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# Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

## Metal induced inhalation exposure in urban population: A probabilistic approach

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### HIGHLIGHTS

- We model health risks caused by inhalation exposure to airborne metals.
- We examine changes in the level of risk between PM<sub>2.5</sub> and PM<sub>10</sub>-bound metals.
- PM<sub>2.5</sub>-bound metals poses a higher risk than PM<sub>10</sub> – associated one.
- Infants and children are especially sensitive to airborne metals.
- Risk value depend on PM composition, as well as the variability of exposure.

### ARTICLE INFO

#### Article history:

Received 1 September 2015  
 Received in revised form  
 22 December 2015  
 Accepted 24 December 2015  
 Available online 29 December 2015

#### Keywords:

Cancer risk  
 Monte Carlo  
 Particulate matter  
 Metals  
 Silesia region  
 Probabilistic assessment

### ABSTRACT

The paper was aimed at assessing the health risk in the populations of three Silesian cities: Bielsko-Biala, Częstochowa and Katowice exposed to the inhalation intake of cadmium, nickel and arsenic present in airborne particulate matter. In order to establish how the exposure parameters affects risk a probabilistic risk assessment framework was used. The risk model was based on the results of the annual measurements of As, Cd and Ni concentrations in PM<sub>2.5</sub> and the sets of data on the concentrations of those elements in PM<sub>10</sub> collected by the Voivodship Inspectorate of Environmental Protection over 2012–2013 period. The risk was calculated as an incremental lifetime risk of cancer (ILCR) in particular age groups (infants, children, adults) following Monte Carlo approach. With the aim of depicting the effect the variability of exposure parameters exerts on the risk, the initial parameters of the risk model: metals concentrations, its infiltration into indoor environment, exposure duration, exposure frequency, lung deposition efficiency, daily lung ventilation and body weight were modeled as random variables. The distribution of inhalation cancer risk due to exposure to ambient metals concentrations was LN ( $1.80 \times 10^{-6} \pm 2.89 \times 10^{-6}$ ) and LN ( $6.17 \times 10^{-7} \pm 1.08 \times 10^{-6}$ ) for PM<sub>2.5</sub> and PM<sub>10</sub>-bound metals respectively and did not exceed the permissible limit of the acceptable risk. The highest probability of contracting cancer was observed for Katowice residents exposed to PM<sub>2.5</sub> – LN ( $2.01 \times 10^{-6} \pm 3.24 \times 10^{-6}$ ). Across the tested age groups adults were approximately one order of magnitude at higher risk compared to infants. Sensitivity analysis showed that exposure duration (ED) and body weight (BW) were the two variables, which contributed the most to the ILCR.

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### 1. Introduction

In recent years, there has been an increasing concern about the exceedance of the permissible concentrations of particulate matter in atmospheric air. The results of epidemiological research reveal

that exposure to PM causes an increase in mortality rate and incidence of vascular and respiratory diseases, including cancer (Pope et al., 2011). Despite ample scientific evidence confirming the correlation between persistent exposure to PM and the increase in malignant cancer incidence, including lung cancer, it is still unknown, which compounds of the particles are responsible for inducing carcinogenesis (Harrison et al., 2004). Studies into environmental hazard indicate however that PM induced cancers can be attributed to its metallic constituents (t Mannetje et al., 2011;

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Yaman, 2012).

In Poland, three metals: lead, cadmium, nickel and one semi-metal, arsenic, are monitored in the air. Three of the above elements: As, Ni and Cd have been classified as factors with sufficient evidence of carcinogenicity in humans (IARC, 2014). Most of the available information about the health effects of those elements is derived from studies, which monitored As, Cd and Ni contents in PM<sub>10</sub> (Sadovska, 2012; Trojanowska and Świetlik, 2012). Scientific investigations do not usually deal with the health effects of exposure to the above metals based on their concentrations in PM<sub>2.5</sub>. This results from the fact that before 2008, PM<sub>2.5</sub> was not required to be monitored. However, since PM<sub>2.5</sub> constitutes approximately 70% of PM<sub>10</sub> mass (Gomiścek et al., 2004) and is deposited in the deepest areas of the respiratory track, it probably enables more accurate prediction of risk (WHO, 2013).

The assessment of the health effects of exposure to PM and metals in urban areas is relevant because of their numerous emission sources and the size of the population exposed. Since metals are widely present in urban air and their carcinogenic properties are widely known, the assessment of their harmfulness to public health is necessary.

The methodological difficulty in assessing the inhalation hazard caused by airborne carcinogenic metals lies in the complexity of their effects on a population, such as variability of metal concentrations in air, indoor/outdoor pollution ratio, exposure duration, *physiological parameters* (lung ventilation rate influencing deposition efficiency in the respiratory) and variability of individual characteristics in a population exposed (age and gender) (Biesiada, 2001). Those factors affect the amount of metals taken in, thus significantly determining the final risk. Monte Carlo technique involving the so called Probability Risk Assessment allows the variability of those risk parameters to be taken into account, while assessing risk and determining their effect on the final health risk value. Such approach gives more complex risk characteristics and constitute a source of additional information for risk managers.

### 1.1. Objectives

The primary objective of this study was: to assess the inhalation risks to the residents of three Silesian cities – exposed to PM<sub>2.5</sub> and PM<sub>10</sub> associated metals by using Monte Carlo approach (1), to determine the influence of exposure parameters variability on health risk value (2), to identify those exposure parameters, which are the key contributors to over all risk value (3).

## 2. Materials and methods

### 2.1. Characteristics of the study area

The Upper Silesian Region (Fig. 1) is one of the most polluted areas in Poland and is home to numerous extractive, electrical, power engineering and metallurgical industries. Its nature based on raw materials and power production, as well as developed transport infrastructure, makes it occupy the first place in terms of excessive PM concentrations. The emission of PM dust in this area accounts for 22.14% of the over all national emission (Śląskie, 2020+).

### 2.2. Sampling protocol

In the presented study authors used the data on PM<sub>10</sub> and associated metals concentrations collected by the Voivodship Inspectorate of Environmental Protection in Katowice (VIEP Katowice) and their own measurements of the above elements in PM<sub>2.5</sub> for the same period (May 2012–April 2013). Locations of the sampling

sites are shown in Fig. 1. More detailed information concerning sampling sites along with samplers specification can be found in the Supplementary Materials. It must be highlighted that PM<sub>2.5</sub> and PM<sub>10</sub> data presented in this work in fact come from different sampling sites, where those fractions were collected separately. Throughout the work inhalation hazards were therefore evaluated independently for PM<sub>2.5</sub> and PM<sub>10</sub>.

#### 2.2.1. PM<sub>10</sub>

Datasets containing PM<sub>10</sub> and associated metal concentrations were downloaded from the Silesian Air Monitoring database ([www.katowice.pios.gov.pl/slmonpow](http://www.katowice.pios.gov.pl/slmonpow)), operated by the Chief Inspectorate for Environmental Protection (CIEP). The CIEPs laboratories carry out a routine assessment of metal contents in PM<sub>10</sub>. Metals assays are regularly done in two-week cumulative samples (14 PM<sub>10</sub> filters in total). Thus, 26 measurements of metal concentrations in atmospheric air are conducted each year (Table 5).

#### 2.2.2. PM<sub>2.5</sub>

Fine particles were collected using low volume samplers (2.3 m<sup>3</sup>/h) equipped with a PM<sub>2.5</sub> measuring head onto Ø47 mm Whatman quartz fiber filters. Diurnal samples were sampled at Bielsko-Biała and Częstochowa urban background sites and additionally at Katowice traffic site. The mass of the sampled particles was determined gravimetrically (Radwag microbalance, resolution 1 µg) according to the BS EN 14907:2006 standard. Before each weighing, the filters were conditioned for at least 48 h at the air temperature of 20 ± 1 °C and air relative humidity of 50 ± 5%.

### 2.3. Metals extraction and samples preparation

Single quarter of each PM<sub>2.5</sub> filter was digested in a Milestone microwave digestion system (MLS 1200 Mega oven) using 2 cm<sup>3</sup> of 65% HNO<sub>3</sub> (Baker). The digestion power was held at 1000 W over all digestion stages (time, 6 min). After cooling, the samples were transferred into flasks and made up to 25 cm<sup>3</sup> with ultrapure water. Samples were transferred into plastic bottles and kept in ventilated room until the instrumental analysis. Determination of the total arsenic was carried out after As(V) reduction into As(III). For that purpose three remaining quarters of each filter were cut down to pieces smaller than 1 cm in length and placed in a tube. In next step exactly 5 cm<sup>3</sup> of HCl (36% w/v), 2.5 cm<sup>3</sup> of urea (25% w/v) and 1 cm<sup>3</sup> of KI (25% w/v) was added to this tube. After 30 min (prereduction time), solution was filled to 25 cm<sup>3</sup> with ultrapure water, filtrated through 0.45 µm cellulose filter and aspirated to HG-AAS. The complete reduction of the arsenous hydride was achieved in VGA reaction loop by the addition of 10 M HCl and sodium tetrahydroborate (III) in 0.05% (w/v) NaOH.

### 2.4. Instrumental analysis

The instrumental analysis was conducted by means of GT-AAS method (in case of Ni and Cd) and by using HG-AAS (for As determination). All metal concentrations were calculated on PM<sub>2.5</sub> mass collected and normalized by the volume of air passed through the filters during the sampling period. Calibration solutions were prepared daily by using Merck single-element stock solutions of 1000 ppm.

### 2.5. QA/QC

Blank filters were mineralized following the same digestion procedure as tested filters. Blank samples have been found to have non-detectable levels of elements of interest. Certified reference material NIES Urban Aerosol was used to verify the accuracy and

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