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Original article

Evaluation of highly mobile fraction of trace elements in PM₁₀ collected in Upper Silesia (Poland): Preliminary results

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ABSTRACT

The amount of the soluble fraction of trace elements released from inhaled particulate matter seems to be one of the key factors of the toxicity of these particles. This study reports the concentrations of PM₁₀ and trace elements in total and water-soluble fractions (bioavailable form). Weekly samples were collected at two rural sites in Upper Silesia, Poland. Measurements were carried out from April to August 2013, divided between heating and non-heating sessions. During heating sessions, the concentrations of PM₁₀ in selected sites varied in the range of 32.88–48.70 $\mu\text{g m}^{-3}$, while for the non-heating sessions the range was 16.14–27.89 $\mu\text{g m}^{-3}$.

Selected PM₁₀ samples (characteristic for both sessions) were determined by means of total and water-soluble content of eight trace elements. The elements are characteristic of carcinogenic (As, Cr, Cd and Ni), probably carcinogenic (Co and Pb) and toxic (Mn and Sb) groups. The analyses of the mineralized samples as well as the water-soluble fractions were carried out by ICP-MS method using a Varian 810 MS.

The total concentration of carcinogenic Cd, Cr and Ni during non-heating sessions was 2.81, 7.97 and 4.82 ng m^{-3} , respectively. While during heating sessions the total content was twice as high. Similar relation was observed for the concentration of PM₁₀. The concentration of the soluble fraction of these elements in the atmospheric air in heating sessions was 1.62, 0.75, 2.20, 1.79, 1.85 ng m^{-3} for As, Cr, Pb, Mn, Sb, respectively and remained almost the same as in non-heating sessions. Lower levels of Ni and Cd (0.15 and 0.11 ng m^{-3}) were determined during heating sessions. The obtained data indicate that during heating periods these elements are probable present mainly in other fractions with lower mobility, so less harmful to human health.

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1. Introduction

On a global scale, the hard and brown coal position is strong, and reveals a clear increasing trend. Hence, problems connected with air quality in the vicinity of coal combustion sources will intensify.

One of the most contaminated pollutants in atmospheric air is the particulate matter (PM). A considerable part of particulate matter comes from anthropogenic sources such as production processes, and coal-based power generation and heat generation industries, processes of coal coking, iron and steel industries, traffic

and resuspension processes from urban surfaces. On the one hand, pollutants emitted from industrial coal combustion processes have been seriously reduced; on the other, the emissions from preparatory processes in power and coking plants have not yet been determined. Less is known about emissions from small-scale combustion utilities for example domestic boilers and resuspended dust. The issue is that of domestic sources cause a low emission problem. Domestic sources are particularly dangerous during winter because they use for heating the coal of low quality or other fuels; biomass, culm or even refuse. PM emitted from domestic sources according to its chemical composition, especially trace elements is a threat to the human population, particularly in terms of their toxic impact (Konieczynski and Zajusz-Zubek, 2011; Konieczynski et al., 2012). Those problems are not confined only Poland, but are characteristic too for other countries in which energy production is based on coal and domestic sources utilizing low-quality fuels.

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Particulate matter is an important subject of studies (Domanska and Wojtylak, 2012; Wei et al., 2012), with urban air quality being of special interest to scientists. Some examples (Wrobel et al., 2000; Gryniewicz-Bylina et al., 2005) indicate elevated concentrations of PM₁₀ and PM_{2.5}, which since the early 1990s have been connected with the growing significance of the vehicular emission of particulate matter. Publications addressing the problem of air pollution are mainly focused on the presentation of data concerning air quality in urban and industrialized areas (Karar et al., 2006; Kulshrestha et al., 2009; Yadav and Satsangi, 2013; Melaniuk-Wolny et al., 2014) as well as the impact of road transport (Pastuszka et al., 2010). The studies on urban particulate matter PM₁₀ and PM_{2.5} (crossroads) have revealed the presence of seven trace elements (Cd, Cr, Cu, Fe, Mn, Ni and Pb) at the elevated level according to the background sites in Zabrze, Poland (Pastuszka et al., 2010). The problem of urban air quality, considering particulate matter, is an important issue for the majority of cities all over the world. However the research on rural areas are uncommon. Generally, there is a shortage of publications concerning suspended dust (PM₁₀) and respirable fraction (PM_{2.5}) concentrations in rural areas where domestic sources are predominant (Kulshrestha et al., 2009; Perrone et al., 2012). In Poland air quality in rural areas is practically unstudied (Konarski et al., 2006; Rogula-Kozłowska et al., 2013). So far, only a few examples concerning rural air pollution in Poland have been reported in the literature (Konarski et al., 2006) and no study concerning air pollution at rural sites in Upper Silesia, Region has been carried out. The reason is a very limited number of rural monitoring stations. As shown in the work of Hlawiczka (2008), the proportion of non-urban (but not necessarily typically rural) monitoring stations to all stations in Poland is approximately 8%.

During the last few years, interest in PM composition as well as its impact on human health has grown. Special attention is put on the influence of trace elements. Several trace elements have been defined as hazardous to humans. The most harmful among trace elements, according to their toxicity, are the following 12 elements: As, Be, Cl, Cr, Cd, Co, Hg, Mn, Ni, Pb, Sb and Se (Hazardous Air Pollutants (HAPs), U.S. EPA, 1998. According to the International Agency for Research on Cancer (IARC), these elements can be classified to one of the following categories: group 1: the agent is carcinogenic to humans – As, Be, Cr, Cd and Ni (IARC, 2012); group 2: the agent is probably carcinogenic to humans – Cl, Co and Pb (IARC, 2006a, b); while Hg, Mn (ATSDR, 2012) and Sb (Amarasiriwardena and Wu, 2011) are toxic elements.

Recently, the scientific interest in the negative impact of respirable dust on human health has increased (Schleicher et al., 2011; Kim et al., 2012; Sughis et al., 2012). Within environment and dust exposure research conducted thus far, the concern has mainly been with the total content of trace elements in suspended dust and dust deposition, without distinguishing their specific chemical forms. While those forms impact on the heavy metal threat to environment and human health. A selected sample can, for example, contain significant amounts of element, but the most crucial question is what part of its total content will be released from the selected material to the environment, and can be dangerous to human health. Tessier's derived general scheme of chemical speciation which was optimised by Fernandez-Espinosa et al. (2002). The speciation scheme distinguishes four fractions depending on element's mobility. There are fractions: soluble – *highly mobile*; bound to carbonates and oxides and reducible metals – *mobile*; bound to organic matter, oxidizable metals and sulphides – *less mobile*; and residual, permanently connected with minerals – *not mobile*.

The availability of scientific data concerning chemical composition of dust, including speciation analyses of trace elements,

remains very limited. This is a result of technical difficulties of analysis, sample collection, and also more recently a lack of detailed definition of the scientific aims of speciation research. The authors of one publication (Sanchez-Rodas et al., 2012) presented results of arsenic speciation analysis in respirable dust near copper smelter. They sited out that As(V) is the dominant form and that the more toxic form of As(III) is linked mainly to the PM_{2.5} fraction, compared with the less toxic form of As(V). This, according to the authors, poses an additional health risk to the local human population. Other authors (Wang et al., 2012) have considered speciation of cadmium in PM_{2.5} and PM₁₀ during the heating period. The samples were collected on the terrain of one Chinese university campus. A higher concentration of Cd in PM₁₀ (3.642 ng m⁻³) than in PM_{2.5} (1.964 ng m⁻³) was found. However, the bioavailability of Cd was higher in PM_{2.5} than in PM₁₀.

The purpose of present study is to outline the levels of PM₁₀ and to preliminary recognise chemical speciation of PM₁₀ samples collected at two rural sites as a possible background locations. Besides assessing the PM₁₀ and trace elements levels in the selected study areas, the identification of water solubility of trace elements was conducted. The significance of present study obtains the bioavailability of carcinogenic, probably carcinogenic and toxic trace elements. The data collected in this study can not only be utilized to validate air quality models in this rapidly developing area, but may be crucial for comparing with datasets from other similar parts of Poland or the world. Moreover, the identification of the bioavailability of selected carcinogenic and toxic elements in the future might be used as output data for potential biological and population research on risk assessment for different forms of trace elements contained in suspended particulate matter. This is important in the context of air pollution hazardous to human health.

2. Experimental

2.1. Sampling

Fig. 1 shows the study area and the sampling locations in Ziemiecice (site 1: 50°22'07.57"N; 18°42'12.59"E) and Tworog Maly (site 2: 50°15'22.84"N; 18°28'2.85"E) situated, respectively, 10 km and 20 km from Gliwice, Upper Silesia, Poland. Site 1 is a rural site in the suburbs of Gliwice. Site 2 is a rural site located on the territory of Cysterski Landscape Park. According to categories of sampling sites proposed by the European Environment Agency (Putaud et al., 2010), the rural background should be located 10–50 km from large pollution sources. Both sites meet this condition.

The major pollutant sources at site 1 are combustion of coal and wood for domestic heating and cooking purposes as well as resuspension from agriculture activities (decreased during winter). Site 2 in addition to site 1 is influenced by dispersion of traffic and industrial pollutants originated in Gliwice city.

The PM₁₀ samples were collected from 29 March to 23 August 2013. In order to gather sufficient amount of PM₁₀ each sample was collected during 7-days sessions and totally it was 21 samples and 21 blank filters stored in sampling area. The samples have been collected with a low-volume PM₁₀ sampler type PNS-15 (Atmoservice) at flow rate 2.3 m³ h⁻¹, compatible with PN-EN 12341:2006. The inlet tube was installed 1.5 m above the ground, which is important for human exposure. PM₁₀ samples were collected continuously each week on high-purity quartz (SiO₂) microfiber filters (QM-A Whatman).

The research has been divided into: heating sessions with combustion of various materials in domestic furnaces (the researchers were informed about combustion episodes), and non-

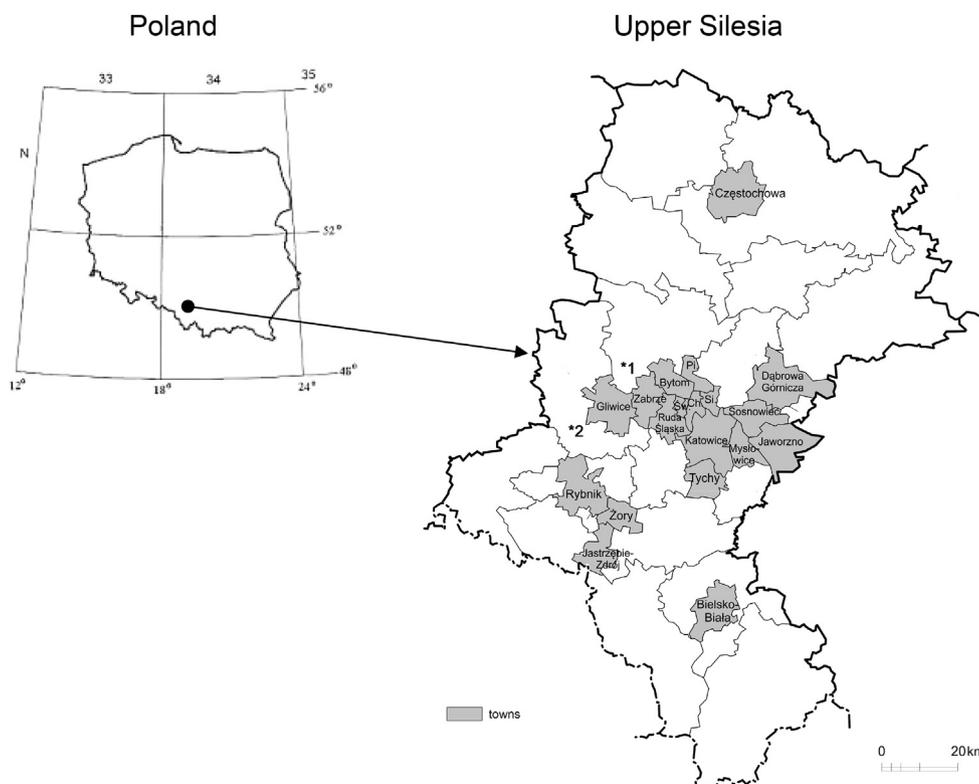


Fig. 1. Localization of two rural sites in Upper Silesia Region, Poland, 1 – Ziemiećice, 2 – Tworóg Mały and Air Monitoring Stations in Gliwice, Rybnik and Zabrze.

heating sessions without combustion in domestic furnaces. The total and water soluble fraction the four samples with four blank filters from April (heating) and four samples with four blank filters from June (non-heating) were selected for recognition of bioavailability of PM10 samples collected at rural side.

2.2. Chemical analysis

First, the concentration of PM10 during both sessions has been measured at sites 1 and 2, as well as at Air Monitoring Stations in Gliwice, Zabrze and Rybnik. Then, in the selected PM10 samples (characteristic for both sessions), eight trace elements were determined by means of a total content of As, Cd, Co, Cr, Mn, Ni, Pb and Sb in PM10.

The next step entailed the determination of bioavailable forms of the enumerated trace elements. The bioavailable form is defined as a highly mobile fraction (fraction 1), which is soluble and exchangeable and, therefore, most dangerous to the environment.

The procedure to determine the total content of selected trace elements in PM10 proceeded in the following way. One half of the QM-A filter was mineralized under high pressure and high temperature in a system for microwave mineralization (Candela) in 8 mL HNO₃ and 2 mL H₂O₂ (according to PN-EN 14902:2010). Ultrapure acid and hydrogen peroxide for trace analysis from Sigma Aldrich TraceSELECTultra[®] were used, which allowed a clear solution to be obtained.

Trace elements are adsorbed on particle matter surfaces and some are easily released to aqueous solutions as soluble fraction. This fraction of the trace elements is readily bioavailable; hence, it is the most dangerous to human health. In order to evaluate the content of selected trace elements in highly mobile (soluble) fraction, the procedure of leaching, based on the scheme of Tessier et al. (1979) and modified by Fernández-Espinoza et al. (2002); Sanchez-Rodas et al. (2012) with single-stage extraction, was as follows: the

second half of the QM-A filter was extracted by 15 mL of ultrapure deionized water (Mili-Q Fisher) in polypropylene tubes, then the tubes were shaken for 3 h at room temperature and then filtrated (DigiFilter System 0.45 μm).

2.3. Quality control

Elemental concentrations of eight elements (As, Cd, Co, Cr, Mn, Ni, Pb, Sb) were analysed for each sample by plasma mass spectrometry (ICP-MS, Varian 810). The instrument is equipped with a multiplier collector and a radio frequency power of 1.4 kW was applied to the plasma. The standard operational conditions of this instrument are a coolant Ar gas flow rate of 17 L min⁻¹, an auxiliary Ar gas flow rate of 1.7 L min⁻¹, and a nebulizer Ar flow rate of 1 L min⁻¹. The sample flow rate is 1 mL min⁻¹. Detection limits for all elements are listed in Table 1. All samples were measured in tenfold repeats.

Certified multi-element standards 1000 μg mL⁻¹ (CPI International Peak Performance™ Standards, USA) were used as calibration solution to determine ⁷⁵As, ¹¹⁴Cd, ⁵⁹Co, ⁵²Cr, ⁵⁵Mn, ⁶⁰Ni, ²⁰⁸Pb and ¹²¹Sb.

Furthermore, quality control was performed by additional accuracy analysis of the As, Cd, Ni and Pb contents using the European Reference Material ERM[®]-CZ120 (Fine Dust PM10-LIKE) from the Institute for Reference Materials and Measurements.

3. Results and discussion

3.1. Concentrations of PM10

In the statistical analysis of PM10 samples collected at two rural sites, Ziemiećice (site 1) and Tworóg Mały (site 2), average positional measures were chosen. Thus, the minimal PM10 concentration value for site 1 is $x_{min} = 16.14 \mu\text{g m}^{-3}$, the maximal value

Table 1
The detection and quantification limits of analysed elements.

Isotope	Limit of detection (LOD) [$\mu\text{g L}^{-1}$]	Limit of quantification (LOQ) [$\mu\text{g L}^{-1}$]
^{75}As	0.20	0.60
^{114}Cd	0.01	0.04
^{59}Co	0.01	0.03
^{52}Cr	0.04	0.14
^{55}Mn	0.03	0.09
^{60}Ni	0.05	0.15
^{208}Pb	0.01	0.03
^{121}Sb	0.01	0.03

$x_{\max} = 48.70 \mu\text{g m}^{-3}$ (so the empirical area variation equals $O_x = 32.56 \mu\text{g m}^{-3}$), the median $M_e = 25.16 \mu\text{g m}^{-3}$ and the variation coefficient $V(x) = 39.9\%$.

In the case of site 2, the average positional measures are: $x_{\min} = 11.05 \mu\text{g m}^{-3}$, $x_{\max} = 22.16 \mu\text{g m}^{-3}$, $O_x = 11.11 \mu\text{g m}^{-3}$, $M_e = 16.45 \mu\text{g m}^{-3}$ and $V(x) = 23.6\%$.

Due to the heterogeneity of the obtained PM10 concentration values, dominants and skewness coefficients were not calculated.

Considering the levels of PM10 concentrations collected for the period from April to June 2013 and from July to August 2013, respectively, at site 1 (during 14 sampling weeks), and site 2 (during seven sampling weeks), and the results reported by selected Polish Air Monitoring Stations in Gliwice, Rybnik and Zabrze during the same period of time (21 weeks), we can conclude:

- there is a strong positive correlation between the results obtained at site 1 and at the monitoring station in Rybnik or Gliwice (Pearson's correlation coefficients $r_{yx} = 0.85$ and $r_{yx} = 0.74$, respectively);
- there is a moderate positive correlation between site 2 and the monitoring station in Zabrze, Rybnik or Gliwice (Pearson's correlation coefficients $r_{yx} = 0.52$, $r_{yx} = 0.51$ and $r_{yx} = 0.45$, respectively);
- there is a weak correlation between site 1 and the monitoring station in Zabrze (Pearson's correlation coefficient equals 0.28).

The authors conclude that relation between the monitoring station and the sampling sites in this study can be a consequence of the closer distance between site 1 and Gliwice downtown (approximately 10 km, while the distance between site 2 and Gliwice is about 20 km), as well as the localization of industry and the dominant wind direction (for the period of measurement the wind direction fluctuated in the range of 135–225°).

The selected sites, given the good localizations as well as the lower concentrations of PM10 observed at both sites in comparison with the nearest monitoring stations in Gliwice ($36.31 \mu\text{g m}^{-3}$), Rybnik ($25.04 \mu\text{g m}^{-3}$) and Zabrze ($37.39 \mu\text{g m}^{-3}$), can preliminary indicate both localizations as future background (reference) sites for evaluating the impact of power and coking plants on their surrounding areas. To confirm the suitability of both locations, it will be reasonable to perform a complete analysis comparing the selected sites and monitoring stations by conducting parallel measurements in both sites during shorter averaging time.

In order to compare the concentrations of trace elements during heating and non-heating sessions the results of total content and highly mobile fraction (soluble fraction) for PM10 collected in April and June have been presented. As it can be seen in Table 2 the average concentration level of PM10 was $40.81 \mu\text{g m}^{-3}$ in April but in June only $20.57 \mu\text{g m}^{-3}$. Since June is a summer month while April belongs to spring, i.e. to the heating season, the almost twice as high level of PM10 in April compared to June agrees well with the general, seasonal pattern of the concentration of atmospheric particles in Poland. The obtained data confirm the seasonal pattern

of the concentration of airborne particles in Poland reported previously in a number of papers (example: Pastuszka et al., 1993; Pastuszka and Okada, 1995 and Klejnowski et al., 2012). Generally, the highest particulate concentrations have been recorded in winter, and next, in spring and are attributed to the use of local coal-based heating sources during that time.

3.2. Heavy metals in PM10

The seasonal changes of the concentration levels of heavy metals contained in the airborne particles are different than the changes of PM levels because they depend on the contributions of main emission sources of these metals. For example, although in 1989 in Katowice, the coal combustion was partially responsible for the emission of all the monitored heavy metals, it was not the main source of airborne Pb, Cd, and Ni. It was estimated that apart from the metallurgical plants, cars and trucks contributed significantly to the emission of Cd in this area. Trucks also appeared to be important sources of Ni. Only Mn, present in ambient air, originated mainly from coal combustion (Pastuszka et al., 1993). Knowing these results and respecting also other factors (example: meteorological factors and seasonal traffic density) it was possible to explain that the ratio of the concentration of the heavy metal in winter to the concentration in summer in 1989 was >1 for Mn and was <1 for Pb, Cd, and Ni, while the ratio $C_{\text{SPRING}}/C_{\text{SUMMER}}$ was >1 for Pb, Cd and Mn.

Our previous research (Konieczynski and Zajusz-Zubek, 2011) revealed that in power plants, the fly ash formed during coal combustion processes contains the highest concentrations of Cr, Cu, Mn, Ni, Pb and Zn. The results obtained in those investigations are in agreement with the present study and confirm the crucial contribution of hard coal used for consumption and heating in rural areas.

Comparing the total content of carcinogenic and toxic elements between two sessions conducted in site 1, the following order of average concentration of eight trace elements was found: for heating sessions, $\text{Pb} > \text{Cr} > \text{Ni} > \text{As} > \text{Sb} > \text{Cd} > \text{Mn} > \text{Co}$; and for non-heating sessions, $\text{Pb} > \text{As} > \text{Cr} > \text{Sb} > \text{Ni} > \text{Mn} > \text{Cd} > \text{Co}$. The denoted decreasing order of the total average concentrations of trace elements was similar to the order presented by Klejnowski (2011). Results presented in the cited publication considered data for the total content of As, Cd, Ni and Pb in PM10 samples collected at a monitoring station in Katowice, Upper Silesia, that indicate the highest concentrations of Pb and the lowest of Cd.

As it is explained above, in Poland, in eighties in the last century, the high emission from the heating sources, mainly from the heating plants, significantly elevated the concentration level of few trace elements, for examples Mn. On the other hand, in these years the number of cars driven, rapidly decreased in winter, which certainly can explain the measured decrease in the concentration level of most heavy metals during that period (Pastuszka et al., 1993). During the last twenty – thirty years the traffic emission has increased significantly while the emission from the heating

Table 2
Results of trace element concentrations (ng m^{-3}) for PM10 samples.

Parameters	PM10 ($\mu\text{g m}^{-3}$)	Total							Soluble fraction (F1)								
		Group 1 – carcinogenic				Group 2 – probably carcinogenic		Toxic		Group 1 – carcinogenic				Group 2 – probably carcinogenic		Toxic	
		As	Cd	Cr	Ni	Co	Pb	Mn	Sb	As	Cd	Cr	Ni	Co	Pb	Mn	Sb
Concentrations of trace elements (ng m^{-3}) during heating sessions																	
Average	40.81	8.45	6.35	14.95	11.88	0.79	93.48	2.21	7.95	1.62	0.11	0.75	0.15	0.06	2.20	1.79	1.85
Max	48.70	11.49	11.51	21.62	18.18	1.43	163.49	3.87	11.75	2.44	0.18	1.05	0.33	0.09	2.89	3.33	3.26
Min	32.88	7.21	2.78	11.36	7.84	0.45	42.19	0.85	4.32	1.23	0.06	0.19	0.04	<LOD	1.04	0.74	0.71
SD	7.57	2.04	3.69	4.56	4.71	0.44	52.94	1.42	4.13	0.56	0.05	0.38	0.14	0.04	0.87	1.27	1.26
Concentrations of trace elements (ng m^{-3}) during non-heating sessions																	
Average	20.57	8.52	2.81	7.97	4.82	0.55	64.10	3.52	4.85	1.70	0.26	0.83	0.19	0.07	1.77	1.71	1.72
Max	27.89	9.54	2.90	9.81	4.89	0.75	87.75	3.68	5.21	1.82	0.46	0.98	0.39	0.10	2.09	2.09	1.95
Min	16.14	7.89	2.69	6.24	4.72	0.34	38.05	3.39	4.35	1.59	0.12	0.69	0.06	0.04	1.42	1.09	1.51
SD	6.39	0.89	0.11	1.79	0.09	0.21	24.94	0.15	0.45	0.12	0.18	0.15	0.17	0.03	0.34	0.54	0.22

<LOD – below limit of detection.

source has been reduced. Knowing that the traffic density remains at the same, high level in all seasons, the emission from the heating sources can only slightly increase the total amount of all trace elements in the ambient air. Therefore, 1.5–2.5 increase in the concentration level of elements in ambient air in April compared to June (Table 2) certainly agrees with this process and with previous reports. There are only two exceptions: the concentration of As in atmospheric air was almost the same in both months, and the concentration of Mn was clearly smaller in April compared to June.

3.3. Soluble fractions in PM10

The concentration of the soluble fraction of these elements in the atmospheric air in April remained almost the same as in June (As, Cr, Pb, Mn, Sb), or was lower (Ni, Co), even significantly (Cd). Since the pathway of exposure of human organisms to airborne particles is mostly through air/lung fluid interface during breathing, the amount of the soluble fraction of elements released from inhaled particulate matter seems to be one of the key factors of the toxicity of these particles. Actually there is common agreement that the soluble fractions are almost completely bioavailable (Vousta and Samara, 2002; Yadav and Satsangi, 2013). Therefore, the obtained data indicate that the prognosis of the adverse health effects resulting from the exposure to increased concentrations of elements in the heating season should be corrected into more positive scenarios. Trying to explain this important result it should be noted first that although the amount of the studied trace elements in ambient air (in μg of the element per cubic meter of air) increased in April compared to June (Table 2), the content of these elements

in the total mass of particulate matter (in μg of the element per g of the suspended dust) decreased (Table 3).

The highest ratio of the content of trace elements in PM10 in April to June was observed for Ni (0.81), while the lowest was for Mn (0.27). Although the trace elements from heating systems may have contributed to the levels of atmospheric particles in spring (and especially in winter), due to the fact that the heating in Poland is still based on the coal combustion which gives also a high emission of sulfates, nitrates and other compounds, the particulate emission from heating could be, paradoxically, the reason for the decrease in relative contribution of trace elements to the winter and spring airborne particles. Surprisingly, this ratio of the soluble fraction of these elements was lower ranging from 0.47 (Pb) to 0.17 (Co). Recent study of Yadav and Satsangi (2013) can cast some light on this problem. They found that trace elements in soluble fraction are possibly adsorbed on particle surfaces and are easily released to aqueous solutions. On the other hand, Rogula-Kozłowska et al. (2011) studying the surface layer of sampled respirable particles (PM2.5) in Upper Silesia, Poland, using the X-ray Photoelectron Spectroscopy (XPS) showed that in heating season the influence of traffic emission on the chemical composition of the surface layer of airborne particles is partially masked by the municipal and heating emission. This phenomenon seems to be responsible for the results presented in Tables 2 and 3 but their precise explanation needs additional studies. Besides, it should be mentioned that the obtained data are closely related with the coal combustion used for the heating in Poland. In other countries producing heat from different sources or located in different climatic zone the contribution of soluble fraction in total amount of trace elements will be

Table 3
Results of trace element content ($\mu\text{g g}^{-1}$) for PM10 samples.

Parameters	Total							Soluble fraction (F1)								
	Group 1 – carcinogenic				Group 2 – probably carcinogenic		Toxic		Group 1 – carcinogenic				Group 2 – probably carcinogenic		Toxic	
	As	Cd	Cr	Ni	Co	Pb	Mn	Sb	As	Cd	Cr	Ni	Co	Pb	Mn	Sb
Concentrations of trace elements ($\mu\text{g g}^{-1}$) during heating sessions																
Average	4.19	2.69	6.72	5.08	0.42	45.71	1.23	4.33	0.82	0.05	0.44	0.06	0.02	1.01	1.01	1.04
Max	7.19	3.65	8.55	5.77	0.90	102.39	2.42	7.44	1.53	0.11	0.66	0.11	0.04	1.81	2.09	2.07
Min	2.29	1.73	4.25	4.12	0.14	21.14	0.28	1.37	0.39	0.02	0.25	0.01	<LOD	0.65	0.23	0.23
SD	2.34	1.09	1.80	0.72	0.35	38.07	1.06	3.38	0.54	0.04	0.20	0.05	0.02	0.55	0.93	0.93
Concentrations of trace elements ($\mu\text{g g}^{-1}$) during non-heating sessions																
Average	11.32	3.65	10.59	6.28	0.72	86.29	4.59	6.30	2.30	0.28	1.03	0.17	0.10	2.15	2.21	2.31
Max	12.09	3.72	12.00	6.34	0.88	104.37	4.71	6.58	2.39	0.43	1.15	0.34	0.14	2.40	2.50	2.49
Min	10.83	3.56	9.27	6.21	0.56	66.38	4.49	5.92	2.21	0.17	0.93	0.05	0.05	1.88	1.73	2.15
SD	0.68	0.08	1.37	0.07	0.16	19.06	0.11	0.34	0.09	0.13	0.11	0.15	0.04	0.26	0.41	0.17

<LOD – below limit of detection.

certainly different. For example, [Heal et al. \(2005\)](#) showed that water-soluble form is the dominant fraction of PM_{2.5}-bound heavy metals in urban atmosphere of developed countries where automobile emission is a major source of PM_{2.5}.

Taking carcinogenesis and toxicity into consideration, particular attention should be directed to arsenic. Comparing the content of selected trace elements in mobile fraction with the total content in PM₁₀, arsenic contributed up to 20%, while the average total concentration of As independent of heating period is about 8 ng m⁻³. Thus, it negligibly exceeds the acceptable value for As in PM₁₀ of 6 ng m⁻³ given by the European Directive on Air Quality ([European Commission Directive, 2004/107/CE](#)).

The results reported by [Spangler and Reid \(2010\)](#) site to the crucial character of Mn as a surrogate marker for other confounding carcinogens, such as As. Following the proposed assumption in our research, Pearson's coefficients between Mn and other trace elements during heating sessions have been calculated. The most meaningful correlations between the content of Mn (μg g⁻¹) and the researched trace elements in the total content, as well as in the content of soluble fraction, were found between Mn and As ($r_{yxTotal} = 0.981$ and $r_{yxF1} = 0.982$), Mn and Co ($r_{yxTotal} = 0.952$ and $r_{yxF1} = 0.981$), Mn and Cr ($r_{yxTotal} = 0.817$ and $r_{yxF1} = 0.995$) and between Mn and Sb ($r_{yxTotal} = 0.962$ and $r_{yxF1} = 0.887$). These correlations indicated the important role of Mn. However, concerning the amount of examined samples, the above conclusion should be treated as a preliminary estimation, requiring further long-term research.

[Table 4](#) gives comparative data on results for PM₁₀ samples collected in the rural and urban atmosphere of different locations of Europe, India as well as other sites in Poland. Total concentrations of trace elements in our study are found to be similar to results

of ([Karar et al., 2006](#) and [Klejnowski, 2011](#)). Other results were in general higher ([Kulshrestha et al., 2009](#)) or lower ([Tyagi et al., 2012](#)) than in the present study.

Assuming that the soluble fractions are labile and completely bioavailable, a bioavailability index (BI) can be calculated according to Eq. (1):

$$BI = \frac{C_S}{C_T} \quad (1)$$

where

$$C_S - \text{mass concentration of soluble fraction sample, ng m}^{-3}, \\ C_T - \text{total concentration of separate trace element, ng m}^{-3}.$$

The calculated BI values are presented in [Fig. 2](#) for eight trace elements. From the results, it is clear that toxic Mn had the highest bioavailability index, reaching 0.8 during heating sessions and 0.5 during non-heating sessions. Carcinogenic As and toxic Sb had intermediate BI (in the range 0.2–0.4). The carcinogenic Cd, Cr, Ni and probably carcinogenic Co and Pb had BI values below 0.1. It is most likely indicative of the fact that these elements are present mainly in other fractions with lower mobility. For example, research on TSP ([Schleicher et al., 2011](#)) found Pb to be dominantly bound to fraction 2 (bond to carbonates – defined as mobile) and Ni to fraction 3 (bond to organic matter – defined as less mobile).

Since there are very few studies based on soluble fractions and almost no studies focusing on Poland, a comparison of trace elements' solubility is quite difficult. Our results were consistent with [Yadav and Satsangi \(2013\)](#) for Mn, Co and Cr; while for Ni, Pb and

Table 4

Comparison of PM₁₀ (μg m⁻³) and trace elements' concentration (ng m⁻³) in the ambient air of different rural and urban sites in the world.

Localization	Concentration of PM ₁₀ , (μg m ⁻³)	Fraction	Concentration (ng m ⁻³)							
			Group 1 – carcinogenic				Group 2 – probably carcinogenic		Toxic	
			As	Cd	Cr	Ni	Co	Pb	Mn	Sb
Rural										
Present study Upper Silesia, Poland	11.50–48.70	Total	6.35–11.49	2.62–11.51	6.24–21.62	4.39–18.18	0.34–1.43	38.05–163.49	0.85–8.65	4.32–11.75
		Soluble F1	1.23–2.44	0.06–1.03	0.19–1.65	0.04–0.33	0.0004–0.09	1.00–4.00	0.74–3.70	0.71–3.26
Montagney, France ^a	–	Total	0.24–1.30	0.09–0.56	0.83–2.23	0.84–2.75	0.02–0.05	3.79–22.03	2.45–7.71	0.68–2.00
Roorkee, India ^b	37–959	Total	0.27–1.48	0.004–0.01	–	0.08–0.15	–	–	0.27–0.56	–
Agra, India ^c	29.8–293	Total	–	–	1300	1700	–	2200	900	–
Kolkata rural Kasba, India ^d	135.1–166.7	Total	–	1.8–4.8	3.2–13.7	4.5–9.5	–	18.5–66.9	1.2–3.8	–
Oporto, Portugal ^e	1–20	Total	–	–	7.64	5.64	–	5.83	4.38	–
Urban										
Katowice, Poland ^f traffic	28.23–110.43	Total	1.13–6.22	0.08–5.13	–	1.69–5.22	–	23.12–129.30	–	–
Zabrze, Poland ^g background (SE)	65.82–512.89	Total	–	0.002–0.02	0.02–0.09	0.005–0.05	–	0.09–0.58	0.01–0.19	–
Zabrze, Poland ^g traffic(SE)	91.14–531.2	Total	–	0.04–0.15	0.68–2.02	0.03–0.55	–	0.46–3.31	0.24–0.64	–
Gdańsk, Poland ^f background	16.20–55.97	Total	0.27–1.81	0.05–2.53	–	0.46–3.71	–	6.38–56.16	–	–
Montagney, France ^a	–	Total	1.99–3.03	0.77–1.91	3.40–6.92	5.76–13.24	0.26–0.35	24.5–39.9	80–122	1.34–2.99
Agra, India ^c	33.2–295.3	Total	–	–	300	200	–	1100	900	–
Pune, India ^h	13.8–236.1	Total	–	242.9	789.0	1315.1	530	69.1	140	–
		Soluble F1	–	195.5	113.0	319.9	90	27.6	60	–
Kolkata urban Kasba, India ^d	154.3–291.9	Total	–	2.5–6.5	4.4–8.3	6.4–10.4	–	41.5–244.4	2.1–3.7	–
Oporto, Portugal ^e traffic	20–110	Total	–	–	8.69	8.29	–	55.5	13.4	–

SE-smog episode.

^a [Gaudry et al. \(2008\)](#).

^b [Tyagi et al. \(2012\)](#).

^c [Kulshrestha et al. \(2009\)](#).

^d [Karar et al. \(2006\)](#).

^e [Slezakova et al. \(2007\)](#).

^f [Klejnowski \(2011\)](#).

^g [Pastuszka et al. \(2010\)](#).

^h [Yadav and Satsangi \(2013\)](#).

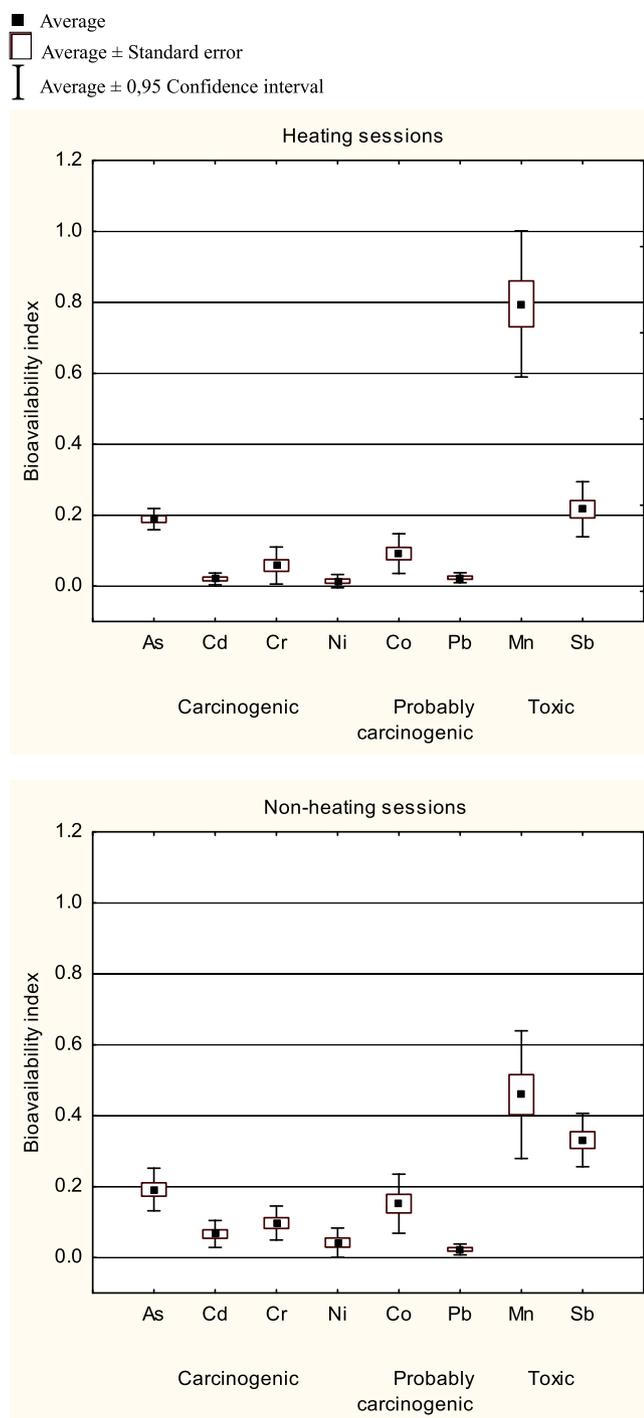


Fig. 2. Bioavailability index of different trace elements in PM10 samples collected at site 1.

Cd, the values are relatively higher than those observed in our study (Table 4).

4. Significance

The concentration of PM10 at the studied sites ranged from 11.05 to 48.70 $\mu\text{g m}^{-3}$. These levels were lower than the PM10 concentration values obtained from the nearest monitoring stations in Gliwice, Rybnik and Zabrze.

The average concentration level of PM10 was 40.81 $\mu\text{g m}^{-3}$ in heating session but in non-heating session only 20.57 $\mu\text{g m}^{-3}$.

Chemical composition of PM10 in the rural areas (Ziemiecie, Upper Silesia, Poland) demonstrates minor differences between heating and non-heating sessions. The highest average concentration of selected carcinogenic elements revealed Cr (14.95 ng m^{-3}). For the second group – probably carcinogenic elements – the highest average concentration was found for Pb (93.48 ng m^{-3}). The highest average concentration of toxic elements was found for Sb (7.95 ng m^{-3}). The total concentrations of carcinogenic and toxic elements divided between the two sessions fell in the following order: for heating sessions, Pb > Cr > Ni > As > Sb > Cd > Mn > Co; and for non-heating sessions, Pb > As > Cr > Sb > Ni > Mn > Cd > Co.

The concentration of highly mobile fraction of trace elements in the atmospheric air in heating session remained almost the same as in non-heating session (As, Cr, Pb, Mn, Sb), or was lower (Ni, Co), even significantly (Cd). Probably, during heating periods these elements are present mainly in other fractions with lower mobility, so less harmful to the human health.

From this research, it appears that the highly mobile trace elements, rather than the total content, of trace elements should be used in order to more precisely assess environmental and health risks. Chemical speciation of trace elements in PM10 is, therefore, important, and should become a routine analysis in the future study of air monitoring in the assessment of toxicological aspects. The bioavailability of carcinogenic and toxic elements in the future might be used as output data for potential biological and population research on risk assessment. It seems clear that the next step should be the biological study of cytotoxicity and genotoxicity of different fractions of particulate matter.

Conflict of interest

The authors declare no conflict of interest.

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References

- Amarasiriwardena, D., Wu, F., 2011. Antimony: emerging toxic contaminant in the environment. *Microchem. J.* 97, 1–3.
- ATSDR, September 2012. Agency for toxic substances and disease registry. Toxicol. Profile. Manganese. <http://www.atsdr.cdc.gov/substances/index.asp> (accessed 01.10.15).
- Domanska, D., Wojtylak, M., 2012. Application of fuzzy time series models for forecasting pollution concentrations. *Expert Syst. Appl.* 39, 7673–7679.
- European Commission Directive, 2004. 2004/107/CE for as, Cd, Hg, Ni, and PAHs.
- Fernández-Espinoza, A.J., Ternero, M., Barragán, F.J., Jiménez, J.C., 2002. A chemical speciation of trace elements for fine urban particles. *Atmos. Environ.* 36, 773–780.
- Gaudry, A., Moskura, M., Mariet, C., Ayrault, S., Denayer, F., Bernard, N., 2008. Inorganic pollution in PM10 particles collected over three French sites under various influences: rural conditions, traffic and industry. *Water Air Soil Pollut.* 193, 91–106.
- Grynkiewicz-Bylina, B., Rakwicz, B., Pastuszka, J.S., 2005. Assessment of exposure to traffic-related aerosol and to particle-associated PAHs, in Gliwice, Upper Silesia, Poland. *Pol. J. Environ. Stud.* 14, 117–123.
- Heal, M.R., Hibbs, L.R., Agius, R.M., Beverland, B.J., 2005. Total and water-soluble trace metal content of urban background PM10, PM2.5 and black smoke in Edinburgh, UK. *Atmos. Environ.* 39, 1417–1430.
- Hlawiczka, S., 2008. Analysis of Air Pollution and PM2.5 PM10 Dust Address the Chemical Composition of Dust, Including Heavy Metals and PAHs. Chief Inspectorate of Environmental Protection. <http://powietrze.gios.gov.pl/gios/site/content/publications>.
- IARC, 2006a. Monographs on the evaluation of carcinogenic risks to humans: metallic cobalt particles (with or without tungsten carbide), Vol. 86, pp. 1–119.

- IARC, 2006b. Monographs on the evaluation of carcinogenic risks to humans: inorganic and organic lead compounds, Vol. 87, pp. 1–529.
- IARC, 2012. Monographs on the evaluation of carcinogenic risks to humans: a review of human carcinogens: arsenic, metals, fibres, and dusts, 100C, pp. 41–93.
- Karar, K., Gupta, K., Kumar, A., Biswas, A.K., 2006. Characterization and identification of the sources of chromium, zinc, lead, cadmium, nickel, manganese and iron in PM10 particulates at the two sites of Kolkata, India. *Environ. Monit. Assess.* 120, 347–360. <http://dx.doi.org/10.1007/s10661-005-9067-7>.
- Kim, S.Y., Peel, J.L., Hannigan, M.P., Dutton, S.J., Sheppard, L., Clark, M.L., Vedal, S., 2012. The temporal lag structure of short-term associations of fine particulate matter chemical constituents and cardiovascular and respiratory hospitalizations. *Environ. Health Perspect.* 120, 1094–1099.
- Klejnowski, K., 2011. Analysis of Air Pollution and PM2.5 PM10 Dust Address the Chemical Composition of Dust and the Influence of Natural Sources. Chief Inspectorate of Environmental Protection. <http://powietrze.gios.gov.pl/gios/site/content/publications>.
- Klejnowski, K., Rogula-Kozłowska, W., Błaszczak, B., Osrodka, L., Krajny, E., 2012. Problems of air pollutants (Problemy zanieczyszczeń powietrza) (in Polish). In: Ziemiański, M., Osrodka, L. (Eds.), *Zmiany Klimatu a Monitoring i Prognozowanie Stanu Środowiska Atmosferycznego*. Institute of Meteorology and Water Management, Warsaw, Poland, pp. 111–124.
- Konarski, P., Haluszka, J., Cwil, M., 2006. Comparison of urban and rural particulate air pollution characteristics obtained by SIMS and SSMS. *Appl. Surf. Sci.* 252, 7010–7013.
- Konieczynski, J., Zajusz-Zubek, E., 2011. Distribution of selected trace elements in dust containment and flue gas desulphurisation products from coal-fired power plants. *Archives Environ. Prot.* 37, 3–14.
- Konieczynski, J., Zajusz-Zubek, E., Jabłonska, M., 2012. The release of trace elements in the process of coal coking. *Sci. World J* 2012, 1–8. <http://dx.doi.org/10.1100/2012/294927>.
- Kulshrestha, A., Satsangi, P.G., Masih, J., Taneja, A., 2009. Metal concentration of PM2.5 and PM10 particles and seasonal variations in urban and rural environment of Agra, India. *Sci. Total Environ.* 407, 6196–6204.
- Melaniuk-Wolny, E., Widziewicz, K., Adamczyk, Z., Nowinska, K., Zak, M., 2014. Single-stage extraction to assess metals bioavailability from smelting dust. *Pol. J. Environ. Stud.* 23, 195–202.
- Pastuszka, J., Hlawiczka, S., Willeke, K., 1993. Particulate pollution levels in Katowice, a highly industrialized Polish city. *Atmos. Environ.* 27B, 59–65.
- Pastuszka, J.S., Okada, K., 1995. Features of atmospheric aerosol particles in Katowice, Poland. *Sci. Total Environ.* 175, 179–188.
- Pastuszka, J.S., Rogula-Kozłowska, W., Zajusz-Zubek, E., 2010. Characterization of PM10 and PM2.5 and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes. *Environ. Monit. Assess.* 168, 613–627.
- Perrone, M.G., Larsen, B.R., Ferrero, L., Sangiorgi, G., De Gennaro, G., Udisti, R., Zangrando, R., Gambaro, A., Bolzacchini, E., 2012. Sources of high PM2.5 concentrations in Milan, Northern Italy: molecular marker data and CMB modeling. *Sci. Total Environ.* 414, 343–355.
- PN-EN 12341:2014-07 Ambient air – standard gravimetric measurement method for the determination of the PM₁₀ or PM_{2.5} mass concentration of suspended particulate matter.
- PN-EN 14902:2010. Ambient air quality – standard method for the measurement of Pb, Cd, as and Ni in the PM10 fraction of suspended particulate matter.
- Putaud, J.P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., 2010. A European aerosol phenomenology – 3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmos. Environ.* 44, 1308–1320.
- Rogula-Kozłowska, W., Pastuszka, J.S., Talik, E., 2011. Properties of Aerosol Related with Traffic Sources (Właściwości Aerozolu ze Źródła Komunikacyjnych) (in Polish). Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze, Poland.
- Rogula-Kozłowska, W., Błaszczak, B., Szopa, S., Klejnowski, K., Sowka, I., Zwodzia, A., Jabłonska, M., Mathews, B., 2013. PM2.5 in the central part of Upper Silesia, Poland: concentrations, elemental composition, and mobility of components. *Environ. Monit. Assess.* 185, 581–601. <http://dx.doi.org/10.1007/s10661-012-2577-1>.
- Sanchez-Rodas, D., Sanchez De La Campa, A., Oliveira, V., De La Rosa, J., 2012. Health implications of the distribution of arsenic species in airborne particulate matter. *J. Inorg. Biochem.* 108, 112–114.
- Schleicher, N.J., Norra, S., Chai, F., Chen, Y., Wang, S., Cen, K., Yu, Y., Stüben, D., 2011. Temporal variability of trace metal mobility of urban particulate matter from Beijing – a contribution to health impact assessments of aerosols. *Atmos. Environ.* 45, 7248–7265.
- Slezakova, K., Pereira, M.C., Reis, M.A., Alvim-Ferraz, M.C., 2007. Influence of traffic emission on the composition of atmospheric particles of different sizes – part 1: concentrations and elemental characterization. *J. Atmos. Chem.* 58, 55–68.
- Spangler, J.G., Reid, J.C., 2010. Environmental manganese and cancer mortality rates by county in North Carolina: an ecological study. *Biol. Trace Elem. Res.* 133, 128–135. <http://dx.doi.org/10.1007/s12011-009-8415-9>.
- Sughis, M., Nawrot, T.S., Ihsan-ul-Haque, S., Amjad, A., Nemery, B., 2012. Blood pressure and particulate air pollution in schoolchildren of Lahore, Pakistan. *BMC Public Health* 12, 378.
- Tessier, A., Campbell, P.G., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844–851.
- Tyagi, V., Gurjar, B.R., Joshi, N., Kumar, P., 2012. PM10 and heavy metals in sub-urban and rural atmospheric environments of northern India. *ASCE Journal of Hazardous, Toxic Radioact. Waste* 16, 175–182.
- U.S. EPA, 1998. Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units—Final Report to Congress. EPA-453/R-98-004a (Utility Air Toxics Study) Exec. Summ. At ES-4.
- Vousta, D., Samara, C., 2002. Labile and bioaccessible fraction of heavy metals in the airborne particulate matter from urban and industrial areas. *Atmos. Environ.* 36, 35–3590.
- Wang, W.Q., Zhu, X.P., Zheng, C.X., Aikebaier, Y., Liu, B., Wei, L.Y., Jan 2012. Speciation analysis of Cd in PM10 and PM2.5 during heating period in Urumqi, 32, pp. 235–238. <http://www.ncbi.nlm.nih.gov/pubmed/22497166#>.
- Wei, S., Huang, B., Liu, M., Bi, X., Ren, Z., Sheng, G., Fu, J., 2012. Characterization of PM2.5-bound nitrated and oxygenated PAHs in two industrial sites of South China. *Atmos. Res.* 109–110, 76–83.
- Wrobel, A., Rokita, E., Maenhaut, W., 2000. Transport of traffic-related aerosols in urban areas. *Sci. Total Environ.* 257, 199–211.
- Yadav, S., Satsangi, P.G., 2013. Characterization of particulate matter and its related metal toxicity in an urban location in South West India. *Environ. Monit. Assess.* 185, 7365–7379. <http://dx.doi.org/10.1007/s10661-013-3106-6>.