

Heavy Metals in PM_{2.5} Aerosols in Urban Sites of Győr, Hungary

Zs. Csanádi, A. Szabó Nagy, J. Szabó, J. Erdős

Abstract—Atmospheric concentrations of some heavy metal compounds (Pb, Cd, Ni) and the metalloid As were identified and determined in airborne PM_{2.5} particles in urban sites of Győr, northwest area of Hungary. PM_{2.5} aerosol samples were collected in two different sampling sites and the trace metal(loid) (Pb, Ni, Cd and As) content were analyzed by atomic absorption spectroscopy. The concentration of PM_{2.5} fraction was varied between 12.22 and 36.92 µg/m³ at the two sampling sites. The trend of heavy metal mean concentrations regarding the mean value of the two urban sites of Győr was found in decreasing order of Pb > Ni > Cd. The mean values were 7.59 ng/m³ for Pb, 0.34 ng/m³ for Ni and 0.11 ng/m³ for Cd, respectively. The metalloid As could be detected only in 3.57% of the total collected samples. The levels of PM_{2.5} bounded heavy metals were determined and compared with other cities located in Hungary.

Keywords—Aerosol, air quality, heavy metals, PM_{2.5}.

I. INTRODUCTION

AIR and ambient atmosphere quality is an important issue for public health, the economy and the environment. One of the most significant components is the particulate matter (PM). It is a complex mixture of solid and liquid particles of several different origins, which can contain a wide range of organic and inorganic materials. They can be emitted from both natural and anthropogenic sources, and can be found both outdoors and indoors [1]. PM is defined according to the diameter/size of the particle. Particulates with aerodynamic diameters smaller than 10 µm are called PM₁₀ and particulates with aerodynamic diameter less than 2.5 µm are defined as PM_{2.5} fractions [2].

Transportation and residence in air and deposition on the respiratory system of these particles is determined by their size. Small airborne particles have a high probability of deposition in the respiratory tract and are likely to cause respiratory, cardiovascular and cancer diseases. [3]. As well as the size distribution, the chemical composition of particles can induce health-related effects [4]. The major components of PM include organic compounds, inorganic ions or metallic components [5]. PM fractions containing different heavy metals regarding the long-term exposure to metals could cause several toxic effects on human health [6], [7].

Metal containing aerosols in the ambient atmosphere are

produced by various anthropogenic and natural sources. Combustion of fossil fuels and wood, exhaust emission from vehicles, industrial activities and energy production are known to be anthropogenic sources [8]. Vehicle traffic is a possible source of Cd, Pb, Mn and Ni as a result of fuel combustion and the wearing of brakes, tires, and other components [9], [10]. Emissions sources as coal burning power plants can be potential sources for As, Cd, Cr, Pb and Ni while metal and ceramic processing facilities could emit a wide variety of trace metals and metalloids [11].

The metal content of PM_{2.5} including lead, nickel, cadmium and arsenic has been suggested as possible factors inducing adverse respiratory health effects according to the International Agency for Research on Cancer (IARC), as potential cancer agents [12]. Several epidemiological and toxicological studies have showed that heavy metals can accumulate in fatty tissues, affecting the functions of organs and destructing the nervous or endocrinal system, or interact with DNA to cause mutations [13], [14]. Pb is typically a cumulative toxin and can be stored in the teeth and bones, where it accumulates during a long-time possession. Chronic Pb exposure commonly can lead to haematological effects, such as anaemia, or neurological disorders, as headache, lethargy, muscle weakness, tremors and paralysis [14]. The respiratory toxicity and carcinogenicity effects of Ni compounds in ambient air were described such as lung cancer, lung inflammation and fibrosis [15]. Inhalatively resorbed Cd usually reaches blood circulation in form of Cd-cysteine complexes [16]. The main organ for long-term Cd accumulation is the kidney and a Cd accumulation can therefore result in a tubulus cell necrosis [17]. The metalloid As is a known carcinogen for bladder, lung, and skin. Inhalation of it may cause lung cancer [18].

Air quality policy and emission regulations are typically based on the size of particle fractions PM₁₀ and PM_{2.5}, because they are the most likely to have impact on human health. In Hungary, only PM₁₀ concentration levels are regularly measured and regulated, and PM_{2.5} fractions are determined insufficiently. Therefore, the aim of this work was to investigate the concentration levels of some heavy metal compounds (Pb, Cd, Ni) and the metalloid As in airborne PM_{2.5} particles in urban sites of Győr, northwest area of Hungary.

II. MATERIALS AND METHODS

A. Study Area and PM_{2.5} Aerosol Sampling

Atmospheric aerosol measurements were performed at the permanent urban sites of Győr located in the northwestern part

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of Hungary in 2014. The location of Győr is shown in Fig 1.

Győr is an important center in the northwestern area of Hungary. It is situated on an important routeway of Central Europe. The number of inhabitants is about 130.000, it is the sixth largest in Hungary. Győr has a good geographic situation and it is a dynamically developing city as an emphasized center in automotive industry. PM_{2.5} samples were taken onto two monitoring sites (Site 1 and Site 2). Site 1 is located at Szent István Street, Site 2 is located at the junction of Szigethy Street and Ifjúság Boulevard. Both of them are busy road junctions of the city, where the main pollution source is traffic [19].



Fig. 1 Schematic map of Hungary showing the location of Győr, as the studied monitoring site

PM_{2.5} and associated metal compounds were monitored, between 04 and 17 of November, 2014. The total of 28 aerosol samples were collected every day for 24-hours over 2 weeks with a Digital High Volume sampler DHA-80 (Digital Elektronik AG, Switzerland) provided with a PM_{2.5} cut-off inlet. Samples were taken onto high purity quartz fiber filters (Whatman QMA, size: 150 mm diameter). The applied flow rate was 30 m³/h. The sampler was loaded with 14 filters, which were changed automatically every 24 hours. About 720 m³ of air was pumped through a filter in every 24 hours [20].

B. Gravimetric Analysis

The filters were conditioned for 48 h at 20±1 °C and 50±5% relative humidity before and after sampling. The total mass of particles was determined by weighing of the sampling filters before and after sampling using a micro-analytical balance and the PM_{2.5} concentration was calculated from the weighed mass on the filter and the sampling volume as previously described in our works [19], [20]. After the sampling, the filters were separately packed into an aluminum foil and stored in a refrigerator at 4 °C until chemical analysis [19], [20].

C. Chemical Analysis of PM_{2.5}-Bound Heavy Metals and Metalloid Arsenic

The concentrations of heavy metals (Pb, Cd, Ni) and the metalloid As in the PM_{2.5} aerosol fraction were measured by graphite furnace atomic absorption spectroscopy (SOLAAR MQZ, Unicam Ltd., Cambridge, UK) equipped with Zeeman

and deuterium background correctors, a graphite furnace GF9 and an autosampler. One half of the filter was cut by a ceramic scissor and the sample was treated with 15 mL aqua regia and digested at temperatures up to 210 °C for 20 min using a CEM Mars 5 microwave. The analytical method was given in details in previous studies [10], [19]. The resulting solution was filtered and diluted to 100 mL with distilled water. A 20 µL volume of the sample was injected into the graphite tube. The sample analysis was conducted in accordance with the MSZ EN 14902:2006 Hungarian standard method procedure [21].

III. RESULTS AND DISCUSSION

A. PM_{2.5}, PM_{2.5}-Bounded Heavy Metal and Metalloid Arsenic Concentrations

Table I represents the concentration levels of PM_{2.5} and PM_{2.5}-bound heavy metals and metalloid arsenic in the urban atmosphere of Győr in November of 2014.

TABLE I
 CONCENTRATION RANGES, MEAN VALUES AND STANDARD DEVIATIONS OF PM_{2.5} AND PM_{2.5}-BOUND HEAVY METALS AND METALLOID ARSENIC AT TWO MONITORING SITES OF GYŐR, HUNGARY IN NOVEMBER 2014

Pollutant	Site 1	Site 2
PM _{2.5} (µg/m ³)	12.22–34.14 22.43±8.20	12.44–36.92 23.90±8.66
Pb (ng/m ³)	2.07–12.83 6.94±3.24	2.14–14.00 8.24±3.88
Cd (ng/m ³)	ND–0.28 0.09±0.10	ND–0.43 0.13±0.13
Ni (ng/m ³)	ND–1.14 0.41±0.36	ND–0.72 0.27±0.29
As (ng/m ³)	ND ^a	ND–0.55 <ND

ND = not detected

^aAs were not detected in all samples

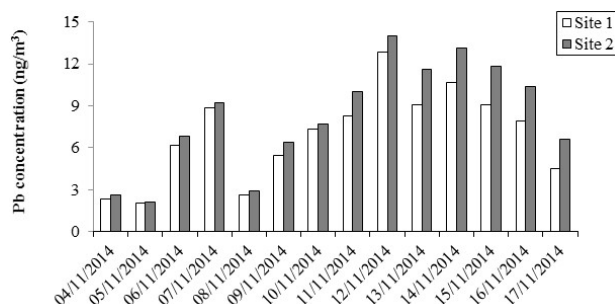


Fig. 2 PM_{2.5}-bound Pb concentrations measured at two monitoring sites of Győr, Hungary in November of 2014

The PM_{2.5} concentrations ranged from 12.22 to 36.92 µg/m³ in the total aerosol samples. The heavy metal mean concentrations was found in decreasing order of Pb, Ni, Cd at the two urban sites of Győr, respectively. The mean values detected at each sampling sites were 6.94 and 8.24 ng/m³ for Pb, 0.09 and 0.13 ng/m³ for Cd and 0.41 and 0.27 ng/m³ for Ni, respectively. The metalloid As could be detected only in 3.57% of the total collected samples with 0.55 ng/m³ value. Figs. 2, 3, and 4 show the individual concentration values of the measured heavy metals during the study period.

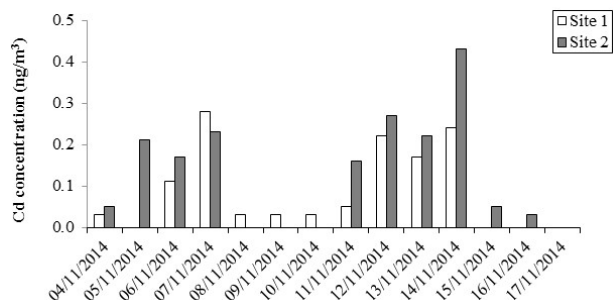


Fig. 3 PM2.5-bound Cd concentrations measured at two monitoring sites of Győr, Hungary in November of 2014

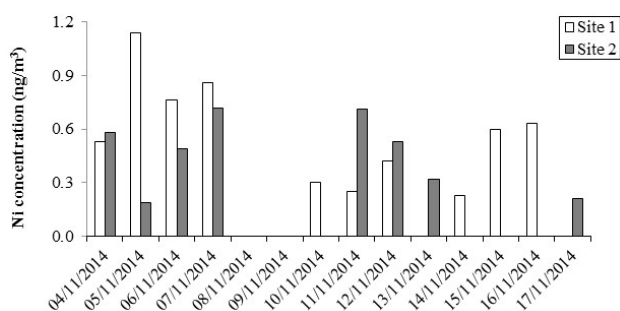


Fig. 4 PM2.5-bound Ni concentrations measured at two monitoring sites of Győr, Hungary in November of 2014

For PM2.5, the EU's Ambient Air Quality Directive in 2008 introduced a target value ($25 \mu\text{g}/\text{m}^3$ annual mean), which became a limit value in 2015 [22]. The WHO's Air Quality Guide (AQG) shows a stricter $10 \mu\text{g}/\text{m}^3$ annual mean and a $25 \mu\text{g}/\text{m}^3$ 24-hour mean value [23]. The Hungarian regulation for PM aerosols is usually equal to the EU Directive, the annual target value for PM2.5 aerosol fraction is $25 \mu\text{g}/\text{m}^3$ [24]. In general, PM10 levels are more regulated in Hungary as well, for this reason it could be reasonable to compare the actual PM10 and PM2.5 target and limit values. For heavy metals, only the PM10 fraction is regulated. Table II summarizes these actual air quality limit and target values in the case of PM10 compared with PM2.5 aerosol particles and the associated heavy metals.

TABLE II
AIR QUALITY LIMIT OR TARGET VALUES AND QUALITY INDEX

Regulation	PM10		PM2.5	
	Daily ($\mu\text{g}/\text{m}^3$)	Annual ($\mu\text{g}/\text{m}^3$)	Daily ($\mu\text{g}/\text{m}^3$)	Annual ($\mu\text{g}/\text{m}^3$)
EU limit or target value [22]	50 ^a	40	–	25
Hungarian limit value [24]	50 ^a	40	–	25
WHO guideline value [23]	50 ^b	20	25	10
PM10-bound heavy metals Annual (ng/m^3)				
	Pb	Cd	Ni	As
EU limit or target value [22]	500	5	20	6
Hungarian limit value [24]	300	5	25	10
WHO guideline value [23]	500	5	–	–

^aNot to be exceeded on more than 35 days/year.

^b99th percentile (3 days/year).

The measured mean concentration of PM2.5 in our study

was $23.17 \mu\text{g}/\text{m}^3$ regarding to the total number of samples collected at the two sampling sites and were under the EU's and Hungarian annual mean target value. However, the daily PM2.5 concentration exceeded the 24-hour AQG value of $25 \mu\text{g}/\text{m}^3$ in 46 % of the total samples. The reason could be the increased emissions from heat combustion in the heating season.

The comparison of PM2.5-bound heavy metal concentrations detected in Győr with the annual mean limit or target values defined for the associated PM10 fraction show very low metal content. Thus, excellent air quality for heavy metals can be identified.

B. Comparison of Heavy Metal Concentrations with other Hungarian Cities

The comparison of the mean PM10 and PM2.5 aerosol particles and bounded heavy metals and metalloid arsenic concentrations observed for Győr with other Hungarian cities is summarized in Table III.

TABLE III
COMPARISON OF PM-BOUND HEAVY METAL CONCENTRATIONS WITH OTHER HUNGARIAN CITIES

Location	Particle size/ mean concentration ($\mu\text{g}/\text{m}^3$)	Period	Mean Concentration (ng/m^3)				Reference
			Pb	Cd	Ni	As	
Győr	PM10/34.94	2008-2012	14.47	0.60	3.73	0.64	[19]
	PM2.5/23.17	2014	7.59	0.11	0.34	<ND	This study
Budapest	PM10/35.36	2014	8.73	0.28	1.85	2.2	[25]
	PM2.5/15.7	2015	–	–	–	–	[24]
Miskolc	PM10/51.98	2014	24.07	0.60	–	1.27	[25]
Debrecen	PM10/27.81	2014	–	–	–	–	[25]
	PM2.5/27.54	2015	–	–	–	–	[24]
Esztergom	PM10/22.31	2014	6.96	0.11	1.82	0.47	[25]
Szombathely	PM10/21.36	2014	5.01	0.11	2.21	0.58	[25]

– = no data available

The measured concentrations in this study are comparable with previously published data of other Hungarian sites based on the Hungarian PM10 Monitoring Program [25] in 2014. Similarly to the results of Győr, it was found that the other Hungarian cities also have excellent air quality with respect to heavy metals based on the air quality guideline values.

IV. CONCLUSION

Atmospheric concentrations of PM2.5 aerosol particles and some PM2.5-bounded heavy metal compounds (Pb, Ni, Cd) and the metalloid As were monitored in Győr. The concentration of PM2.5 fraction was varied between 12.22 and $36.92 \mu\text{g}/\text{m}^3$ regarding to the two sampling sites. The heavy metal mean concentrations at the two urban sites of Győr was measured for Pb, Ni and Cd. The metalloid As could be detected only in a small amount of 3.57% of the total collected samples. The levels of heavy metals were compared with the relevant regulated limit and target values and published data for other cities located in Hungary. These results indicated excellent air quality for heavy metals in the Győr atmosphere.

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