

Seasonal variations of PM_{2.5} and PM₁₀ concentrations and inhalation exposure from PM-bound metals (As, Cd, Ni): first studies in Poznań (Poland)

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Abstract: Results of measurements of suspended particulate matter concentrations – PM₁₀ and PM_{2.5} (ambient particles with aerodynamic diameter not greater than 10 and 2.5 μm respectively) in Poznań, Poland in years 2010–2016 alongside the results of cancer risk assessment analysis in relation to inhalation exposure to selected heavy metals: As, Cd and Ni related to PM₁₀ are presented in this work. The data originated from measurements (4 sampling sites) of Voivodeship Inspectorate of Environmental Protection (VIEP). Average yearly concentrations of PM in 2010–2016 are displayed together with an analysis of its seasonal variability. In order to determine the cancer risk a methodology of risk assessment of the United States Environmental Protection Agency (US EPA) is used.

Average yearly concentrations of PM₁₀ ranged from 21 μg/m³ in 2010 at the measurement station on Szymanowskiego street to 39 μg/m³ in 2016 at measurement stations on Polanka and Dąbrowskiego streets. Mean concentrations in the heating season were twice higher than in non-heating season at stations on Szymanowskiego street, Polanka street and Dąbrowskiego street. In the case of heavy metals, the highest average seasonal concentrations were: 3.34 ng/m³ for As in the heating season of 2016 (Chwiałkowskiego street), 0.92 ng/m³ for Cd in the heating season of 2012 (Chwiałkowskiego street), 10.82 ng/m³ for Ni in the heating season of 2016 (Szymanowskiego street). We have shown that the presence of As in PM in Poznań is connected with fossil fuel emission from home fireplaces. Road traffic and industry were a potential source of Cd and Ni. The highest risk values for residents of Poznań were acquired for average concentrations in the heating seasons from 2012–2016 of As and they were: 24.27·10⁻⁶ for children, 11.87·10⁻⁶ for women and 9.94·10⁻⁶ for men. Received risk value on an acceptable level according to US EPA is 1·10⁻⁶.

Introduction

Negative influence of particulate matter (PM) and heavy metals contained within, on human health, environment and materials has already been proved and described many times (Atkinson et al. 2001, Bates 1992, Calvo et al. 2009, Cembrzyńska et al. 2012, Colville et al. 2001, Dobrowolski et al. 2002, EEA 2016, Friberg 1984, Krzyżanowski et al. 2015, Ramanathan et al. 2013, Sadowiecki and Gawroński 2013, Trojanowska and Świetlik 2012, WHO 2013 i 2016, Widziewicz et al. 2016, Wilk et al. 2013). Recently, in Europe, the concentration of PM and other air pollutants (including the precursors of PM) is systematically decreasing, which results in improvement of the quality of lives of residents. However, in many areas,

the concentrations of PM are still on a high level, which is dangerous for life and health of residents. Exceeding PM amount standards are usually observed in cities, where the majority of the people live (EEA 2016, Widziewicz et al. 2017). Only in a few European cities air quality meets standards established by WHO. Central and eastern parts of Europe are an area where standards are exceeded most often. This situation is mostly influenced by low emission from community and household sectors. However, the climatic factors, geographical location and the type of city household development are also significant (Błaszczak et al. 2016, Chlebowska-Styś et al. 2017b, Czarnecka and Kalbarczyk 2013, EEA 2016, Juda-Rezler i in. 2011, Majewski et al. 2013, Rogula-Kozłowska et al. 2011, Widziewicz and Rogula 2017). On the other hand,

in Western Europe road transport is considered to be the main source of pollutant emission. (Jeong et al. 2016, Chlebowska-Styś et al. 2017a, Karagulian et al. 2015, Kozińska et al. 2013, Li et al. 2013, Rogula-Kozłowska et al. 2016). According to the EEA data, the highest concentrations of particulate matter pollutants are present in Poland, Italy, Bulgaria and Slovakia (Chlebowska-Styś et al. 2017b, EEA 2016).

In Polish cities, a clear seasonal variability in PM concentrations is noticed. Difficulties with high concentrations of pollutants are present in autumn and winter season and are visibly correlated with meteorological conditions (Błaszczak et al. 2016, Chlebowska-Styś et al. 2016, Rogula-Kozłowska et al. 2011; 2016). The lower the air temperatures are and the higher the number of windless periods is, the higher the concentrations of PM are. The concentrations of PM during the heating season are nearly twice as high as the ones outside the heating season, which is connected with meteorological conditions and hard/brown coal burning (Błaszczak et al. 2016, Chlebowska et al. 2016, Rogula-Kozłowska et al. 2011; 2016). Another important source of suspended PM emission is also its secondary uplifting, i.e. dust resuspension. In cities, the resuspension of PM is mostly attributed to road transport (Badyda and Majewski 2006, Rogula-Kozłowska et al. 2011; 2014; 2016).

Recent research also indicates that the concentrations of PM and its properties may differ not only on a large, continental scale but also on a very small scale. PM varies not only within some areas of one country/region but also is different within one, quite small city (Rogula-Kozłowska et al. 2014, Widziewicz et al. 2017). As it was shown in previous works, even two points located only a few dozens of meters from each other are characterized by PM having different concentrations and chemical properties (Rogula-Kozłowska et al. 2011). This is why it is important to study the properties of PM where its concentrations and chemical properties determine influence on large populations and where present knowledge about PMs is scarce.

The aim of this work is analysis of seasonal variability of concentrations of PM_{2.5} and PM₁₀ (ambient particles with aerodynamic diameter not greater than 2.5 and 10 µm, respectively) in Poznań, with first accompanied assessment of inhalation influence of PM – bound metals on so called carcinogenic risk.

Area and methodology of the research

Locations of measurement stations

Concentration of PM₁₀ in Poznań was measured at 4 measurement stations belonging to the Voivodeship Inspectorate of Environmental Protection (VIEP). Two of them were subject to automatic measurement of air pollutants (Polanka street and Dąbrowskiego street – measurement station no. 1 and 2), and two remaining measurement stations were subject to manual measurement (Chwiałkowskiego street and Szymanowskiego street – measurement stations no. 3 and 4) – Fig. 1. Automatic collection of samples was performed in accordance with the method of beta Ray attenuation; the time of result averaging was equal to 1 hour. Measurement of PM_{2.5} was conducted with use of the manual method at station on Polanka street (measurement station no. 1; result averaging time of 24 hours). In order to carry out a comparative analysis,

the results of automatic measurements – the 1 hour averages were transformed into an average 24 hour concentrations. The manual method as well as the automatic method of PM measurement accord with the requirements of the Directive of European Parliament and of the Council 2008/50/EC of May 21, 2008 on ambient air quality and cleaner air for Europe (Official Journal of the European Union L152 of June 11, 2008, page 1).

All of the VIEP Poznań stations where PM₁₀ and PM_{2.5} are monitored meet the requirements for urban background stations. Multi-family housing with local boiler rooms (in the distance of 200 m) and Lake Malta (in the distance of 500 m) from the North, multi-family housing connected to city heating network from the East (150 m), multi-family and single-family housings with local boiler rooms again from the West (150 m) (in the distance of about 200 m) constitute the surroundings. The area located South and South-West of the measurement station on Polanka street (Fig. 1, measurement point no. 1) was a wasteland covered with vegetation for many years. In 2014, the authorities began to build a huge shopping mall there, whose construction was finished near the end of 2016. The surroundings of the measurement stations on Dąbrowskiego street (Fig. 1, measurement point no. 2) are constituted by single-family housings from the West in the distance of 300 m and from the South (130 m), by the area of the Adam Mickiewicz University Botanical Garden from the East (5 m), by the Rusałka Lake together with its recreational areas (350 m) from the North. Moreover, the vicinity of the measurement station on Chwiałkowskiego street (Fig. 1, measurement point no. 3), from each direction, is mainly constituted by old apartment buildings heated with coal in local boiler rooms. In addition, there are allotment gardens South-East of the measurement point, which may be a source of air pollution in the spring and summer season because of such activities as burning leaves and grass or grilling. Urban heating network in this region is not highly developed. The closest surroundings for the station located on Szymanowskiego street (Fig. 1, measurement point no. 4) are constituted by multi-family housings connected to the urban heating network from the North and East in the distance of 100 m and a single-family houses with possibility to connect it to gas network and from the South and West in the distance of about 100 m. Most of the households in this region use their own heat sources. There are also several industrial sources of PM Southwest of the measurement station.

Methodology of particulate matter sampling

MetOne BAM-1020 (at the sampling point no. 1) and MP101M (at the sampling point no. 2) were used for PM₁₀ measurements. The aforementioned detectors were produced by Environment S.A. The results were generated and sent to the central base of the VIEP in Poznań in real time via internet. The inlets of both samplers were located 5 m above the ground level.

DERENDA PNS 16T-3.1. samplers were used for manual measurements of PM₁₀ (at sampling points 3 and 4) and of PM_{2.5} (at sampling point 1). The samplers were characterized by a flow rate of 30 m³/h. All manual samplers had a filter storage for no more than 14 items. Their inlets were located 5 m above the ground level. Samples of PM_{2.5} and PM₁₀ were collected on Whatman® quartz fiber filters (QM-A) with a diameter of 150 mm (in the case of PM₁₀) and 47 mm (in the case of PM_{2.5}).

The filters were transported to/from the VIEP in Poznań, where they were subject to conditioning and weighing, before and after the exposure, in a weighing room (with the constant air humidity of $45 \pm 5\%$ and the temperature of air equal to $20 \pm 2^\circ\text{C}$), from/to a measurement station. The weighing was carried out using an analytical balance of Xa 60/220 type, manufactured by RADWAG company (weighing resolution $0,1\mu\text{g}$). Filters were conditioned after the exposure in the same temperature and relative humidity conditions, in which they were prepared before the exposure, for at least 48 hours. After the conditioning, the filters were weighed two times, with a 24 hour break.

Analysis of the heavy metals content in particulate matter

Determination of As, Cd and Ni in PM_{10} samples from sampling site no. 3 was performed in certified laboratory of the VIEP in Poznań. The samples subject to the analysis were gathered in the period between 1 January 2012 and 31 December 2016. Circa 1800 samples were collected. Determination was carried out on consolidated samples from each week. The combined samples were subject to mineralization in a microwave digestion system. They were placed in Teflon containers and mineralized gradually by successive adding concentrated acids, HNO_3 , HF, HClO_4 and HCl to be precise. Then, the amount of each metal was determined with use of Atomic absorption spectrometer – AA 240 DUO (Agilent Technologies, Inc.) with atomization in a graphite furnace (accordance to PN-EN 14902.2010 standard).

Also, 28 samples of PM_{10} selected from station on Szymanowskiego street (from the periods: between 21 October 2016 and 22 November 2016 and between 5 June 2017 and 2 July 2017) were subject to analysis for As, Cd and Ni amount in the author's own investigations. In this case, 24-h samples were analysed. The microwave mineralization of samples was conducted in accordance with the standard PN-EN 14902:

the content of As, Cd and Ni was measured using inductively coupled plasma-mass spectrometry (ICP MS; 6100 DRC-e spektrometer produced by Perkin-Elmer) in accordance with PN-EN 14385:2005 standard. In the case of 24-h PM_{10} samples analyses were conducted in a certified laboratory, which can mark metals in lower concentrations than the VIEP's certified laboratory in Poznań. For specific heavy metals the authors established limits of determination of elements: $\text{As} < 0.023 \mu\text{g/sample}$, $\text{Cd} < 0.002 \mu\text{g/sample}$ and $\text{Ni} < 0.008 \mu\text{g/sample}$. Since both laboratories where metal analyses were carried out are certificated and possess an accreditation certificate for marking As, Cd and Ni, the correctness of markings performed is guaranteed in both cases. Therefore, the comparability of the results obtained in both laboratories is also ensured.

Health risk analysis

In order to determine cancer risk related to inhalation exposure resulting from the presence of selected PM-bound metals (As, Cd, Ni) adsorbed from a surface of suspended particulate matter PM_{10} the authors used the methodology of risk assessment of the United States Environmental Protection Agency (US EPA). This methodology includes the so-called whole-life chronic exposure of a child and an adult person to a PM-bound element or substance (US EPA 1986, 1989). The calculation scenario assumed, on the basis of the literature data, a 24-hour exposure of an adult person and a child during 365 days per year to an influence of polluted air. For tested population the project assumed the following data: average time of exposure was respectively equal to 6 years for a child and 70 years for an adult (Biesiada 2006, Trojanowska and Świetlik 2012; 2013).

The United States Environmental Protection Agency's (US EPA) method for health risk assessment enables one to calculate predicted and existing health risks present in relation to specific concentration of polluted air – in this case the

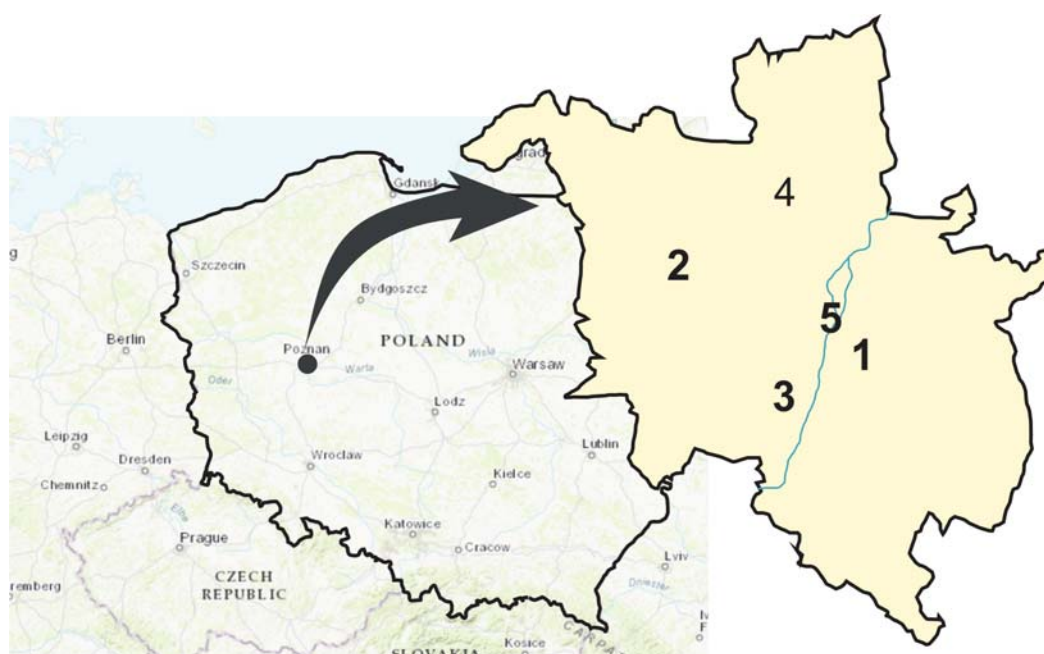


Fig. 1. Location of measurement stations: 1 – Polanka street, 2 – Dąbrowskiego street, 3 – Chwiałkowskiego street, 4 – Szymanowskiego street

inhalation exposure. In the described scenario, the level of As, Ni and Cd, present in a studied area, has an influence on the size of a dose.

The collected sample of a specific heavy metal, which accesses the organism of a human during respiration processes, during 24 hours, with respect to 1 kg of human body weight was calculated with use of the following formula (1).

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

where:

EDI – estimated daily intake [mg/d·kg]

C – average concentration of the substance in the air [mg/m³]

IR – 24 hour lung ventilation [m³/d]

AF – bioavailability factor [unitless]

F – contact frequency [d/year]

ED – time of exposure [year]

BW – average body weight [kg]

AT – averaging period [d]

The values of specific parameters used in the work to calculate the value of collected sample amount to average body weight – 16 kg for children, 65.4 kg for women, 78.1 kg for men, assumed values of 24-hour lung ventilation – 10 m³/day for children, 20 m³/day for adults. The remaining parameters were equal to contact frequency – 24 hours – 365 d/year, time of exposure – 365 days a year, bioavailability factor equal to 1 (meaning that 100% of inhaled pollution is bioavailable by person). The data is based on 50-percentile of the body weight distribution in anthropometric data (Biesiada 2006, Gruszecka-Kosowska 2017, Trojnowska and Świetlik 2012; 2013). Average concentration of the selected heavy metals per resident was assumed as an average value of concentrations of the determined metals in 24-hour samples of PM₁₀ particulate matter, collected during the authors' own studies in campaigns in the heating season and non-heating season and also on the grounds of data of the VIIEP in Poznań. Carcinogenic influence of As, Ni and Cd (table 3) was calculated with a following formula: (2).

$$CR = EDI \cdot SF \quad (2)$$

where:

CR – cancer risk

EDI – estimated daily intake [mg/d·kg]

SF – slope factor

The slope factor, being factor of the strength of carcinogenic activity, was assumed on the grounds of toxicological database (IRIS) for inhalation exposure to As: 15.1; Cd: 6.3 and Ni: 0.84 [mg/kg·d]⁻¹ (<https://www.epa.gov/iris>). The acquired values were compared with acceptable level of cancer risk, which is equal to 1·10⁻⁶ (Trojanowska and Świetlik 2012; 2013, US EPA 1991).

Results of the studies and discussion

According to the Polish law, an acceptable annual average concentration for PM₁₀ is equal to 40 µg/m³ and for PM_{2.5} – 25 µg/m³ (Journal of Polish Laws of 2012, item 1031).

During the years between 2010 and 2016 the acceptable annual average level of PM₁₀ at each of the analyzed stations in Poznań was not exceeded. In the analyzed period, the average annual concentrations had shown a downwards tendency. In the case of Polanka street (sampling point no. 1) the concentration of PM₁₀ in 2010 was 14% higher than the concentration in 2016; at the measurement station on Dąbrowskiego street (sampling point no. 2) it was 19% higher (Table 1). In the case of two remaining measurement points decreases were also observed, but they were insignificant. Annual average concentration of PM_{2.5} exceeded the limit in 2011 and 2014 (Table 1).

Basing on the analysis of annual average concentrations of PM₁₀ and PM_{2.5}, one may assume that the air quality in Poznań is quite good. However, for the PM₁₀, another standard was established – namely, an allowed number of days in a year (35) where 24-h concentration exceeded 50 µg/m³ (L>50). In the considered period, with few exceptions, the standard was exceeded at every measurement station in Poznań (Table 1). An exception was observed only at the measurement station on Polanka street (measurement point no. 1) in 2013 and at the measurement station on Chwiałkowskiego street (measurement point no. 3) in the years between 2013 and 2016. However, also at these measurement stations the number of days during a year where value exceeded 50 µg/m³ was near to the standard (35 days). Days with 24-hour concentrations of PM₁₀ greater than 50 µg/m³ are more frequently observed in the autumn-winter period.

The analysis of data in the heating period (H) and non-heating period (NH) (Table 1), clearly indicates that higher 24-h concentrations of PM₁₀ as PM_{2.5} are observed in the heating season. The highest average PM₁₀ concentration during the heating season was observed in 2010 at posts on Polanka street (measurement point no. 1) and Dąbrowskiego street (sampling point no. 2). The observed concentration amounted to 53 µg/m³. Average PM₁₀ concentration during the non-heating season ranged across 13 µg/m³ (observed in 2013 at the sampling point by Szymanowskiego street) and 31 µg/m³ (2014, on Chwiałkowskiego street). As of PM_{2.5}, average concentrations during the heating season (Polanka st, sampling point no. 1) was highest in 2011, amounting to 39 µg/m³, and lowest in 2013 and 2016, being equal to 32 µg/m³ in both these years. The highest PM_{2.5} average concentration occurred in 2014 (18 µg/m³) and the lowest – in 2010 (14 µg/m³). This data allows one to draw the conclusion that in Poznań during the heating season the annual dust concentration standards (40 µg/m³ for PM₁₀ 25 µg/m³ for PM_{2.5}) are exceeded.

In Poznań, the air quality in winter is mainly shaped by emission caused by energy production in coal-fired power and heating plants and in domestic stoves. Also, meteorological conditions in the winter season (frequent windless periods, temperature inversion) are not favorable to dispersion of PM in the atmosphere. The analysis performed by Sówka et al. (2018) confirmed the presence of negative correlations between PM concentration in Poznań and the wind speed and air temperature in winter and between PM concentrations and relative air humidity in summer. The similar problem with aggravating air quality during the winter season is observed in other Polish cities (powietrze.gios.gov.pl). The worst situation is observed in the southern region of Poland (Błaszczak et al. 2016, Chlebowska-Styś et al. 2017b, Rogula-Kozłowska et al.

2014, 2016). In contrast, the cities located in Northern Europe (Helsinki, Copenhagen, Stockholm, London) are characterized by a lack of variability in concentrations of PM during the year; in Western Europe the seasonal variation of PM concentration is not so clear like in Poland (Błaszczak et al. 2016, Cusack et al. 2012, Rogula-Kozłowska et al. 2014, Rouil and Meleux 2016).

Table 2 presents average concentrations of selected heavy metals in the years between 2012 and 2016 in selected measurement points in Poznań. In accordance with the Directive 2004/107/EC of the European Parliament and of the Council, acceptable levels of selected PM₁₀-bound heavy metals are 20 ng/m³ for Ni, 6 ng/m³ for As and 5 ng/m³ for Cd (Journal of Laws of 2012, item 1031, Official Journal of the European Union L 152 of June 11, 2008; page 1).

The highest annual concentration of As was observed in 2015 at the measurement station no. 3 (Chwiałkowskiego street). Higher seasonal concentrations of As were noted in heating season (H), rather than in non-heating (NH) season. In the case of Cd, the highest annual concentration was observed

in 2012 at Chwiałkowskiego street (measurement point no. 3) and again – the higher seasonal concentrations were obtained in the heating period. The highest annual concentration of Ni was noted in 2012 (Chwiałkowskiego street, measurement point no. 3). In 2012 and 2014 higher seasonal concentrations of Ni were noted in the heating period. On the other hand, at the measurement station on Chwiałkowskiego street (measurement point no. 3) the mid-term concentration of Ni was higher in the non-heating period in 2013 and 2016. According to the literature data, the presence of PM-bound As could have been correlated with emission from combustion of fossil fuels in home fireplaces/stoves or/and in heating/power plants. Road traffic and industry could be considered as the major sources of Cd and Ni (Birmili et al. 2006, Lough et al. 2005, Rogula-Kozłowska 2016, Sternbeck et al. 2002). The closest surroundings of the station no. 4 (Szymanowskiego street), where the concentrations of Ni were the highest, are single-family housing, multi-family housing and industry (e.g. carpentry, production of building materials, chocolate factory).

Table 1. Values of annual average concentrations (Sa) and average concentrations in the heating (H) and non-heating (NH) seasons of PM₁₀ and PM_{2.5} in Poznań in 2010–2016

| Year | Season | Concentration of PM ₁₀ [µg/m ³] | | | | | Concentration of PM _{2.5} [µg/m ³] | |
|------|--------|--|------------------|---------------------|--------------------|-------------------|---|-------------------|
| | | Polanka St. | Dąbrowskiego St. | Chwiałkowskiego St. | Szymanowskiego St. | Jana Pawła II St. | Polanka St. | Jana Pawła II St. |
| 2010 | Sa | 38 | 37 | – | – | – | 25 | – |
| | H | 53 | 53 | 49 | – | – | 37 | – |
| | NH | 24 | 23 | 31 | – | – | 14 | – |
| 2011 | Sa | 39 | 39 | – | – | – | 28 | – |
| | H | 53 | 53 | – | – | – | 39 | – |
| | NH | 27 | 25 | – | – | – | 16 | – |
| 2012 | Sa | 36 | 33 | – | 29 | – | 24 | – |
| | H | 49 | 46 | – | 39 | – | 34 | – |
| | NH | 24 | 22 | – | 21 | – | 15 | – |
| 2013 | Sa | 30 | 25 | 32 | 21 | – | 23 | – |
| | H | 40 | 31 | 41 | 26 | – | 32 | – |
| | NH | 20 | 19 | 23 | 13 | – | 16 | – |
| 2014 | Sa | 36 | 37 | 35 | 26 | – | 26 | – |
| | H | 45 | 41 | 48 | 37 | – | 35 | – |
| | NH | 27 | 18 | 22 | 18 | – | 18 | – |
| 2015 | Sa | 35 | 31 | 33 | 26 | – | 24 | – |
| | H | 43 | 43 | 42 | 34 | – | 34 | – |
| | NH | 27 | 20 | 24 | 18 | – | 15 | – |
| 2016 | Sa | 33 | 30 | 32 | 27 | – | 24 | – |
| | H | 38 | 37 | 38 | 31 | 25 | 32 | 15 |
| | NH | 29 | 23 | 26 | 22 | – | 16 | – |
| 2017 | Sa | – | – | – | – | – | – | – |
| | H | – | – | – | – | – | – | – |
| | NH | – | – | – | – | 17 | – | 10 |

Sa – annual average concentration

H – heating season (January, February, March, October, November, December)

NH – non-heating season (April, May, June, July, August, September)

Table 2. Values of annual average concentrations and average concentrations in the heating (H) and non-heating (NH) seasons of As, Cd and Ni in PM₁₀ in Poznań in 2010–2016

| Selected metals | Sampling site | Concentration [ng/m ³] | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2012–2016 |
|---------------------|---|------------------------------------|------|------|------|------|-------|------|-----------|
| As | Chwiałkowski St. -VIEP Poznań station (measurement point no. 3) | the average concentration | 2.10 | 1.82 | 1.23 | 2.34 | 1.95 | – | 1.89 |
| | | the average concentration in H | 2.81 | 2.55 | 1.81 | 2.34 | 3.34 | – | 2.57 |
| | | the average concentration in NH | 1.50 | 1.08 | 0.75 | – | 0.55 | – | 0.97 |
| As (own studies) | Jana Pawła II St. (measurement point no. 5) | the average concentration | – | – | – | – | – | – | – |
| | | the average concentration in H | – | – | – | – | 2.14 | – | – |
| | | the average concentration in NH | – | – | – | – | – | <go | – |
| As (own studies) | Szymanowskiego St. (measurement point no. 4) | the average concentration | – | – | – | – | – | – | – |
| | | the average concentration in H | – | – | – | – | 1.83 | – | – |
| | | the average concentration in NH | – | – | – | – | – | <go | – |
| Cd | Chwiałkowski St. -VIEP Poznań station (measurement point no. 3) | the average concentration | 0.65 | 0.45 | 0.35 | 0.45 | 0.41 | – | 0.46 |
| | | the average concentration in H | 0.92 | 0.65 | 0.55 | 0.45 | 0.52 | – | 0.62 |
| | | the average concentration in NH | 0.43 | 0.24 | 0.18 | – | 0.25 | – | 0.28 |
| Cd (own studies) | Jana Pawła II St. (measurement point no. 5) | the average concentration | – | – | – | – | – | – | – |
| | | the average concentration in H | – | – | – | – | 0.84 | – | – |
| | | the average concentration in NH | – | – | – | – | – | – | – |
| Cd (own studies) | Szymanowskiego St. (measurement point no. 4) | the average concentration | – | – | – | – | – | – | – |
| | | the average concentration in H | – | – | – | – | 0.25 | – | – |
| | | the average concentration in NH | – | – | – | – | – | <go | – |
| Ni | Chwiałkowski St. -VIEP Poznań station (measurement point no. 3) | the average concentration | 2.15 | 1.30 | 1.00 | 1.04 | 0.69 | – | 1.24 |
| | | the average concentration in H | 2.66 | 1.19 | 1.13 | 1.04 | 0.62 | – | 1.33 |
| | | the average concentration in NH | 1.78 | 1.40 | 0.88 | – | 0.79 | – | 1.21 |
| Ni (own studies) | Jana Pawła II St. (measurement point no. 5) | the average concentration | – | – | – | – | – | – | – |
| | | the average concentration in H | – | – | – | – | 5.28 | – | – |
| | | the average concentration in NH | – | – | – | – | – | 0.60 | – |
| Ni (own studies) | Szymanowskiego St. (measurement point no. 4) | the average concentration | – | – | – | – | – | – | – |
| | | the average concentration in H | – | – | – | – | 10.82 | – | – |
| | | the average concentration in NH | – | – | – | – | – | <go | – |

The cancer risk considered to be acceptable or negligible according to US EPA is $1 \cdot 10^{-6}$. The risk which is serious and requires protective measures to be taken for residents of a specific studied area is equal to $1 \cdot 10^{-3}$ (Biesiada 2006, Trojanowska and Świetlik 2012; 2013). Taking the same assumptions for input data for calculations as in the literature (Gruszecka-Kosowska 2017, Trojanowska and Świetlik 2012), we were able to compare the acquired values of doses collected through inhalation for As. The calculation results of arsenic intake in Poznań for annual average concentrations obtained between 2012 and 2016 collated in table nr 3 show higher values for point no. 3 (Chwiałkowskiego street) than the values obtained in the literature for the agglomeration of Poznań (Trojanowska and Świetlik 2012). In the completed studies basing on the data from 2007–2009, the authors acquired the following estimated daily intake of As collected through

the means of inhalation: $0.20 \cdot 10^{-6}$ [mg/d·kg] for children, $0.09 \cdot 10^{-6}$ [mg/d·kg] for women and $0.08 \cdot 10^{-6}$ [mg/d·kg] for men (Trojanowska and Świetlik 2012). In Legnica (in the years 2007–2009), where ambient concentrations of As are much higher than in Poznań, the following estimated daily intakes of As were computed: $1.86 \cdot 10^{-6}$ [mg/d·kg] for men, $2.22 \cdot 10^{-6}$ [mg/d·kg] for women and $4.53 \cdot 10^{-6}$ [mg/d·kg] for children (Trojanowska and Świetlik 2012). These values are higher than the values determined for the residents of Poznań, for whom the following values were obtained: men: $0.48 \cdot 10^{-6}$ [mg/d·kg], women: $0.58 \cdot 10^{-6}$ [mg/d·kg], children: $1.18 \cdot 10^{-6}$ [mg/d·kg].

In the completed calculations the highest values of risk for residents of Poznań (Table 4) for the years 2012–2016, in the heating period obtained for the measuring point no. 3 (Chwiałkowskiego street) were: $24.27 \cdot 10^{-6}$ for children,

Table 3. Estimated daily intakes by inhalation for selected heavy metals

| Selected metals | Sampling site | Season | Adults men | | | Adults women | | | Children | | |
|---------------------|--|--------|--------------------------------|------|-----------|--------------|------|-----------|----------|------|-----------|
| | | | 2016 | 2017 | 2012–2016 | 2016 | 2017 | 2012–2016 | 2016 | 2017 | 2012–2016 |
| | | | EDI [$\cdot 10^{-6}$ mg/d·kg] | | | | | | | | |
| As | Chwiałkowskiego St. -VIEP Poznań station (measurement point no. 3) | yr | – | – | 0.48 | – | – | 0.58 | – | – | 1.18 |
| | | H | – | – | 0.66 | – | – | 0.79 | – | – | 1.61 |
| | | NH | – | – | 0.25 | – | – | 0.30 | – | – | 0.61 |
| As (own studies) | Jana Pawła II St. (measurement point no. 5) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 0.55 | – | – | 0.65 | – | – | 1.34 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| As (own studies) | Szymanowskiego St. (measurement point no. 4) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 0.47 | – | – | 0.56 | – | – | 1.15 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| Cd | Chwiałkowskiego St. -VIEP Poznań station (measurement point no. 3) | Sa | – | – | 0.12 | – | – | 0.14 | – | – | 0.29 |
| | | H | – | – | 0.16 | – | – | 0.19 | – | – | 0.39 |
| | | NH | – | – | 0.07 | – | – | 0.08 | – | – | 0.17 |
| Cd (own studies) | Jana Pawła II St. (measurement point no. 5) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 0.21 | – | – | 0.26 | – | – | 0.52 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| Cd (own studies) | Szymanowskiego St. (measurement point no. 4) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 0.06 | – | – | 0.08 | – | – | 0.16 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| Ni | Chwiałkowskiego St. -VIEP Poznań station (measurement point no. 3) | Sa | – | – | 0.31 | – | – | 0.38 | – | – | 0.77 |
| | | H | – | – | 0.34 | – | – | 0.41 | – | – | 0.83 |
| | | NH | – | – | 0.31 | – | – | 0.37 | – | – | 0.76 |
| Ni (own studies) | Jana Pawła II St. (measurement point no. 5) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 1.35 | – | – | 1.61 | – | – | 3.30 | – | – |
| | | NH | – | 0.15 | – | – | 0.18 | – | – | 0.38 | – |
| Ni (own studies) | Szymanowskiego St. (measurement point no. 4) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 2.77 | – | – | 3.31 | – | – | 6.76 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |

H – heating season (January, February, March, October, November, December)

NH – non-heating season (April, May, June, July, August, September)

Table 4. Inhalation cancer risk for selected heavy metals in specific groups

| Selected metals | Sampling site | Season | Adults men | | | Adults women | | | Children | | |
|---------------------|--|--------|------------------------|------|-----------|--------------|------|-----------|----------|------|-----------|
| | | | 2016 | 2017 | 2012–2016 | 2016 | 2017 | 2012–2016 | 2016 | 2017 | 2012–2016 |
| | | | CR [$\cdot 10^{-6}$] | | | | | | | | |
| As | Chwiałkowskiego St. -VIEP Poznań station (measurement point no. 3) | yr | – | – | 7.29 | – | – | 8.71 | – | – | 17.80 |
| | | H | – | – | 9.94 | – | – | 11.87 | – | – | 24.27 |
| | | NH | – | – | 3.75 | – | – | 4.48 | – | – | 9.16 |
| As (own studies) | Jana Pawła II St. (measurement point no. 5) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 8.28 | – | – | 9.88 | – | – | 20.20 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| As (own studies) | Szymanowskiego St. (measurement point no. 4) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 7.09 | – | – | 8.47 | – | – | 17.31 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| Cd | Chwiałkowskiego St. -VIEP Poznań station (measurement point no. 3) | Sa | – | – | 0.75 | – | – | 0.89 | – | – | 1.82 |
| | | H | – | – | 1.00 | – | – | 1.19 | – | – | 2.44 |
| | | NH | – | – | 0.45 | – | – | 0.53 | – | – | 1.09 |
| Cd (own studies) | Jana Pawła II St. (measurement point no. 5) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 1.35 | – | – | 1.61 | – | – | 3.30 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| Cd (own studies) | Szymanowskiego St. (measurement point no. 4) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 0.41 | – | – | 0.49 | – | – | 1.00 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |
| Ni | Chwiałkowskiego St. -VIEP Poznań station (measurement point no. 3) | Sa | – | – | 0.27 | – | – | 0.32 | – | – | 0.65 |
| | | H | – | – | 0.29 | – | – | 0.34 | – | – | 0.70 |
| | | NH | – | – | 0.26 | – | – | 0.31 | – | – | 0.64 |
| Ni (own studies) | Jana Pawła II St. (measurement point no. 5) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 1.14 | – | – | 1.36 | – | – | 2.77 | – | – |
| | | NH | – | 0.13 | – | – | 0.16 | – | – | 0.32 | – |
| Ni (own studies) | Szymanowskiego St. (measurement point no. 4) | yr | – | – | – | – | – | – | – | – | – |
| | | H | 2.33 | – | – | 2.78 | – | – | 5.68 | – | – |
| | | NH | – | – | – | – | – | – | – | – | – |

H – heating season (January, February, March, October, November, December)
NH – non-heating season (April, May, June, July, August, September)

$11.87 \cdot 10^{-6}$ for women and $9.94 \cdot 10^{-6}$ for men, whereas the risk values obtained for the measuring point no. 4, situated on Szymanowskiego street, amounted to: for As: men: $7.09 \cdot 10^{-6}$, women: $8.47 \cdot 10^{-6}$, children: $17.31 \cdot 10^{-6}$, Cd: men: $0.41 \cdot 10^{-6}$, women: $0.49 \cdot 10^{-6}$, children: $1.00 \cdot 10^{-6}$, Ni: men: $2.33 \cdot 10^{-6}$, women: $2.78 \cdot 10^{-6}$, children: $5.68 \cdot 10^{-6}$, respectively. Cancer exposition risk values obtained among the inhabitants of Wrocław, for selected metals marked in PM₁₀ suspended dust: As: men: $6.11 \cdot 10^{-6}$, women: $7.30 \cdot 10^{-6}$, children: $14.90 \cdot 10^{-6}$, Cd: men: $0.37 \cdot 10^{-6}$, women: $0.44 \cdot 10^{-6}$, children: $0.91 \cdot 10^{-6}$ and Ni: men: $1.91 \cdot 10^{-6}$, women: $2.29 \cdot 10^{-6}$, children: $4.67 \cdot 10^{-6}$ (Pachurka et al. 2017) were lower than the values obtained in the examined area of Poznań.

To conclude, it has been proved that cancer risk caused by an inhalation of PM-bound As, Ni and Cd in Poznań is on an acceptable level (Trojanowska and Świetlik 2012; 2013, US EPA 1991).

Conclusions

Polish cities are troubled with poor air quality of air, which is mainly caused by low quality of soild/fossil fuels used in energy production, wide-range use of coal-fired domestic stoves and emission from old vehicles. Completed analysis aimed at determining the influence of the aforementioned sources of PM emission on the quality of air in Poznań together with indication of negative influence of selected metals on its residents.

The analysis of seasonal variability of PM concentrations in Poznań has confirmed that concentrations in the heating seasons are twice as high as in the non-heating period. Higher concentrations of As, Cd and Ni were also noted in heating periods. Acquired cancer risk values for residents of Poznań were on an acceptable level as compared to the guidelines by US EPA (US EPA 1991) and their highest values were found in the heating season for As.

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Analiza zmienności stężeń PM_{2.5} i PM₁₀ wraz z oceną narażenia inhalacyjnego na metale ciężkie w PM₁₀ (As, Cd i Ni) – pierwsze badania w Poznaniu

Streszczenie: Celem pracy była analiza zmienności sezonowej stężeń PM_{2.5} i PM₁₀ w Poznaniu wraz z oceną wpływu inhalacyjnego wybranych metali ciężkich związanych z PM₁₀ (As, Cd i Ni) na mieszkańców. W pracy przedstawiono wyniki pomiarów stężenia pyłu zawieszonego PM₁₀ i PM_{2.5} w Poznaniu w latach 2010–2016 oraz wyniki analizy oceny ryzyka zachorowania na raka w odniesieniu do ekspozycji inhalacyjnej na wybrane wartości PM: As, Cd, Ni. Dane wykorzystane w zestawieniu pochodzą z pomiarów WIOŚ i badań własnych. Przedstawione zostały średnie roczne stężenia PM w rozpatrywanym okresie wraz z analizą jego sezonowej zmienności. W celu określenia ryzyka autorzy wykorzystali metodologię oceny ryzyka US EPA. Średnie roczne stężenia PM₁₀ kształtowały się w przedziale od 21 µg/m³ w 2010 r. (ul. Szymanowskiego) do 39 µg/m³ w 2016 roku (ul. Polanka i Dąbrowskiego). W przypadku metali ciężkich najwyższą wartość stężenia As (3,34 ng/m³) określono w sezonie grzewczym 2016 r. (ul. Chwiałkowskiego), stężenia Cd (0,92 ng/m³) w sezonie grzewczym w 2012 r. (ul. Chwiałkowskiego) oraz stężenia Ni (10,82 ng/m³) w sezonie grzewczym 2016 roku (ul. Szymanowskiego) Przeprowadzone obliczenia wskazały na najwyższe wartości ryzyka dla danych zebranych w latach 2012–2016 w sezonie grzewczym i wyniosły odpowiednio dla dzieci: 24,27·10⁻⁶, kobiet: 11,87·10⁻⁶ i mężczyzn: 9,94·10⁻⁶. Wartość ryzyka na poziomie akceptowalnym zgodnie z US EPA wynosi 1·10⁻⁶.