

EXPERIMENTAL STUDY ON ELEMENTAL COMPOSITION OF PM₁₀ IN SOFIA, 2012-2014

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ABSTRACT

Particulate matter, PM₁₀ and PM_{2.5} is a serious problem for the urban air pollution in many Bulgarian cities. PM₁₀ harmful health effect is well known and depends on the concentration, size and chemical composition. The present study is focused on the elemental composition of PM₁₀ applying ED-XRF technique. Six experimental campaigns were organized at the NIMH, Sofia in winter and summer periods of 2012, 2013 and 2014. The results of PM₁₀ mass concentration and the elemental composition of more than 20 elements (P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Y, Zr, Cd, Sn, Sb, I, Ba, Pb) have shown that there are significant variations in maximum and mean concentrations. The concentrations of PM₁₀ and most components are lower in the summer periods. The maximum and average concentrations of Ca tended to increase from 2012 to 2014. The mean concentrations of S, K, Fe, Ti, Cu and Zn measured during the winter and summer periods of 2013 are lower than those in 2012 and 2014. Basic statistical parameters obtained for the entire data set are summarized for the winter and summer periods.

Keywords: urban air pollution, PM₁₀, elemental composition, X-ray fluorescence analysis, ED-XRF.

Introduction

The city of Sofia has the highest health risk of air pollution in comparison with other Bulgarian cities, because of the topography of the closed valley *Sofiisko pole* surrounded by mountains, and the presence of different industrial, traffic and domestic pollutant sources which could affect the most populated area in the country. The toxicity of particulate matter (PM) depends not only on the size but to a significant extent on the chemical composition of the aerosol particles. Therefore it is an important task to characterize the chemical composition of the particulate matter, including macro and micro elements.

PM is a mixture of aerosol particles (solid and liquid) covering a wide range of sizes and chemical compositions. PM₁₀ (PM_{2.5}) refers to particles with a diameter of 10 (2.5) micrometers or less. Particulate matter is either directly emitted as primary particles or is formed from SO₂, NO_x, NH₃, NMVOCs gasses as secondary aerosol. PM is emitted from many anthropogenic sources, including both combustion and non-combustion sources. Important natural sources of PM are sea salt and natural re-suspended dust (Air pollution fact sheet 2014, Bulgaria, EEA).

Crustal elements like Si, Al, Fe, Ca and partly K could be mainly attributed to airborne soil and road dust. Vehicle traffic is a potential source of cadmium, lead, manganese, and nickel as a result of fuel combustion and the wearing of brakes, tires, and other components (Johansson et. al., 2009; Gao et al., 2015). Arsenic, cadmium, chromium, lead, nickel and other trace elements could be emitted from coal-burning and metal-processing facilities.

Experimental

Sampling and mass concentration measurements

PM₁₀ sampling was carried out with a certified sampler at the site of NIMH Central Meteorological Observatory (CMO) in Sofia during the field campaigns: 6–25.02.2012; 2–26.07.2012; 21.01–11.02.2013; 1–21.07.2013; 6.02–26.02.2014 and 21.07–13.08.2014. The CMO of

NIMH is situated in the sought-eastern part of the city with coordinates 42.655 N, 23.384 E, at 586 m a.s.l (Fig.1). Twenty-four hour samples were collected on 47mm quartz fiber filters (*Whatman 1851-047-QMA*) using low volume air sampler Tecora Echo PM (flow rate of 38.33 l/min). The filters were changed at 8:00 LST and mass concentration was measured gravimetrically according to EN-12341 standard. Filters were weighed before and after sampling with an analytical balance (*Mettler Toledo, AG135*). The conditioning of the filters is for at least 48 hours in a temperature and humidity controlled room ($T= 20\pm 2^{\circ}\text{C}$, $RH=50\pm 5\%$). Average weight of at least 3 repetitive weightings (blank /loaded) is used further.

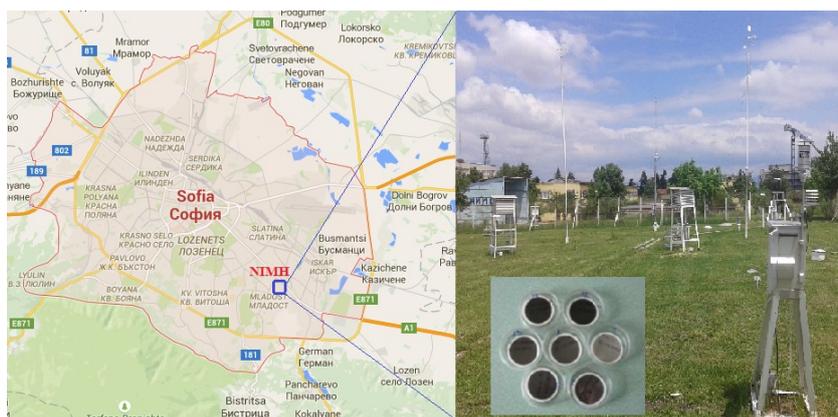


Fig.1 Sampling site, sampling device and examples of exposed filters

EDXRF analyses of elemental composition in PM₁₀

Energy dispersive XRF technique with 3 spectrometric systems of the XRF laboratory of INRNE-BAS was applied to determine more than 20 macro and micro elements in the PM₁₀ filter samples. The spectra were analyzed with specialized software X-Ray-Fit1 (Nikolova and Valcheva, 2006). This way it was possible to determine the elements P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Y, Zr, Cd, Sn, Sb, I, Ba, Pb in the PM₁₀ samples. To calibrate the systems, primary reference materials were used, followed by participation in inter-comparison exercises and proficiency tests. The method detection limit (MDL) varies from one element to the other being substantially high for Fe, As and Pb.

Results and discussions

The seasonal variations of the air particulate are characterized with high PM₁₀ values in winter (exceeding often daily limit value) and much lower mass concentrations in summer (EEA Rep. 2012, Veleva et al., 2013). The PM₁₀ concentrations in summer campaigns are below limit value of $50\mu\text{g}\cdot\text{m}^{-3}$. In winter campaigns the PM₁₀ daily concentration exceeded this limit value 9 times out of 20 days in February 2012, in 4 days in January-February 2013 and in 7 out of 17 days in February 2014.

Periods with $\text{PM}_{10} > 50\mu\text{g}\cdot\text{m}^{-3}$ in several consecutive days are 13-15, 19-23 of February 2012, 5.02-6.02.2013, 6-7.02.2014 and 16-18.02.2014. Single days with very high concentration of PM₁₀, above $130\mu\text{g}\cdot\text{m}^{-3}$, are observed during days of anticyclonic weather and cold, calm conditions only in winter time. In general PM₁₀ average and maximum values are lower in January-February 2013 compare to the winter field campaigns in 2012 and 2014. The reason for this could be explained with the different meteorological conditions. The days with precipitations in the winter period of 2013 were more frequent (15 days, 60 mm precipitation amount in total) compare to 2012 (11 days, 18.4 mm) and to 2014 (only 3 days with total of 9.7 mm precipitation).

Another important factor for the observed high PM₁₀ concentration is the bigger number of days with anticyclonic weather conditions in February 2012 (7 days with high pressure conditions under the influence of anticyclone and ridges). In comparison, there were relatively high pressure

weather conditions influenced by ridge only in 2 days of the winter experiment of 2013. Unfavorable conditions of high air pollution levels prevailed in six days of February 2014 when relatively high atmospheric pressure is observed, influenced by ridges.

The knowledge of elemental composition could be very helpful in identification of the source contribution to PM₁₀ concentration.

The summarized results from elemental analyses of PM₁₀ are presented on Fig. 2 and Fig. 3. Mean values of macro and micro elements are grouped for winter and summer experiments. The macro elements are measured almost in all PM₁₀ samples. The number of elements with concentrations below Detection Limit (DL) is higher in summer samples.

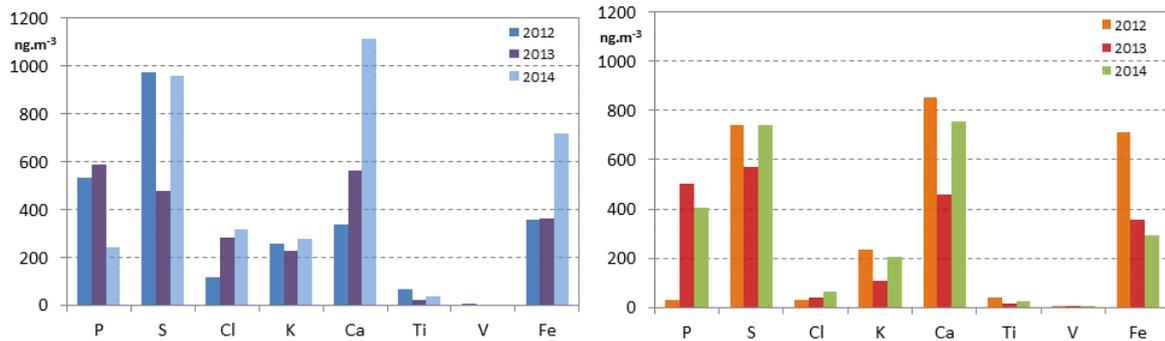


Fig.2. Macro elements in PM₁₀ for winter (left) and summer (right) campaigns

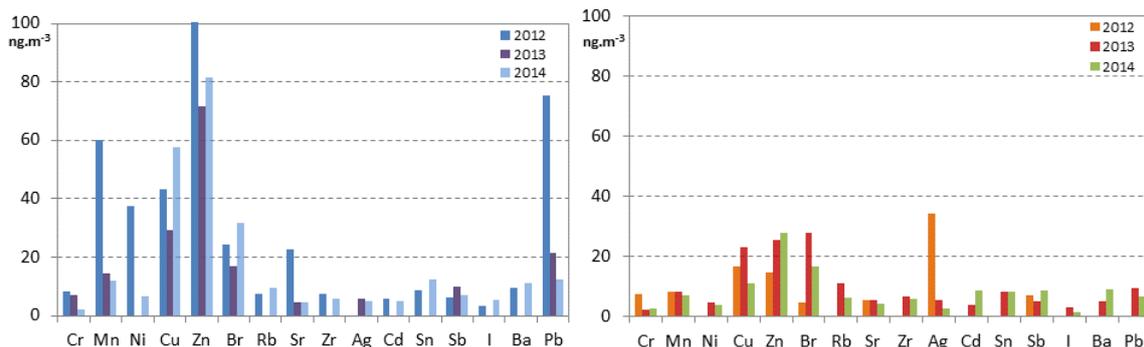


Fig.3. Micro elements in PM₁₀ for winter (left) and summer (right) campaigns

There is a tendency of increase of the Ca and Fe concentrations in winter PM₁₀ samples during the period 2012-2014. These elements are mainly of crustal origin, and the increase of soil and road dust resuspension could be one of the reasons for the observed tendency. The concentrations of Cl, K and almost all of the microelements are lower in summer PM₁₀ samples compare to the winter ones.

The highest mean concentrations of S, Mn, Ni, Zn, Sr and Pb are registered in February 2012, in correspondence to the high PM₁₀ mass concentration.

Some of the microelements As, Cd, Mn, Ni and Pb, are of higher importance because of their potential health effect. Cadmium is measured in 8 daily samples in 2012, in 11 samples in 2013 and more frequently in 2014, in 27 days. There is an increase in the Cd average concentration from 4-6 ng.m⁻³ in 2012 and 2013 to 9 ng.m⁻³ in the summer of 2014. The maximum measured concentration is 21ng.m⁻³ on 3.08.2014. The mean and maximum values are higher than reported for other urban regions in EU and USA (Johanson et al., 2009; Limbeck et al., 2009; Foley et al., 2012; Contini et al., 2014). Mean annual air quality target value of Cadmium is 5ng.m⁻³ in EU countries (Directive 2004/107/EC). Similar tendency of increase is observed for the average Ca concentration. Arsenium was detected only in 3 days in July 2012.

Manganese average concentration in five of the campaigns varies from 7 to 14ng.m⁻³. These values are close to the 12.8 ng.m⁻³ measured in PM₁₀ in Tucson, Arizona (Foley et al., 2012) and to 6.3-14 ng.m⁻³ in three sites in Vienna (Limbeck et al., 2009). Nickel, in range of 1 to 62ng.m⁻³, is measured in about 30% of the PM₁₀ samples. Mean and maximum lead concentrations in PM₁₀ are far below of mean annuals limit value of 0.5µg.m⁻³.

The correlations between analysed by EDXRF elements and PM₁₀ mass concentration are presented in Table 1 for winter and in Table 2 for summer experiments.

Weak correlation between PM₁₀ and Fe, K and Ti is observed in winter periods. No correlation is found between PM₁₀ and P, Ca, Mn, Sb and Ba. The temporal variations of these elements are influenced probably by different sources contribution and source profiles. Significant correlation is obtained between elements pairs: Fe-Ca; Fe-K; Fe-Cl; Ti-V; Ti-Sr; Ti-Pb; Sr-V; Ca-K; Ca-Cl; Ca-Ba; K-Cl; K-Ba; Sr-Pb (Table 1).

Table1. Correlation between analysed elements in winter PM₁₀ filter samples.

	PM10	P	S	Cl	K	Ca	Ti	V	Mn	Fe	Cu	Zn	Sr	Sn	Sb	Ba	Pb
PM10	1,00																
P	0,11	1,00															
S	0,60	-0,14	1,00														
Cl	0,44	-0,02	0,18	1,00													
K	0,61	-0,04	0,53	0,58	1,00												
Ca	0,19	-0,08	0,05	0,57	0,66	1,00											
Ti	0,52	0,40	0,15	0,20	0,47	0,33	1,00										
V	0,46	0,67	0,15	0,08	0,25	-0,03	0,85	1,00									
Mn	0,08	-0,11	0,37	-0,11	0,36	0,02	0,17	0,35	1,00								
Fe	0,50	-0,15	0,23	0,62	0,78	0,90	0,38	-0,01	0,03	1,00							
Cu	0,43	0,11	0,27	0,51	0,41	0,45	0,38	0,30	-0,18	0,53	1,00						
Zn	0,50	0,01	0,28	0,34	0,26	0,10	0,13	0,17	-0,10	0,28	0,37	1,00					
Sr	0,51	0,57	0,13	-0,13	0,11	-0,10	0,73	0,72	0,25	0,01	0,02	0,39	1,00				
Sn	0,41	-0,37	0,46	0,38	0,31	0,04	-0,14	-0,31	0,09	0,26	0,16	0,43	-0,03	1,00			
Sb	-0,05	-0,32	-0,15	0,29	0,06	-0,03	-0,24	-0,43	0,17	0,01	-0,19	0,15	-0,31	0,05	1,00		
Ba	0,22	-0,18	0,05	0,38	0,57	0,50	0,31	0,02	0,09	0,50	0,19	0,12	-0,04	0,05	0,15	1,00	
Pb	0,48	0,32	0,11	-0,01	0,20	-0,17	0,59	0,64	0,14	0,09	0,12	0,35	0,73	0,15	-0,06	-0,07	1,00

*Correlations in bold are significant at p < 0,05

The correlation between PM₁₀ and Fe, K, Ca and Ti in summer experiments is stronger (r>0.65) than in winter, Table 2.

Significant correlation is obtained between elements pairs: Fe-K; Fe-Ca; Fe-Ti; Ti-K; Ti-Ca; K-Ca; Significant negative correlation coefficient is calculated for Cl-Fe; Sn-S, P-K, P-Ca, P-Ti and Cl – Cu pairs indicating difference in source term and transport processes.

Table 2. Correlation between analysed elements in summer PM₁₀ filter samples.

	PM10	P	S	Cl	K	Ca	Ti	V	Mn	Fe	Cu	Zn	Sn	Sb	Ba
PM10	1,00														
P	-0,29	1,00													
S	0,53	-0,06	1,00												
Cl	-0,23	0,14	-0,06	1,00											
K	0,78	-0,41	0,38	-0,01	1,00										
Ca	0,69	-0,33	0,33	-0,06	0,73	1,00									
Ti	0,81	-0,33	0,31	-0,12	0,79	0,77	1,00								
V	0,17	0,49	0,22	0,14	0,31	0,33	0,23	1,00							
Mn	-0,07	-0,02	-0,06	0,39	-0,04	0,09	-0,01	0,07	1,00						
Fe	0,78	-0,43	0,10	-0,34	0,68	0,65	0,80	0,00	0,04	1,00					
Cu	-0,04	0,31	-0,01	-0,52	-0,17	-0,06	-0,18	-0,16	0,21	0,14	1,00				
Zn	-0,21	0,56	0,04	0,16	-0,16	-0,09	-0,07	0,24	0,21	-0,28	0,27	1,00			
Sn	-0,35	-0,02	-0,50	0,05	-0,22	-0,19	-0,21	0,19	0,26	-0,22	-0,20	0,11	1,00		
Sb	0,14	-0,21	0,23	0,01	0,15	0,16	-0,04	0,22	-0,37	-0,02	-0,25	-0,14	0,19	1,00	
Ba	0,04	-0,05	0,35	-0,10	0,37	0,45	0,49	0,67	-0,01	-0,20	-0,17	0,27	0,04	0,19	1,00

*Correlations in bold are significant at $p < 0,05$

Conclusions

In this study results for more than 20 elements concentrations (P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn Br, Rb, Sr, Y, Zr, Cd, Sn, Sb, I, Ba, Pb) in airborne PM₁₀ are obtained in winter and summer periods of 2012, 2013 and 2014 in Sofia.

Average concentrations of macro and micro elements, determined by EDXRF measurements, are summarized to characterize PM₁₀ urban air pollution. Most of the values and their range could be considered as reference once for the 2012-2014. The variations between the mean and maximum daily concentrations in winter and summer present broad range of dispersion influenced by different meteorological conditions and different sources emissions. The higher concentrations in winter can be explained with the weak vertical mixing of pollutants in the surface atmospheric layer during the days with winter inversions and the contribution of emissions from domestic heating. The variations of the elemental concentrations in the different years are influenced by the frequency and amount of precipitations, the prevailing weather type and the atmospheric dynamic.

References

1. Air pollution fact sheets 2014. Bulgaria, European Environmental Agency, www.europe.eu.
2. Contini, D., D. Cesari, A. Donato, D. Chirizzi, F. Belosi, 2014, Characterization of PM₁₀ and PM_{2.5}, and their metals content in different typologies of sites in South-Eastern Italy, *Atmosphere*, 5, 435-453
3. EEA Report No 4, 2012, Air Quality in Europe-2012, European Environmental Agency, Copenhagen, 2012, ISSN 1725-9177.
4. E. Nikolova, R. Valcheva, X-Ray Fit - Windows based Program for Energy Dispersive X-Ray Fluorescent Analysis, EXRS 2006, European Conference on X-Ray Spectrometry, Paris, France, June 19-23, 2006.
5. Foley T., E. A. Betterton and A. Wolf. 2012. Ambient PM₁₀ and Metal Concentrations Measured in the Sunnyside Unified School District, Tucson, Arizona. *Journal of the Arizona-Nevada Academy of Science*, 43(2):67-76. 2012. <http://www.bioone.org/doi/full/10.2181/036.043.0202>
6. Johansson C., M. Norman, L. Burman, 2009, Road traffic emission factors for heavy metals, *Atmospheric Environment*, 43, 4681–4688.
7. Gao J., H. Tian, Ke Cheng, L.Lu , M. Zheng, S. Wang, J. Hao, K. Wang, S. Hua, C. Zhu, Y. Wang, 2015, The variation of chemical characteristics of PM_{2.5} and PM₁₀ and formation causes during two haze pollution events in urban Beijing, China, *Atmospheric Environment*, 107, 1-8.

8. Limbeck A., M. Handler, Ch. Puls, J. Zbiral, H. Bauer, H. Puxbaum, 2009, Impact of mineral components and selected trace metals on ambient PM10 concentrations. *Atmospheric Environment*, 43, 530–538.

9. Veleva, B., Hristova, E., Nikolova, E., Kolarova, M., Valcheva, R., 2013, PM₁₀ concentration and elemental composition by EDXRF techniques in Sofia, *Journal of International Scientific Publications: Ecology & Safety*, 7, 1, 83-96. <http://www.scientific-publications.net>.