spectrally pure (Merck, Ultrapur) acids. Before mineralization, samples were flooded with 5 ml of nitric acid HNO_3 (65%), 1 ml of hydrofluoric HF (40%) and 1 ml of perchloric acid $HClO_4$ (70%). Mineralization was carried out in a microwave reaction system Multiwave 3000 from Anton Paar, in the sealed polytetrafluoroethylene PTFE vessels under pressure (mineralization furnace parameters: a pressure rise of 0.3 bar/s; 240°C; pressure 60 bar; mineralization time 50 minutes).

Chemical analysis was carried out using ICP spectrometer MS Elan DRCE produced by Perkin Elmer. Certified multielement standard stock solutions Periodic table mix 1 and Transition metal mix 2 (Fluka) were used as calibration solutions. The limits of quantification of elements were as follows: Ni -<0.01 µg/sample, As <0.025 µg/sample, Cd <0.003 µg/sample. The analytical method was validated by determination of As, Cd, and Ni in the Standard Reference Material, SRM 1649a, (Urban Particulate Matter Dust), obtained from the National Institute of Standard and Technology (NIST). Recovery rates were as follows: As (80%); Cd (83%); Ni (118%).

In order to determine the risk of cancer through inhalation on PM_1-bound Ni, As and Cd the methodology of risk assessment developed by US Environmental Protection Agency (US EPA) was applied. This methodology includes the so-called lifelong chronic adults and children exposure to selected PM-bound heavy metal [12, 13]. Based on the literature [7, 14, 15], in the scenario calculation, it was assumed that both adults and children may be exposed 24 hours a day and 365 days a year to the impact of polluted air. Among the data of the age of the population, the average time of exposure for children and adults were assumed as 6 and 70 years respectively [7, 14, 15, 16].

The use of methods of health risk assessment described by the US EPA allows of estimation the expected risks and health at a certain concentration of air pollution - in this case of inhalation. In this scenario, the daily intake depends on the concentration level of Ni, As and Cd in the study area.

The sampled amount (estimated daily intake) of the chosen heavy metal, defining the amount of substance entering the body throughout the day, based on 1 kg of body weight, was calculated from the formula (1).

$$EDI = (C \cdot IR \cdot AF \cdot F \cdot ED)/BW \cdot AT \tag{1}$$

where:
EDI - estimated daily intake [mg/d·kg]
C - the average concentration in the air [mg/m^3]
IR - the daily lung ventilation (intake rate) [m^3/d]
AF - bioavailability factor [unitless]
F- the frequency of exposure [d/year]
ED - the duration of exposure [year]
BW - the average body weight [kg]
AT - the averaging time [d]

The following parameters were assumed in the study for calculation of average weight for women: 65.4 kg, men: 78.1 kg and children: 16 kg. Daily ventilation was assumed as following: for adults 20 m^3/d, for children - 10 m^3/d. Other parameters were: 24 hours a day, the bioavailability factor – 1, the frequency of exposure - 365 d/year, the duration of exposure - 365 days a year. These figures are based on a 50-percentile distribution of body weight in anthropometric data [7, 14, 15]. The average concentration of the heavy metal for the resident was defined as the average value of the metal concentrations determined in the 24-hour samples of PM_1 collected during the heating and non-heating season. The assessment included the carcinogenic effects of As, Cd, and Ni on the basis of the formula (2).

$$CR = EDI \cdot SF \tag{2}$$

where:
CR - cancer risk
EDI - estimated daily intake [mg/d·kg]
SF - slope factor

DOI: 10.1051/e3sconf/20171700071

Slope factor was assumed from the toxicological database (IRIS): inhalation exposure to As 15.1, Cd 6.3 and Ni: 0.84 [kg·d·mg^{-1}] [17]. The values obtained were compared with an acceptable level of risk of cancer of $1\cdot10^{-6}$ to $1\cdot10^{-4}$ [7, 14, 15].

3 Results and Discussion

Average concentration levels of PM_1 in selected European cities recorded in the summer and winter were listed in Table 1. In Wroclaw for both winter and spring season, the average concentrations of PM_1 are lower than those obtained in studies conducted in Zabrze (Poland) and selected European cities (Table 2). Average concentration of PM_1 in Wroclaw in winter is approximately 63 and 41% lower than the levels recorded in Milan and Zabrze, while for the spring season, the average concentration of PM_1 in Wroclaw is about 27; 54, 58 and 38% lower than the PM_1 concentrations in Melplitz, Genoa, Milan and Zabrze.

Table 1. Concentrations of PM_1 [µg /m^3] in selected European cities [18, 19].

City (country)	Sampling point	The average concentration in winter [µg/m^3]	The average concentration in summer [µg/m^3]
Zabrze (Poland) [18]	Urban background	30.8	13.1
Melplitz (Germany) [19]	Rural background	10.0	11.0
Genoa (Italy) [19]	Urban background	11.5	17.4
Milan (Italy) [19]	Urban background	48.8	19.4

Table 2. Descriptive statistics for 24-hour concentrations of PM_1.

Parameter	Concentration [µg/m^3]
the average concentration in heating season – winter (09.01- 26.01.2016) (the range of 24-h concentrations)	18.16 (2.84-38.20)
median (09.01- 26.01.2016)	15.55
standard deviation (09.01- 26.01.2016)	10.66
the average concentration in non-heating season – spring (09.05- 23.05.2016) (the range of 24-h concentrations)	8.05 (3.21-11.53)
median (09.05- 23.05.2016)	9.31
standard deviation (09.05- 23.05.2016)	2.88
the average concentration in heating and non-heating season – winter (09.01- 26.01.2016); spring (09.05- 23.05.2016) (the range of 24-h concentrations)	13.76 (2.84-38.20)
median (09.01- 26.01.2016) and (09.05- 23.05.2016)	10.64
standard deviation (09.01- 26.01.2016) and (09.05- 23.05.2016)	9.73

In accordance with European and Polish regulation, the levels of some PM_{10}-bound heavy metals in the framework of the State Environmental Monitoring (SEM) should not exceed nickel - 20 ng/m^3, arsenic - 6 ng/m^3 and cadmium - 5 ng/m^3 [20, 21].

Table 3 presents the average concentrations of PM_1-bound Ni, As and Cd in selected European cities. Based on the literature data in other European cities and own studies, there were no exceedances of selected metals in a fraction PM_1 (in relation to the value of the permissible level set for a fraction of PM_{10}).

Table 3. Concentrations of heavy metals indicated in particulate matter PM_1 in various European cities [7, 22, 23 and own studies].

Place of sampling, country	Site location	Nickel [ng/m^3]	Arsenic [ng/m^3]	Cadmium [ng/m^3]
Wrocław (Poland): Kosiby St., heating season (09.01- 26.01.2016)	Urban background	8.90 (0.21-52.89)	1.58 (0.51-4.26)	0.23 (0.08-1.01)
Wrocław (Poland): Kosiby St., non-heating season (09.05- 23.05.2016) [22]	Urban background	2.72 (0.34-7.35)	1.52 (0.71-4,19)	0.27 (0.07-0.91)
Zabrze (Poland), January-March 2008 [23]	Urban background	0.17	2.14	0.75
Barcelona (Spain), 2005-2006 [23]	Urban background	-	0.6	0.3
Milan (Italy), winter 2002 [23]	Residential-commercial area	7.0	2.0	-
Upper Silesian Agglomeration (2007-2009) [7]	-	3.29	2.15	1.52

Table 4 summarizes the calculated values of the estimated daily intake by inhalation of PM_1-bound Ni, As and Cd in Wroclaw. The highest daily intake of Ni taken by inhalation may be received by children ($5.56 \cdot 10^{-6}$ mg/d·kg) - due to the fact of 50% more inspired air than adults per kilogram of body weight. The respiratory system of children is also not fully developed compared with one of the adults. In a study conducted in the Upper Silesian Agglomeration, part of the Upper Silesian Industrial Region, on the basis of data from the Regional Inspectorate of Environment Protection (RIOP) from 2007-2009, dosage amount of Ni was calculated which amounted to: for children: $2.06 \cdot 10^{-6}$ mg/d·kg; women: $1.01 \cdot 10^{-6}$ mg/d·k; men: $0.84 \cdot 10^{-6}$ mg/d·kg [7]. The values obtained for daily intakes in non-heating season in Wroclaw are 17 (children), 18 (women) and 17 (men)% lower than those obtained in the Upper Silesian Agglomeration. In the case of the heating season, the values obtained were 270 (children), 269 (women) and 271 (men)% higher than those obtained in the Upper Silesian Agglomeration. The higher dosage amounts of Ni collected by the human body in the Silesian Agglomeration could depend on the industrial character of the region.

Table 4. Daily intakes by inhalation for selected heavy metals.

Place of sampling	Nickel Daily intake [$\cdot 10^{-6}$ mg/d·kg]			Arsenic Daily intake [$\cdot 10^{-6}$ mg/d·kg]			Cadmium Daily intake [$\cdot 10^{-6}$ mg/d·kg]		
	children	adults		children	adults		children	adults	
		women	men		women	men		women	men
Wrocław: Kosiby St., heating season (09.01- 26.01.2016)	5.56	2.72	2.28	1.00	0.48	0.40	0.14	0.07	0.06
Wrocław: Kosiby St., non-heating season (09.05- 23.05.2016)	1.70	0.83	0.70	0.95	0.47	0.39	0.17	0.08	0.07

Based on the daily intakes, the value of cancer risk (Table 5) for the analysed heavy metals was calculated. The highest potential inhalation cancer risks associated with exposure to As and for the group of children, which is associated with the value of the slope factor were found for As: 15.1; cadmium 6.3 and nickel: 0.84 [kg·d·mg^{-1}] [17].

Table 5. Inhalation risk of cancerous on selected heavy metals in each group.

Place of sampling	Nickel CR [·10^{-6}]			Arsenic CR [·10^{-6}]			Cadmium CR [·10^{-6}]		
	children	adults		children	adults		children	adults	
		women	men		women	men		women	men
Wrocław: Kosiby St., heating season	4.67	2.29	1.91	14.90	7.30	6.11	0.91	0.44	0.37
Wrocław: Kosiby St., non-heating season [14]	1.43	0.70	0.59	1.43	0.70	0.59	1.06	0.52	0.44

Risk considered insignificant or acceptable by the US EPA is at a value of 1·10^{-6} to 1·10^{-4}. The high risk requiring protective action is 1·10^{-3} [7, 14, 15]. The calculations showed the highest risk values for the residents of the study area in Wroclaw during the heating season, respectively for children: 14.90·10^{-6}, women: 7.30·10^{-6} and men: 6.11·10^{-6}. The values of the risk of cancer associated with exposure to As for the selected area of the city of Wroclaw were higher in winter than the values obtained on the basis of studies conducted in the years 2007-2009, where the potential cancer risks of exposure to arsenic for the residents of Wroclaw Agglomeration amounted to 0.93·10^{-6} for men, 1.11·10^{-6} for women and 2.27·10^{-6} for children [7].

Determined cancer risk values for inhalation exposure in the measurement campaign in the winter season for individual metals amounted to As - men: 6.11·10^{-6}, women: 7.30·10^{-6}, children: 14.90·10^{-6}, Ni - men: 1.91·10^{-6}, women: 2.29·10^{-6}, children: 4.67·10^{-6}, Cd - men: 0.37·10^{-6}, women: 0.44·10^{-6} children: 0.91·10^{-6}

The comparison of the obtained value of daily intakes taken was possible by the assumption of the same input data for the calculation, as in the literature [7]. The values of As daily intakes for the residents of Wroclaw in both the heating (children: 1.0; women: 0.48, men 0.40 [·10^{-6} mg/d·kg]) as well as non-heating season (children: 0.95, women: 0.47, men 0.39 [·10^{-6} mg/d·kg]) were lower due to the less contribution of industrial sources than in other city (Legnica: children: 4.53, women: 2.22, men: 1.86 [·10^{-6} mg/d·kg] located in the industrial region [7].

The calculations in this study showed that the results obtained in the cancer risk are at an acceptable level for the selected site in Wroclaw.

4 Summary

Exposure to heavy metals such as cadmium, arsenic, and nickel may in the future be a potential cause of cancerous changes. The increase in the concentrations of heavy metals in the air is mostly related to human activities, including a large proportion of low-emissions from fuels in households.

In Wroclaw, children are the most exposed to the inhalation cancer risks due to the presence of arsenic in the air, and obtained results may indicate the potential risk of cancer (14.90·10^{-6}). Beyond the level of concentration of analysed heavy metals, the risk of cancer is affected by the size of the slope factor (for arsenic: 15.1 [kg·d·mg^{-1}]). To fully determine the scale of the health risks for selected heavy metals, other means of exposure to contamination, i.e. the oral route and through the skin, should be considered in the future.

Current regulations regarding concentration levels of some heavy metals refer to the average annual values for particulate matter PM_{10}. Components of the sub-micron fraction can be transported to the alveoli in the human body. Therefore, steps should be taken to identify targets of annual and daily average concentrations of PM_1. None of the heavy metals show average concentrations higher than acceptable levels (Ni - 20 ng/m^3, As - 6 ng/m^3 and Ca - 5 ng/m^3).

The investigations were co-financed within the framework of the order No. B50601 with the specific subsidy granted for the Faculty of Environmental Engineering Wroclaw University of Science and Technology (W-7) by the Minister of Science and Higher Education to conduct research and development work and related tasks contributing to the development of young scientists and doctoral students in 2015/2016 and within the project No. 2012/07/D/ST10/02895 (ID 202319) financed by the National Science Centre, Poland (NCN).

References

1. A. Malec, A. Borowski, Inżynieria Ekologiczna = Ecological Engineering, **50**, 161-170, Dec. (2016)
2. J. Krzeszowiak, A. Michalak, K. Pawlas, Medycyna Środowiskowa = Environmental Medicine, **18 (2)**, 66-73 (2015)
3. L. Ryden, J. Martin, S. Volqvartz, Eur J Cardiov Prev R, **14 (3)**, 355-356 (2007)
4. M. Marek, A. Chłoń Damińczak, Kaleta, J. Mazur, P. Miśkiewicz, D. Poznańska, J. Stokwiszewski, B. Wojtyniak, T. Zdrojewski, *Social inequalities in health in Poland,* The European Office of the World Health Organization, Copenhagen (2012)
5. G. Dziubanek, E. Marchwińska-snatched, A. Piekut, M. Rusin, I. Hajok, Hygeia Public Health, **49 (1)**, 75-80 (2014)
6. Chief Inspectorate of Environmental Protection (CIEP), *Fine dust in the atmosphere. A compendium of knowledge about air pollution particulate matter in Poland*, http://www.gios.gov.pl/images/aktualnosci/Pyly_drobne_w_atmosferze.Kompendium_wiedzy.pdf, (2016), [Access: 22.1.2017]
7. M. Trojanowska, R. Świetlik, Medycyna Środowiskowa = Environmental Medicine, **15 (2)**, 33-41 (2012)
8. M.N. Bates A.H. Smith, C. Hopenhaym-Rich, Am J Epidemiol, **135 (5)**, 462-476 (1992)
9. K. Widziewicz, W. Rogula-Kozłowska, K. Loska, Atmospheric Pollution Research, **7 (5)**, 884–894 (2016)
10. Ł. Pachurka, I. Sówka, W. Rogula-Kozłowska, B. Mathews, A. Chlebowska-Styś, A. Zwoździak, [in:] Health determinants/ editors J. Chmielewski, M. Florek-Łuszczki, M. Szpringer, Warsaw: Environmental Institute: National Research Institute, 133-141 (2016)
11. I. Sówka, Ł. Pachurka, M. Przepiórka, W. Rogula-Kozłowska, A. Zwoździak, Rocznik Ochrona Środowiska = Annual Set The Environment Protection, **18 (2)**, 603-614 (2016)
12. US EPA: Guidelines for Human Health Risk Assessment of Chemical Mixtures, Federal Register (51 FR 34014-34025), Washington, D.C. (1986).
13. US EPA: Risk Assessment Guidance for Superfund, Vol. I, Human Health Evaluation Manual (Part A), EPA/540/1-89 /002, Office of Emergency and Remedial Response, Washington, D.C. (1989)
14. M. Biesiada, *Health risk assessment of Wiślinka inhabitants of the effects heaps of phosphogypsum,* Institute of Occupational Medicine and Environmental Health (2006)
15. M. Trojanowska, R. Świetlik, Medycyna Środowiskowa= Environmental Medicine, **16 (2)**, 14-22 (2013)
16. W. Szymczak, N. Szeszenia-Dabrowska, *Estimating health risks associated with environmental pollution*, Library Environmental Monitoring (1995)

17. https://www.epa.gov/iris, [Access: 22.1.2017]
18. A. Zwoździak, M.I. Gini, L. Samek, W. Rogula-Kozłowska, I. Sówka, K. Eleftheriadis, J Aerosol Sci, **103**, 38-52 (2017)
19. W. Rogula-Kozłowska, K. Klejnowski, P. Rogula-Kopiec, L. Ośródka, E. Krajny, B. Błaszczak, B. Mathews, Air Quality, Atmosphere and Health, **7**, 41-58 (2014)
20. Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. (2004)
21. Regulation of the Minister of Environment of 24 August 2012 on the levels of certain substances in the air, OJ 2012 item. 1031. (2012)
22. Ł. Pachurka, I. Sówka, W. Rogula-Kozłowska, A.Chlebowska-Styś, A. Zwoździak, [in:] Ukrainian- Polish Conference: the problems of air pollution and purification: control, monitoring, catalytic, photocatalytic and Sorption methods of treatment: proceedings, November 6-8, 2016 Kyiv/ [editors: NV Vlasenko, E.V.Gubarenì]. Dnipro: Serednâk T.K., 51 (2016)
23. W. Rogula-Kozłowska, B. Kozielska, K. Klejnowski, S. Szopa, Arch Environ Prot, **39** (1), 53-65 (2013)