



Speciation of arsenic: a case study of PM1 in Zabrze

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Abstract

The aim of the study was to determine ambient concentrations of soluble, inorganic form of As ((As(III) and As(V)) in submicron atmospheric particles (PM1) in one of the most polluted region of Europe (Upper Silesia, Poland). Quantitative analyses of soluble As, soluble As (III) and As (V) after chromatographic separation and total As in digested PM1 samples were performed on the Elan 6100 DRC-e ICP-MS spectrometer. Results of analysis of the 15 randomly selected daily samples of PM1 from summer to winter season were presented. We showed that As(V) is dominating soluble, inorganic form of As in ambient air of selected city in Upper Silesia (Zabrze). Ambient concentrations of As(III) and As(V) as well as their mass percentages in water-soluble and total As changed seasonally. In winter season, when emissions from coal combustion prevailed, ambient concentration of soluble As(V) was about three times higher than in summer and accounted for 55% of total As. Ambient mass of As(III) was about 3.7% of the total As mass. During summer, when the sources of As may be more differentiated (industry, traffic, secondary emission from some surfaces, e.g., soils, roads, farmlands and dumps), soluble As(V) accounted for 23% of total As while soluble As(III) 6.7%.

Keywords Arsenic (V) · Arsenic (III) · Water-soluble arsenic · PM1

1 Introduction

Arsenic (As), belonging to toxic elements, is a metalloid widely spread in environment. As in the air originates both from natural and anthropogenic sources. Anthropogenic emissions (metal smelting, burning of some fuels, e.g., gas and carbon coal) are responsible for approximately two-thirds of the total As emissions to the atmosphere; their natural sources are: volcanoes, forest fires and sea spray [1]. It was reported that As concentration in urban and industrial atmosphere was significantly higher than in rural areas. The typical concentration of As in Europe ranges 0.2–1.5 ng/m⁻³ in rural areas and 0.5–3 ng/m⁻³ in urban areas, and usually is below 50 ng/m⁻³ in industrial areas [2]. It is known that particulate matter (PM) generated by anthropogenic sources consists mostly of fine particles, with the domination of particles below 1 µm, PM1 [3, 4]. The fine PM

particles, due to its well-developed surface area, has ability to cumulate metals and metalloids [5]. For instance, studies on fractionated PM have shown that in the Polish urban areas, PM1-bound metal mass is approximately 70–90% of total PM-bound metal mass [6–8]. Moreover, PM1, due to its physical properties, is characterized by long residence time in the atmosphere and the tendency to migrate over long-distances. Depending on meteorological conditions, PM1-bound toxic elements can be spread to distant places from the one in which they were emitted, and remains airborne for days or even weeks, as washout processes are least efficient for cleansing particles in these size bins [9, 10]. In a densely populated industrial area, during period when residential heating is active, increase in fine PM and fine PM-bound As were observed. This factor affects the state of air quality, unfavorable from the point of view of human health, because fine PM including PM1 can be deeply inhaled into the

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unciliated airways of the lung (the alveolar region) and absorbed directly into the pulmonary circulation system [11]. However, As toxicity and mobility are significantly correlated with its speciation and oxidation state in the environment. In general, inorganic As species are more toxic than organic As species. As(III) is both more toxic and more mobile in the environment compared to As(V) [12]. Depending on the environmental conditions (especially pH and oxydo-reduction conditions) as well as on chemical nature of particular groups of As compounds, different forms of arsenic may be interconverted. Ambient air is a specific part of environment, which is under dynamic physical and chemical transformation affected mainly by meteorological conditions (such as humidity, temperature and insolation). Possible oxidation of As(III) to As(V) by atmospheric oxygen has to be considered, especially at high pH [13]. Probably, atmospheric ozone could play a similar role as oxygen. Although its concentration in the air is less than oxygen and changeable, it has stronger oxidizing properties. Most of As in the atmosphere can be found in the particulate phase; < 10% is present in the vapor phase. Anthropogenic emissions, e.g., from smelting or fossil fuel combustion, introduce considerably amounts of the volatile As to the atmosphere (mainly As oxides), which preferentially adsorbs or condenses on the fine particles. Therefore, PM can be significantly enriched in As compared to the continental crust [13]. The source of particulate As can also resuspend dust from roads and soils. Concentrations and chemical composition of PM and PM-bound species of As are very site-dependent. They are shaped by regional and local emission sources; As bound to fine PM can be transported also from distant areas. In the regions with significant industrial emission, concentrations of As (and their species) will be determined by it. In areas with diversified sources of emissions (suburban areas, city centers, etc.), concentrations of As (and their species) are shaped mainly by municipal emission or time-stable road traffic emissions [14]. X-ray analysis of PM from industrial area showed that As bound to PM occurs as: $\text{Ca}_3\text{Sr}_2(\text{AsO}_4)_2.5(\text{PO}_4)0.5(\text{OH})$, As_2O_3 and As_2O_5 [15]. Analysis of PM has revealed that inorganic arsenic species, in particular As(V), is the predominant species in atmospheric PM [2016]. Their ambient concentrations are higher in PM from industrial areas than in PM from semi-urban sites [14–17]. For example, high concentrations of PM2.5-bound As (6.4 ng/m³ for total As, 0.9 ng/m³ for As(III) and 5.5 ng/m³ for As(V)) were noted in area close to Spain cooper smelter [17]. Another research showed domination of As(III) in PM2.5-bound As and higher share of As(III) with increasing concentration of PM2.5-bound As [15]. Studies on As speciation in size-resolved PM shown that more toxic As(III) tends to

concentrate in the fine fraction of PM (PM1 or PM2.5), and the shares of As(III) in total PM-bound As increased with decreasing PM diameter [14–16].

Summarizing the above, the speciation of As in fine PM is of great significance because it may provide information about their species amounts available for living organisms, thus potentially harmful, e.g., after inhaled exposure and also that more stable in environment, thus less danger for ecosystem.

Although urban PM belongs to the most frequently investigated environmental matrices, the As speciation in fine PM samples is still rather scarce, especially speciation of their water-soluble compounds in PM1.

The aim of the study was to conduct speciation of soluble form of inorganic As (As(III) and As(V)) in PM1 samples from one of the most polluted region of Europe (Zabrze in Upper Silesia, Poland). Upper Silesia is the most industrialized and urbanized region of Poland. Important industries in Upper Silesia include coal mining, iron and steel production, power plants, cokeries, waste incinerators and chemicals production. In the last 30 years, in this region, emissions have been significantly reduced; however, PM concentrations are there still one of the highest in the EU, mainly because of dense and obsolete housing, where poor-quality hard coal, scrap and household garbage are burnt in inefficient ovens to warm flats [18, 19]. Since late autumn (the beginning of heating season), the fossil fuel and biomass combustion grows significantly and lasts all heating period. Such annual emission state is reflected in seasonal changes in concentrations of PM and of the PM-related elements including As [6–8]. For this reason, authors decided to check if and how the growing emission from fuels combustion in winter affects results of the speciation of water-soluble PM1-bound inorganic As.

2 Materials and methods

2.1 Sampling area and the collection of PM1 samples

PM1 samples were collected at an urban background station in central Zabrze (50_1805800N, 18_4601800E). The neighborhood of the sampling site consisted of a trunk road (approx. 500 m to the north), blocks of flats and residential houses (to the east), Zabrze city center with residential and commercial housing (to the south and south-east) and blocks of flats and allotments (to the west). The surrounding houses were either connected to the district heating network or heated with local coal-, gas- or electricity-powered boilers [7].

PM1 was collected onto Quartz air-sampling filters (Whatman, Ø 4.7 cm; QM-A) using a low-volume (2.3 m³/h)

air sampler, (Twin Dust; Zambelli Milan, Italy) equipped with the PM1 sampling head (TSI; MN, USA). The 24-h PM1 samples were collected in summer from 24 June to 24 August 2014 and in winter from January 8 to March 8, 2015. In the paper, analysis results for 15 samples for each season are presented. Samples of PM1 for the study were randomly selected.

PM1 samples were conditioned and weighed in a weighing room at the air temperature of 20 ± 1 °C and air relative humidity of $50 \pm 5\%$ by means of an MYA 5.3YF microbalance (1 mg resolution, RADWAG, Radom, Poland). A methodology of gravimetric analysis is described in detail in [20]. After weighting, the filters with PM were cut into four equal pieces with ceramic knife. One part, which used for PM-bound As speciation and determination of soluble As, was placed in the refrigerator at -20 °C under conditions of As species preservation. The next was used in determination of total As. The other two were used in another study [20, 21].

2.2 Chemical analysis

2.2.1 Chemicals and reagents

To perform total As analysis, the following suprapure acids (Merck, Darmstadt, Germany) were used: nitric acid (65%), hydrofluoric acid (40%) and perchloric acid (70%).

To perform As speciation analysis, the following substances were used: ultrapure ammonium nitrate (Merck, Darmstadt, Germany), ammonium solution 25%, suprapure (Merck), sodium arsenate dibasic heptahydrate (Sigma-Aldrich, St Louis, MO, USA) and sodium arsenite (Sigma-Aldrich).

Stock solutions of As compounds containing 1000 mg/l As were prepared in water and maintained at 4 °C (in a fridge). Appropriate dilutions by weight of the stock solutions with distilled water were prepared daily to obtain the required concentration. Mobile phase was prepared from ultrapure ammonium nitrate (Merck, Darmstadt, Germany), and the pH was adjusted by the addition of ammonium solution (25%, suprapure (Merck)). This solution was filtered through a 0.45- μ m membrane filter before use.

All solutions and standards were prepared with the Milli-Q-Gradient ultrapure deionized water (Millipore, Merck Darmstadt, Germany), whose electrolytic conductivity was < 0.05 μ S/cm.

2.2.2 Extraction procedure

Total content (acid extraction/digestion)

PM1 samples collected on filters and blank filters were placed in PTFE vessels and flooded with 5 mL of nitric acid,

1 mL of hydrofluoric acid and 1 mL of perchloric acid and subjected to microwave mineralization (Multiwave 3000 microwave digestion system, Anton-Paar, France). Mineralization furnace parameters were: a pressure rise of 0.3 bar/s; 240 °C; pressure 60 bar and mineralization time 50 min. The digested samples along with several washings were transferred to polypropylene flask with a volume 25 mL.

The arsenic content in the empty filter was 0.11 ppb. This value was subtracted from the arsenic content determined for each of the PM1 samples on filter.

Water-soluble fraction (water extraction)

PM1 samples collected on filters and blank filters were extracted with 25 mL of deionized water (pH ~ 5.6) first in ultrasonic bath (15 °C) for 40 min and then were shaken overnight (60 rpm, 18 °C). Water extracts of PM and of blanks were filtered through a 0.22- μ m PSE membrane filter and analyzed as described below. Arsenic content in empty filter water extract was below limit of detection.

2.2.3 Apparatus

Chromatographic separation of As was performed on high-performance liquid chromatography (HPLC) system (series 200 LC, PerkinElmer). The system consisted of Series 200 LC gradient pump, Series 200 LC autosampler and Series 200 LC Peltier Column Oven.

Quantitative analyses of soluble As, its species after chromatographic separation and total As in digested PM1 samples were performed on the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Elan 6100 DRC-e (Perkin Elmer, Waltham, MA, USA).

Chromatographic and ICP-MS operating parameters are presented in Table 1.

2.2.4 Quality control

By definition, the limit of quantitation is the smallest concentration of the analyte determined in the sample, which can be quantitated with the assumed accuracy and precision [22]. For this purpose, a series of measurements ($n = 6$) for As(III) and As(V) calibration solution (0.2 μ g/l), a lower concentration solution (0.15 μ g/l) and solutions of higher concentrations (0.25 μ g/l and 0.30 μ g/l) were made. The measure of precision was the value of the relative standard deviation of repeatability (RSD %) of the obtained results of As peak area. It was assumed that the precision of 8% will be sufficient. This assumption was met in the case of As(III) for a solution with a concentration of 0.2 μ g/l, and for As(V) for a solution with a concentration of 0.30 μ g/l. It was assumed that the limit of detection is

Table 1 Operating conditions for HPLC and ICP-MS systems

<i>HPLC parameters</i>	
Column	Hamilton PRP-X100; 150 mm × 4.6 mm, 5 μm
Mobile phase	A: 20 mM NH ₄ NO ₃ pH=8.7 B: 60 mM NH ₄ NO ₃ pH=8.7
Flow rate during the analysis	1.1 ml/min
Elution program	0–2.0 min. 100% A 2.0–3.0 min from 100% A to 100% B 3.0–6.5 min 100% B Rinsing 6.5–9.5 min 100% A
Volume of sample	100 μl
Column temperature	30 °C
<i>ICP-MS parameters</i>	
Generator power RF	1125 W
Plasma gas flow	15 l/min
Nebulizer gas flow	0.76–0.82 l/min
Auxiliary gas flow	1.15 l/min
Nebulizer	Cross
Torch	Quartz
Cones	Nickel
Scan mode	Peak hopping
Dwell time	250 ms
Sweeps	20

Table 2 Validation parameters

Parameter	As(III)	As(V)
Limit of detection (μg/l)	0.07	0.1
Limit of quantitation (μg/l)	0.2	0.3
Repeatability (as RSDs) %	7.6	6.8
Recovery %	91	104

equal to one-third of the limit of quantitation. The recovery efficiency was measured by spiking quartz filter and 2 mg of Reference Material (CRM 1648a urban particulate matter; obtained from the National Institute of Standard and Technology (NIST)), put on it previously, with a As(III) and As(V) standard solution (0.5 μg/l) and subjecting them to the same extraction and analysis methods that used collected PM1 samples.

Parameters mentioned above are presented in Table 2.

The accuracy of the method for the total As content was calculated as As recovery from the mineralized CRM 1648a PM sample (according to the methodology described in 2.2.2). Arsenic recovery was 80%.

2.2.5 Statistical analysis

The obtained results were analyzed using the Statistica for Windows package, version 8.0 (StatSoft, Poland). Summary statistics (mean, standard deviation, minimum and

maximum) were determined for each PM1, PM1-bound total As, PM1-bound water-soluble As, PM1-bound water-soluble As(V) and As(III), As(V)/As(III) ratio, percentage of water-soluble PM1-bound As(III) and As(V) in PM1-bound total As. Since the concentrations of the measured analytes were not normally distributed, a nonparametric Mann–Whitney U test was used to compare winter-summer differences in the concentrations ($\alpha_{\text{assump.}} = 0.05$).

3 Result and discussion

In winter season the mean concentration of PM1 was 38.12 μg/m³; that was 3.5 times higher than in summer season (differences were statistically significant; $p < 0.05$; Table 3). In winter, mean concentration of total and soluble As were 3.26 and 1.86 ng/m³, respectively; they were 1.2 and 3 times higher than in summer (Table 3). In earlier research of PM1 from Zabrze, similar seasonal changes of concentrations of PM1 and PM1-bound total As were found [6, 8].

Results of water-soluble PM1-bound As speciation are presented in Table 4. They show higher daily ambient concentration of PM1-bound As(V) than As(III) in Zabrze in both measuring periods (winter/summer). An example of chromatogram of As species in PM1 water extract from summer and winter season is presented in Fig. 1. The mean ambient concentrations in summer season were 0.15 ng/m³ for As(III) and 0.54 ng/m³ for As(V) and 0.12 and

Table 3 Ambient concentrations of PM1 ($\mu\text{g}/\text{m}^3$), PM1-bound total and soluble As (ng/m^3)

Summer season				Winter season			
Collection date	PM1*	As total*	As soluble*	Collection date	PM1*	As total*	As soluble*
	$\mu\text{g}/\text{m}^3$	ng/m^3	ng/m^3		$\mu\text{g}/\text{m}^3$	ng/m^3	ng/m^3
24-06-2014	10.30	2.74	0.57	09-01-2015	24.20	3.02	1.84
28-06-2014	12.46	3.59	0.34	13-01-2015	14.82	2.96	0.81
02-07-2014	9.23	3.78	0.69	17-01-2015	38.98	5.35	0.87
06-07-2014	16.78	5.05	1.29	21-01-2015	29.66	3.30	2.14
11-07-2014	8.15	2.22	0.45	24-01-2015	17.68	1.62	1.30
16-07-2014	11.40	4.90	1.38	29-01-2015	34.83	2.67	2.02
21-07-2014	18.92	2.14	0.63	03-02-2015	67.84	3.56	1.86
25-07-2014	9.22	1.47	0.28	06-02-2015	32.49	1.76	1.38
28-07-2014	12.56	1.68	0.83	14-02-2015	93.48	7.37	5.24
02-08-2014	13.21	1.08	0.62	19-02-2015	56.91	3.38	2.28
07-08-2014	6.47	1.45	0.44	23-02-2015	38.62	3.49	2.14
11-08-2014	6.49	1.53	0.39	26-02-2015	34.37	3.02	1.27
16-08-2014	10.41	1.46	0.47	02-03-2015	18.76	1.80	1.00
20-08-2014	4.58	4.22	0.42	05-03-2015	20.06	2.40	1.06
24-08-2014	7.68	2.32	0.87	07-03-2015	49.12	3.27	2.65
Minimum	4.58	1.08	0.28	Minimum	14.82	1.62	0.81
Maximum	18.92	5.05	1.38	Maximum	93.48	7.37	5.24
Mean	10.52	2.64	0.64	Mean	38.12	3.26	1.86
SD	3.88	1.34	0.33	SD	21.39	1.46	1.09

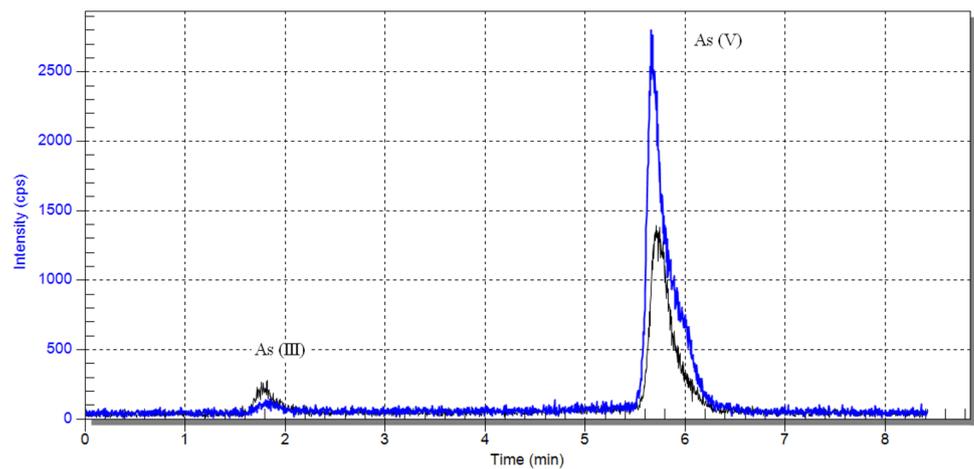
*Element whose summer and winter concentrations in Zabrze are statistically significantly different (according to the Mann–Whitney U test; $\alpha = 0.05$, $p_{\text{comp}} < 0.05$)

Table 4 Ambient concentration of water-soluble PM1-bound As(III) and As(V) (ng/m^3) and their percentage in PM1-bound total As (%)

Summer season					Winter season				
Collection date	As(III)	As(V)*	As(III)	As(V)	Collection date	As(III)	As(V)*	As(III)	As(V)
	ng/m^3	ng/m^3	%	%		ng/m^3	ng/m^3	%	%
24-06-2014	0.05	0.51	1.99	18.56	09-01-2015	0.09	1.74	2.88	57.57
28-06-2014	0.07	0.29	1.82	8.18	13-01-2015	0.19	0.60	6.54	20.43
02-07-2014	0.12	0.59	3.30	15.68	17-01-2015	0.34	0.49	6.41	9.16
06-07-2014	0.23	1.16	4.60	23.02	21-01-2015	0.17	1.94	5.05	58.87
11-07-2014	0.10	0.32	4.38	14.59	24-01-2015	0.07	1.21	4.15	74.66
16-07-2014	0.30	1.04	6.02	21.08	29-01-2015	0.07	1.91	2.60	71.63
21-07-2014	0.26	0.74	12.15	34.71	03-02-2015	0.11	1.75	3.08	49.22
25-07-2014	0.11	0.14	7.28	9.70	06-02-2015	0.06	1.33	3.43	75.51
28-07-2014	0.24	0.61	14.55	36.38	14-02-2015	0.25	5.26	3.40	71.43
02-08-2014	0.15	0.48	13.95	44.65	19-02-2015	0.05	2.26	1.57	66.78
07-08-2014	0.10	0.38	6.97	26.15	23-02-2015	0.09	2.08	2.45	59.61
11-08-2014	0.14	0.30	8.94	19.86	26-02-2015	0.06	1.22	2.08	40.36
16-08-2014	0.12	0.37	8.48	25.44	02-03-2015	0.06	1.01	3.22	56.40
20-08-2014	0.11	0.37	2.61	8.70	05-03-2015	0.07	0.99	2.78	41.33
24-08-2014	0.09	0.79	3.95	34.20	07-03-2015	0.11	2.61	3.29	79.87
Minimum	0.05	0.14	1.82	8.18	Minimum	0.05	0.49	1.57	9.16
Maximum	0.30	1.16	14.55	44.65	Maximum	0.34	5.26	6.54	79.87
Mean	0.15	0.54	6.73	22.73	Mean	0.12	1.76	3.53	55.52
SD	0.08	0.29	4.18	10.97	SD	0.08	1.14	1.45	20.50

*Element whose summer and winter concentrations in Zabrze are statistically significantly different (according to the Mann–Whitney U test; $\alpha = 0.05$, $p_{\text{comp}} < 0.05$)

Fig. 1 Chromatogram of As(III) and As(V) in PM1 water extract (summer-black and winter-blue)



1.76 ng/m³ for As(III) and As(V), respectively, in winter season. So, in the winter season, the mean concentration of As(V) was on average about three times higher than in the summer season, while the mean concentration of As(III) was on average 1.4 times lower. The mass percentages of water-soluble As(III) and As(V) in the total As mass were about 3.5 and 55% in winter; in summer season, they were about 6.7 and 23%, respectively. The total mass share of water-soluble inorganic As species (As(III) + As(V)) was two times higher in winter than in summer (Tables 3 and 4). Currently, there are no data available to compare to water-soluble PM1-bound As(III) and As(V) that were collected anywhere. It can be found in literature a study with different origins of samples, their grain size and characteristics of test sites. The case study, conducted in Czech Republic, presents results of water-soluble As species in two urban dust samples collected in Prague: one was collected in automobile tunnel Letna (particles between 3 and 4 μm; jet-milled and homogenized in blender before analysis) and second one sampled from filters of the air conditioner system in building close to the highway (particles < 63 μm; dried and sieved before analysis). As(III) represented 0.8% and 2.5% of the total As content in the water extract of tunnel dust and building dust, respectively (extraction time = 16 h). As(V) concentrations in analyzed samples were below detection limit [23].

On the basis of the ratio of oxidized and reduced water-soluble As specie, a greater predominance of As(V) over As(III) in winter than in summer can be seen (Table 4). Daily values of the As(V)/As(III) ratio did not exceed 10 in summer season (mean value was about 4); in winter, they were higher than 10 in 13 per 15 analyzed samples of PM1 (mean value was about 19). We tried to compare the seasonal differences of As(V)/As(III) ratio in PM1 from Zabrze and Katowice (city located about 15 km from Zabrze and roughly under the influence of similar PM emission sources). As species in PM1 from Zabrze was extracted

with water, and from Katowice, As(III) was extracted with citric acid/sodium citrate buffer and As(V) calculated as As total—As(III). Mean value of As(V)/As(III) ratio in PM1 in Katowice was higher in winter (4.60 = 5.56/1.21) than in summer (2.86 = 1.92/0.67) [14]. So, mean As(V)/As(III) ratio in PM1 both from Zabrze and Katowice was higher in winter than in summer, but in both seasons, the predominance of As(V) over As(III) in those PM1 was greater in Zabrze than in Katowice.

In environment, the common pentavalent compounds of inorganic arsenic are arsenic pentoxide, arsenic acid and arsenates (e.g., lead arsenate and calcium arsenate) and trivalents: arsenic trioxide, sodium arsenite and arsenic trichloride [2]. In ash from coal combustion, As is present mainly as halides, oxides, sulfides and hydride compounds [24]. X-ray analysis of PM collected in area near a metallurgical industrial plants showed that As was present in most as: Ca₃Sr₂(AsO₄)₂·5(PO₄)_{0.5}(OH), As₂O₃ and As₂O₅ [15].

Solubility of PM-bound As species is dependent on which chemical compounds they are present. There are other factors than can influence the leaching behavior of As species. In the opinion of some authors, trace elements in soluble fraction are possibly adsorbed on particle surfaces and are easily released to aqueous solutions. [25]. So, based on this supposition, also the composition of the PM surface layer could be important factor influencing As leachability. Analysis of the chemical composition of a surface layer of PM1 in Zabrze showed that carbon is a dominating element (mean about 79% of all detected elements). Mean shares of the rest of analyzed chemical elements were: oxygen: 14–16%, silicon and aluminum: 1.5–4%, nitrogen and sulfur: 0.4–1.0%, calcium and chloride: 0.12–0.31% [26].

Dominating carbon probably primarily play a role of sorbent, on which As compounds such as oxides are surface-absorbed, although As can be present as carbonate-bound too.

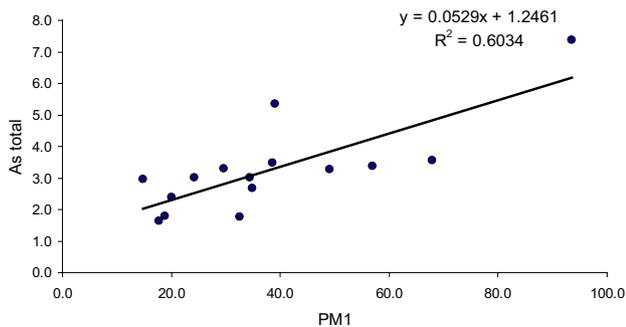


Fig. 2 As total versus PM1 in winter

The differences in seasonal concentrations of water-soluble As(III) and As(V) in PM1 in Zabrze could be also connected with different concentrations of soluble macro-components in PM1 in both seasons. In PM1 samples collected during measuring campaign (described in 2.1), also organic and elemental carbon (OC and EC), selected water-soluble ions were determined and presented in previous paper [20]. The study has shown that the means of the winter concentrations of PM1-bound OC , NO_3^- and Cl were 5, 7 and 20 times higher than the summer ones, those of PM1-bound EC , F^- , K^+ , and NH_4^+ —from 2 to 4 times, respectively, and those of PM1-bound SO_4^{2-} and PO_4^{3-} less than 2. During runoff, the PM sample with water and easily soluble macro-components can affect the pH of leaching solution; pH in turn can affect the leaching behavior of As. It is obvious that As compounds may vary depending on their sensitivity to a pH solution changes; some can be released under neutral pH conditions; some has a tendency to dissolve into acid solution, e.g., arsenic in carbonate-bound, surface oxide-bound ions [24].

Significance of emission sources in shaping As(III) and As(V) solubility can be seen especially in winter season, when emission from fuels combustion (mainly hard and brown coal) prevails in total emission. There has been found positive correlation between PM1 concentrations and As concentrations (Fig. 2), As total and As soluble concentrations (Fig. 3), As soluble and As(V) concentrations (Fig. 4) and negative between As(III) and As soluble (Fig. 5) in winter season. The correlations suggest that PM1-bound As comes from combustion emission (probably municipal emission—heating with use coal) and As compounds from combustion influence not only amounts of soluble As(V) in the ambient air but also its share in total PM1-bound As. As from combustion process is emitted mainly as arsenic trioxide, and prevailing oxidative As forms in PM are explained by oxidation of trivalent forms by oxidants such as ozone [27, 28]. Seasonal changes in PM2.5-bound As(III) and As(V) had been noticed in research conducted in Jinan city situated in Shandong Province of China (area under

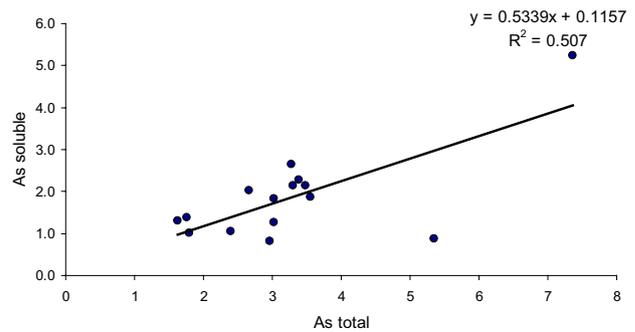


Fig. 3 As soluble versus As total in winter

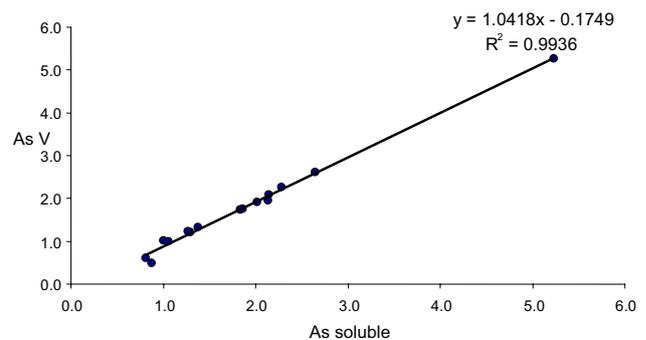


Fig. 4 As(V) versus As soluble in winter

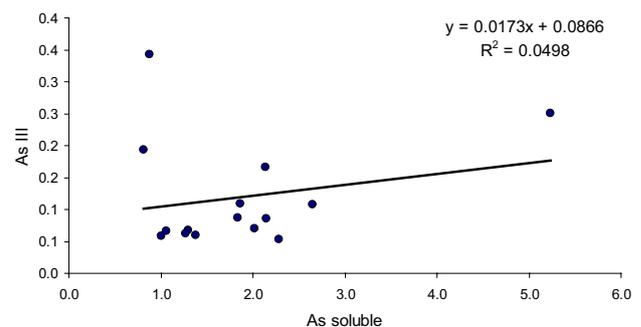


Fig. 5 As(III) versus As soluble in winter

the influence of coal combustion emissions, especially in winter). Analysis of As species in PM showed that only in some winter samples of PM2.5, As(III) was determined; the rest of As was present as As(V) [27].

In winter, water-soluble As(III) also may come from coal combustion (not oxidized arsenic trioxide) and from the other As sources like road traffic, industry and re-suspended dust. In summer season, both As(III) and As(V) were positively correlated with As soluble (Figs. 6, 7), but As soluble was not correlated with As total (Fig. 8) and As total was not correlated with PM1 (Fig. 9). The percentage

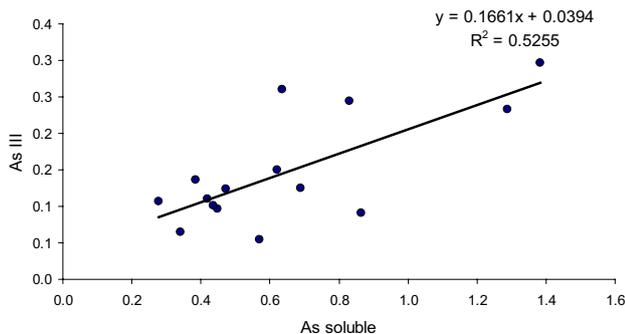


Fig. 6 As(III) versus As soluble in summer

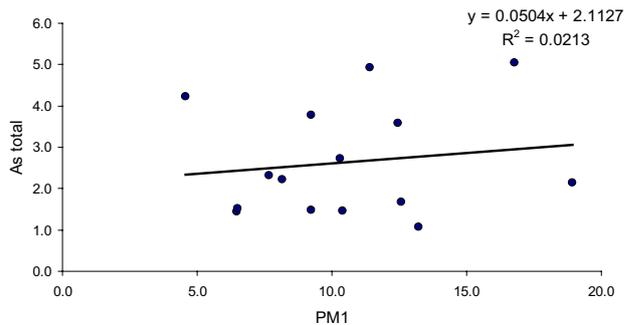


Fig. 9 As total versus PM1 in summer

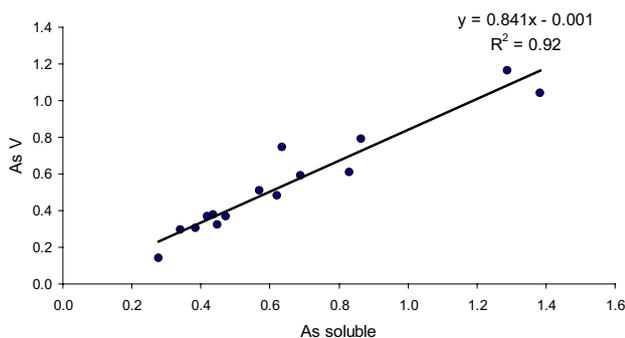


Fig. 7 As(V) versus As soluble in summer

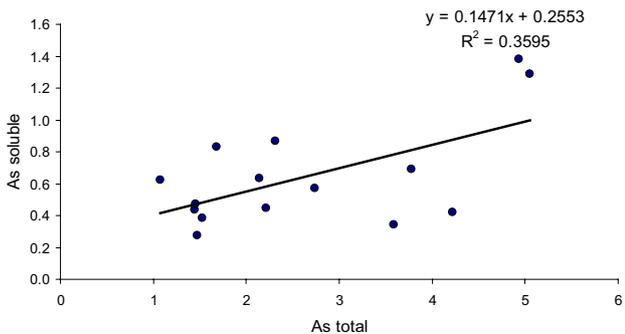


Fig. 8 As soluble versus As total in summer

amount of water-soluble fraction of As(III) in relation to total As amount were almost two times higher and As(V) was 2.5 times less compared to that in winter season.

The seasonal differences mentioned above probably can be a consequence of both prevailing emission from fuel combustion in winter and a various shares such as emissions from industry, traffic and re-suspended dust in the total emission in winter and summer.

In summer, water-soluble As(III) and As(V) in PM1 can also come from second emission from surfaces such as farmlands and dumplings. In winter, this kind of emission

is limited because of snow cover. It should be taken into account that PM1 may be transported from distant regions, being under influence of different sources of emission, than considered.

4 Summary

The research on speciation of inorganic water-soluble As in PM1, collected in industrial city Zabrze, showed that As(V) was dominating soluble species and the ambient concentration of soluble As(III) and As(V) as well as their mass percentage in water-soluble and total As changed seasonally.

In winter season, when emissions from solid fuels combustion (mainly coal) prevailed, ambient concentration of soluble As(V) was about three times higher than in summer and accounted for 55% of total As. Ambient mass of As(III) was about 3.7% of the total As mass. We recorded several times higher concentrations of OC and some water-soluble ions, especially Cl^- and NO_3^- , than in summer. During summer, when the sources of As may be more differentiated (industry, traffic, secondary), emission from some surfaces, e.g., soils, roads, farmlands and dumps, soluble As(V), accounted for 23% of total As, while soluble As(III) 6.7%.

Significant increase in the mean concentrations of PM1, PM1-bound As and PM1-bound soluble As(V) in winter may indicate that prevailing amount of soluble As(V) was coming from solid fuel (coal) combustion and originally appeared as trivalent until it has been oxidized in atmosphere. Additionally recorded several times higher concentrations of OC and some water-soluble ions (especially Cl^- and NO_3^-) in winter can have impact on more effective water solution extraction of PM-bound As (V) than in summer.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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