Journal of International Scientific Publications: Ecology and Safety

Volume 8, ISSN 1314-7234 (Online), Published at: http://www.scientific-publications.net

SEASONAL VARIATION OF PM10 ELEMENTAL COMPOSITION IN URBAN ENVIRONMENT

Blagorodka Veleva[1], Elena . Hristova[1], Emilia Nikolova[2], Maria Kolarova[1], Raliza Valcheva[2]

[1]National Institute of Meteorology and Hydrology, NIMH-BAS, Tsarigradsko sh. 66, Sofia

[2]Institute of Nuclear Research and Nuclear Engineering, INRNE-BAS, Tsarigradsko sh. 72, Sofia

Abstract

This study presents the results from experimental investigation of urban aerosol (PM10 fraction) at Central Meteorological Observatory of NIMH in Sofia. Four experimental campaigns were organised in February, July, October and December, 2012. The sampling of 24 hour average concentration was performed by TECORA sampler on quartz filters according to the European Standards. ED-XRF technique was applied to determine more than 20 macro and micro elements from phosphorus to lead in the PM10 filter samples. The measured PM10 daily concentrations are, in general, higher in the winter season. In February they range from 17.7 to 160.1μg.m^{-3}, compared to the lower summer values of 15.5-42.7μg.m^{-3} in July. In October PM10 varies from 8.43 to 78.3μg.m^{-3}. The highest PM10 concentration, measured on 25 of December (232.6μg.m^{-3}) corresponds to the highest values of most analysed elements. The higher PM10 and elemental concentrations are related to the stagnant meteorological conditions in winter days with calm conditions.

Key words: *urban air pollution, PM10 measurement, elemental composition, EDXRF technique*

1. INTRODUCTION

Geographic and climatic conditions in the region of the closed Sofia valley lead to unfavorable meteorological conditions for pollutants dispersion, emitted by a number of different industrial, traffic and domestic sources. In the recent years the pollution related to the intensive traffic in the city forms high urban background of air particulate due to direct exhausted gases, secondary aerosol and road dust resuspension from the motor vehicles.

Air pollution with air particulate, including PM10, in the atmosphere of Sofia continues to be a significant factor for unfavourable conditions in the urban environment. This problem requires effective measures to improve the air quality (AQMP of Sofia, 2011), because of the large population of about 1.5 million citizens exposed to high concentrations of PM10 including about 17% population of age 0-19 years old.

Studies on the health effects of Suspended particulate matter (SPM) in ambient air are focused on particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter less than 10μm (WHO, 2000). Depending on the particle size SPM are divided in TSP (total suspended particulate), PM10, PM2.5 and PM1 (particles equal to or less then 1 μm). EU Directive 2008/50/EC and national legislation determine the limit daily values of 50μg/m^3, not to be exceeded more than 35 times per calendar year. During 2012, the year of this experimental study, the exceedance days of PM10>50 μg/m^3 vary from 59 for "Pavlovo" to 108 days for "Orlov most" station.

Aerosol is considered as primary or secondary depending on its formation. "Primary" particles (as dust from roads or elemental carbon from wood combustion) are emitted directly into the atmosphere. Secondary aerosols are produced as a result of the reaction and transformation between the emitted primary gaseous pollutants in air, with example S and N as sulphates and nitrates (Seinfeld and Pandis 2006).

The main sources of most trace elements in air particulate are soil or crustal dust, marine aerosols (sea salts), vehicle emissions, industrial sources, biomass burning.

- *Soil dust* includes most of the crustal elements with high concentrations of Si, Al, Fe, Ca and partly of K with an important contribution to coarse aerosol (Gugamsetty et al. 2012);
- *Vehicles* emit elements such as Cu, Zn, V, Sb, Pb and Ni. Zn is widely used as a chemical fingerprint for tire wear, and Cu and Sb are used for break wear (Gugamsetty et al. 2012);
- *Biomass burning* is a source of K, Ca, Mn and Sr, important during the periods of wild fires (Argyropoulos et al. 2012);

- *Industrial source:* Ti, V, Cr, Cu, Zn, Sb, Fe, Ni and As is associated with metallurgical and chemical industries. Fly-ash particles resulting from coal burning are sources of Ti, Cr, Fe, Ni, As, Rb, Sn and Ba, with element composition similar to crustal material in some cases (Wang et al. 2013);
- *Sea salt* is the main source of Na, Cl and K (Seinfeld and Pandis 2006).

To identify the source contribution to PM10 concentration, investigation of elemental composition is important. In the present study the EDXRF techniques are applied to evaluate the number of macro and micro elements concentration in PM10 aerosol, collected during several field campaigns in 2012.

2. EXPERIMENTAL

2.1. Sampling

PM10 sampling was carried out with certified PM10 samplers at the site of NIMH Central Meteorological Observatory (CMO) during February, July, October and December 2012. Twenty-four hour samples were collected on 47mm quartz fiber filters (Whatman 1851-047-QMA) according to EN-12341, using Tecora low volume air sampler at flow rate of 38.33 l/min. Filters were weighed before and after sampling with an analytical balance (Mettler Toledo, AG135). The conditioning of the filters is for 48 - 96 hours in a temperature and humidity controlled room (T= 20±2^{o}C, RH=50±5%). Temperature differences between pre-sampling and post-sampling weighing were usually within 1°C and relative humidity - within 10%. Average weight of at least 3 repetitive weightings (blank /loaded) is used further.

In October parallel sampling was organized with TECORA low volume PM10 samplers, one stationary, placed at CMO of NIMH in Sofia, inlet at 2m above the ground (site 1) and other placed in the mobile laboratory of ExEA at MoEW with inlet at 4m height (site 2), see Fig.1. The distance between the two sampling sites was about 250m. The sampling in December was done by mobile laboratory of ExEA at MoEW, placed at site 2.

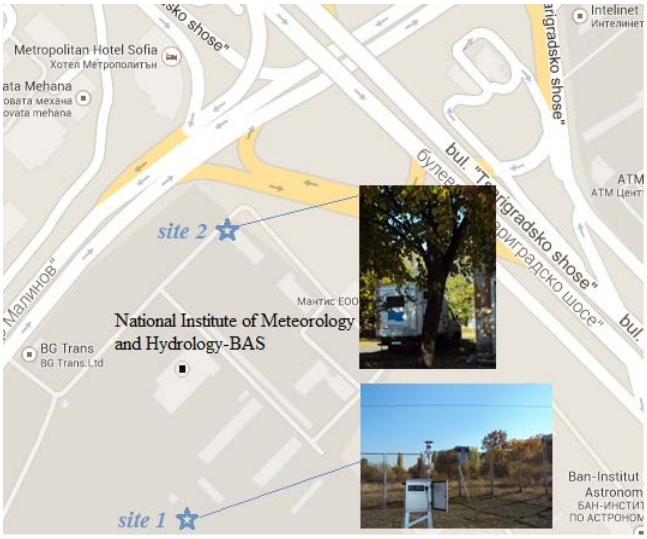


Fig.1.Map with sampling sites location in the NIMH-BAS, Sofia.

The sampling procedure and used equipment are of the same type and follow the EN-12341 standard. Therefore comparative assessment of the data set can be performed for PM10 and TSP (Hristova & Veleva, 2013).

2.2. Elemental analyses

The exposed quartz fiber filters were analyzed by EDXRF in INRNE-BAS. Three spectrometric systems were applied:

- The first one is equipped with Si (Li) detector with 25μ Be window and 170eV energy resolution at 5,9keV Mn-Ka line (PGT). This system is combined with an exciting head, based on an annular source Am-241 and three secondary targets (Mo, Dy, Sn).

- The second system is equipped with Si pin diode detector, Peltier cooling, with 7 µBe window a 140eV (KETEK). An exciting head, especially designed for low Z elements determination is supplied with three radionuclide sources Fe-55.

- The third system is equipped with Si pin diode detector, Peltier cooling, with 7µ Be window a 140 eV (KETEK). An exciting head with source of Pu-238 is especially designed for analyzing elements with Z between 17 and 35.

The XRF spectra are analyzed with specialized software X-Ray-Fit1 (Nikolova and Valcheva, 2006). By these three spectrometric systems it was possible to determine 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. The low concentrations on the filter samples require long measurement time - 10000s.

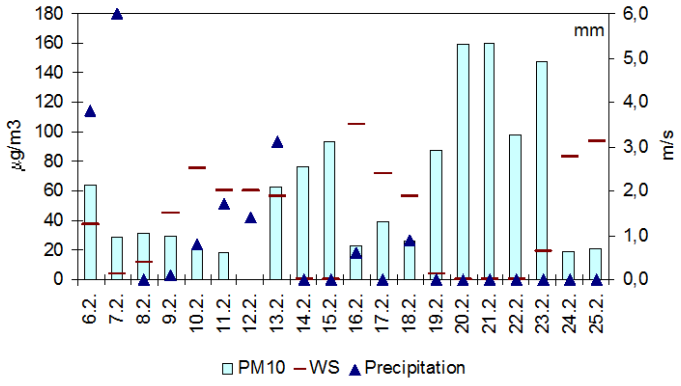
Available suitable standard for XRF analysis of aerosols filters in INRNE Lab is Community Bureau of Reference BCR, Reference material 128, Fly ash on filter. In this reference material only a few elements are present. Therefore 5 filters from the experimental campaign in February 2012 with different mass load were chosen, corresponding to different atmospheric conditions and used as “internal standards”. These 5 filters were analyzed in AGH University laboratory, Krakow, and after that on spectrometric systems in INRNE-BAS. In addition the same 5 filters were measured in the laboratory in IMI, Zagreb, and in the Albanian Centre of Applied Nuclear Physics. This intercomparison exercise helped to evaluate further the elemental concentration in the PM10 samples collected in 2012 increasing the number of analyzed elements.

In the frame of the IAEA Project RER1/008 inter laboratory proficiency test was performed.18 laboratories from 12 countries participated. The INRNE laboratory took part producing reliable results for Ca, Fe, K, Mn, Pb and Zn. The calibration coefficients for Cu were adjusted as a result of this proficiency test.

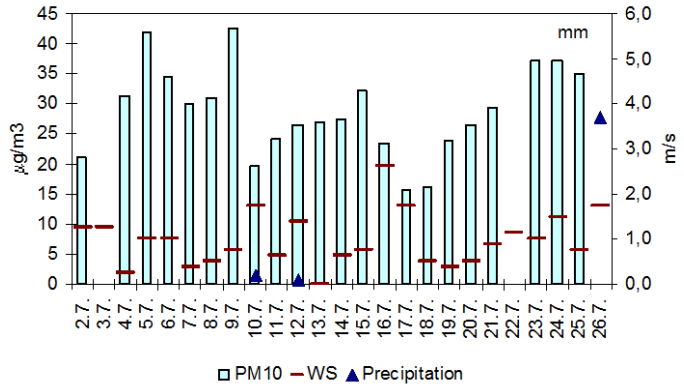
3. RESULTS AND DISCUSSIONS

3.1. Comparative assessment of the PM10 and meteorological conditions

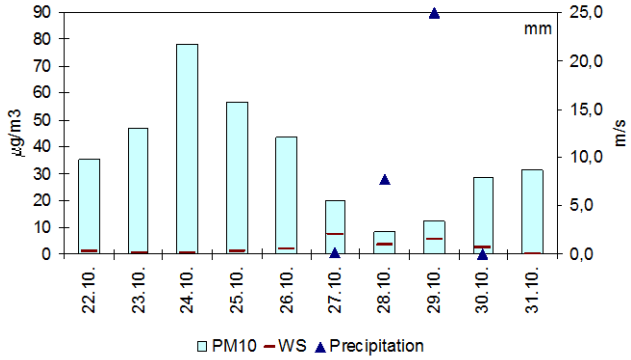
In the previous studies seasonal pattern in PM10 mean monthly and quarterly values from the urban monitoring stations of the Executive Environmental Agency (ExEA) of MoEW is well distinguished (Ilieva, 2012; Veleva et al, 2013). Daily, monthly and quarterly maximums are registered in the cold period of the year (first and fourth quarter of the year) for all urban background stations during the period 2010-2012 (Veleva et al, 2014). Minimums are observed in summer months, when mixing conditions in the atmosphere are better due to more intensive turbulent diffusion that results in lower measured concentrations. The seasonal variation of PM10 is well seen in our data presented in Fig.2 from 4 field campaigns. The averaged meteorological data are based on synoptic data from the NIMH-CMS Sofia and analyses. February 2012 was colder than the normal (with -3.4°C mean monthly value) and July was warmer (25°C) than normal (Monthly Bulletin of NIMH, 2012). October is warmer than normal with 14.1°C mean monthly temperature and 115% precipitation norm. December is colder than the average (with -0.8°C mean monthly value) and 114% precipitation norm.



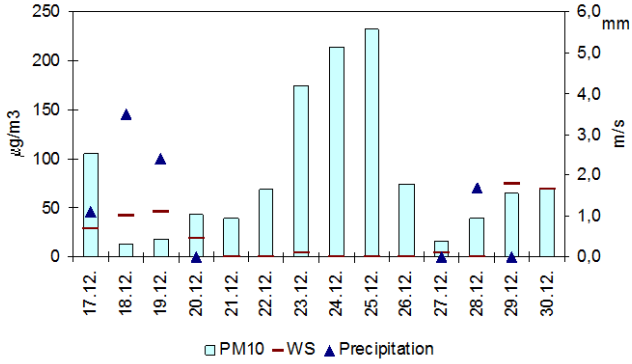
a)



b)



c)



d)

Fig.2. Daily PM10 concentration, mean wind speed (WS) and daily precipitation in

a) February, b) July, c) October and d) December 2012.

There are no days with PM10 concentration above 50 µg/m^3 in July (Fig. 2b), while in February in 9 of 20 days the PM10 concentration exceeded the limit value. In December PM10 is above the limit in 8 of 14 days.

During the PM10 experiments in October the meteorological situation is characterized with calm weather and weak winds from East and Southeast, varying RH from 60 to 90 %. At the end of the month, after October 27, a Mediterranean cyclone with precipitation and westerly winds diminished the pollution levels of PM10 and the concentrations of macro and microelements correspondingly.

In December, during the experimental campaign the weather was cloudy, with calm winds and weak precipitations in the first 3 days. The highest PM10 concentrations, measured at NIMH in 2012 are on 23, 24 and 25 December, days with calm weather partially cloudy, RH>80%. The daily average temperature changes from -3.5 to +3.1°C, because of advection of warmer air above relatively colder surface - typical meteorological situation for high pollution levels, reported for other EU cities (Kukkonen et al., 2005).

3.2. Results from the Parallel small scale experimental study of the variation of PM10 and elemental composition in October 2012

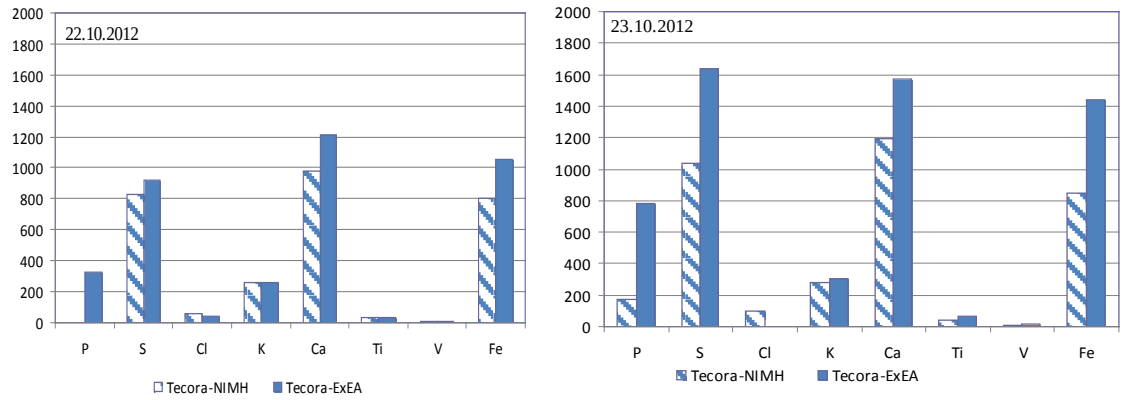
The data comparison from the October parallel sampling at site1 and site2 is presented in Fig.3.

The concentrations of Ca, S, K and Cu are very similar (Fig.3 a,b), and the difference between the two stations is in the region of 1 sigma uncertainties of the XRF analyses (8-12%). Higher variability is observed in Fe values, where the concentrations measured at site 2 are 20 to 30 % higher that for site 1. That might be due to the fact that site 2 is situated closer to the intensive crossroad of two boulevards (Fig.1). The difference between the two sites is more pronounced for Zn concentrations - up to 5 times higher at the mobile laboratory on October 22. The calm conditions and occasional NNE wind of 1-2m.s^{-1} enhance the transport of traffic related pollutants such as zink (Misaelides et al, 1993). Sb and Zn could be of traffic origin being essential components of anti-friction alloys and car tires. The contribution of polluted road-side dust to the elemental concentration in the atmosphere was found to be more significant for As, Co, Cr and Zn. The concentration of Fe and Zn and most of the other elements show closer values on 24, 25, 26 of October, days with prevailing calm weather and wind from S, SE and SSE directions observed only in 1-2 synoptic standard times of observations.

The influence of meteorological conditions and particularly of the wind and precipitation is clearly demonstrated on 27 and 28 of October, when all the concentrations of micro and macro elements dropped several times at both sites.

The trickiest element is Phosphorus, showing similar presence on 23 and 25, absent, or below Detection Limit (DL) of 8ng.m-3, on 24 and 27 October at both sites. In some days P is measured in one site only: on site 1 –on 26 and 28, on site 2 on October 22. Phosphorus has no significant gaseous phase under standard temperature and pressure conditions and is therefore almost entirely particle-associated in the atmosphere (Pierrou, 1976). In some studies long range transport is considered as a source of Total Phosphorous (TP), associated to the fine PM (<3.2um) (Vicars et al.2010, Srinivas and Sarin, 2012). This behavior of P in this experiment could be explained if the sources have local character and probably can be connected to the dry autumn vegetation. In the winter conditions of February 2012 with permanent snow cover, the main source for high P concentrations is related to the biomass and coal burning (Mahowald et al., 2008).

The results discussed above show that the measured concentrations at site 1 (Central Meteorological Observatory of NIMH) for most of the elements can be considered as representative for the region of Sofia. Data about elements like Fe, Zn, P, show that additional study for other urban background stations in Sofia is needed.



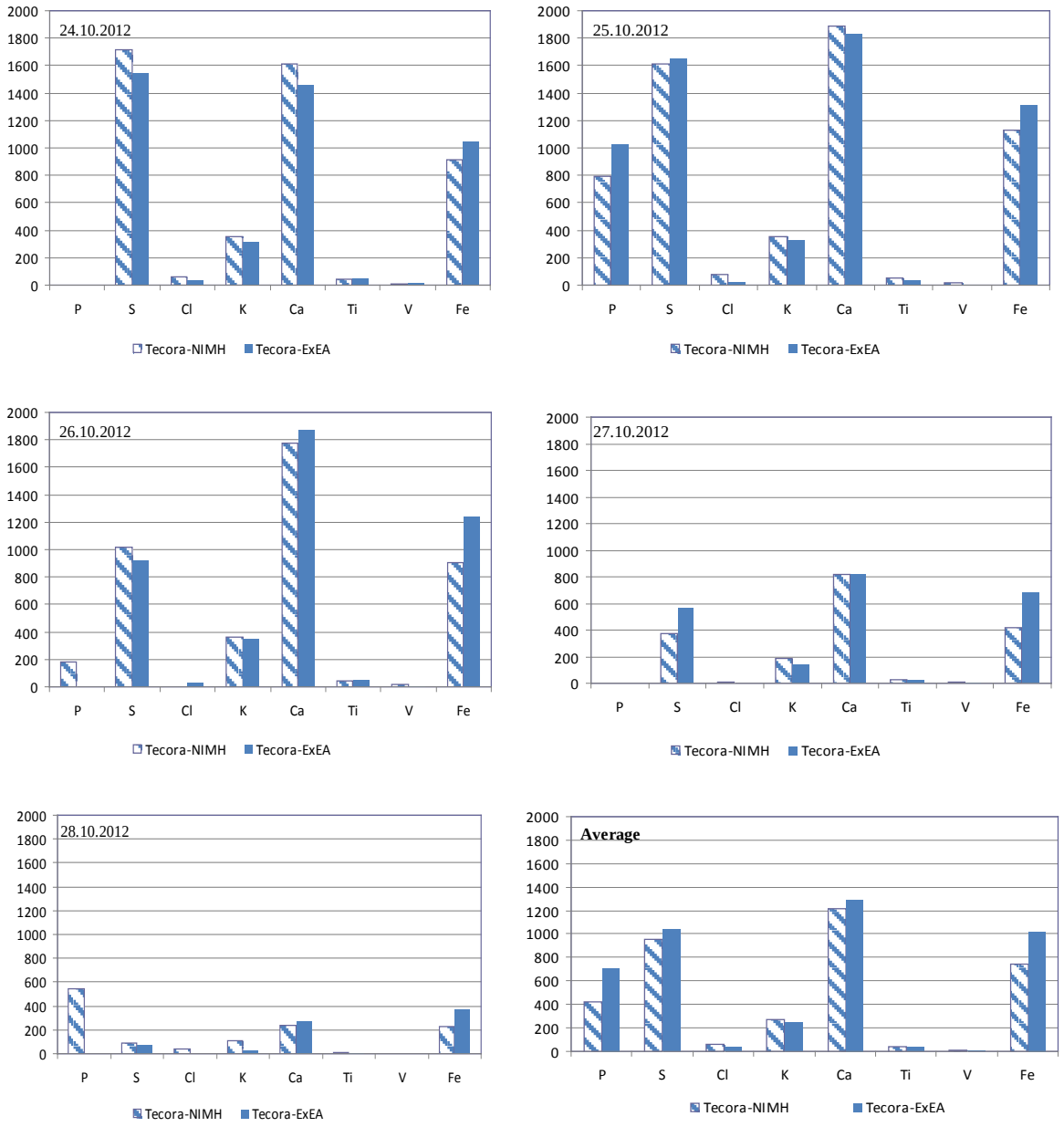


Fig. 3a. Daily concentration of macro-elements in ng.m^{-3}, measured at site 1 and site 2 in October 2012 and averaged over the period of measurements.

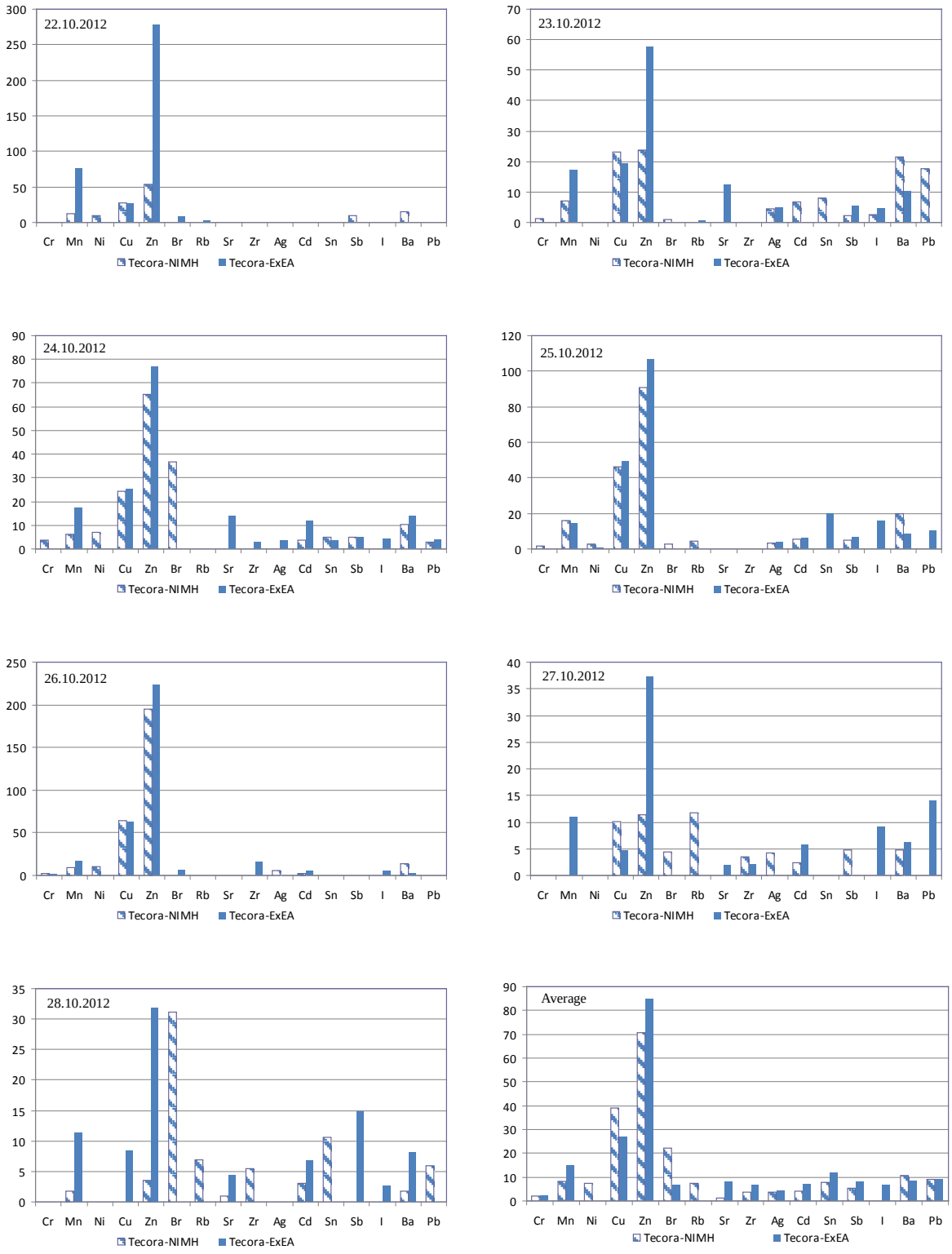
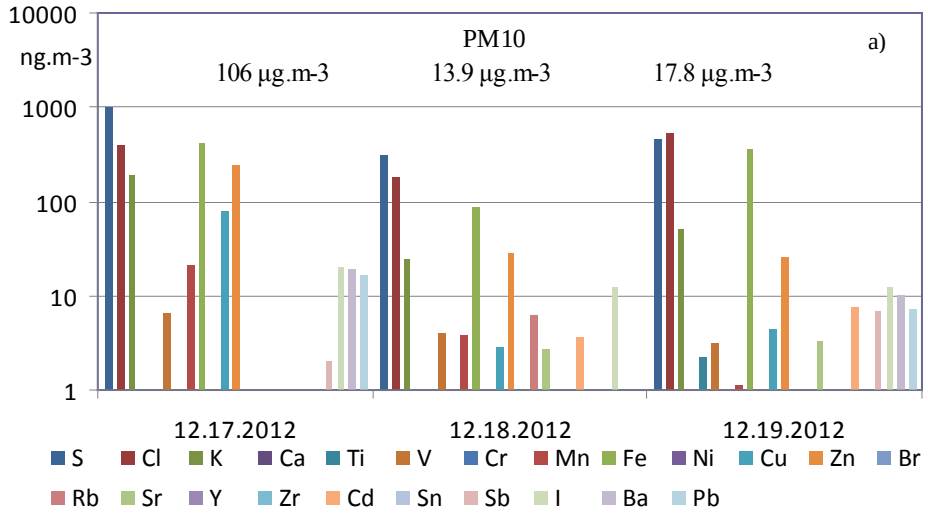


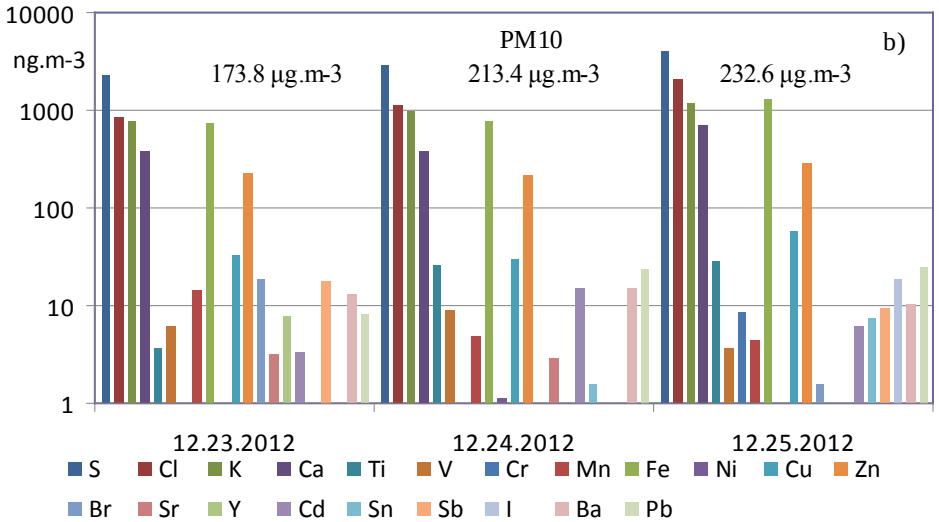
Fig. 3b. Daily concentration of micro-elements in ng.m^{-3}, measured at site 1 and site 2 in October 2012 and averaged over the period of measurements.

3.3. High PM10 pollution episode in December 2012

According to the monitoring data of ExEA (Rep. RIEW, 2012), daily concentrations of PM10, measured in the end of December 2012 at all Sofia urban air quality background stations, are between the highest values registered during the year. The high pollution episode is observed during several days after December 23, when the maximum PM10 value at Drujba monitoring station is 7 times higher than the daily limit value of 50μg.m^{-3}. The variation of PM10 concentrations, presented in Fig.2, demonstrate clear PM10 maximum during the same December period at site 2 of NIMH. The results from the EDXRF analyses of those filters, show highest concentrations of most of the elements compared to the previous ones (see Table 1).

Concentration of elements grouped in 3 consecutive days for different PM10 concentration and meteorological conditions is presented in Fig.4.





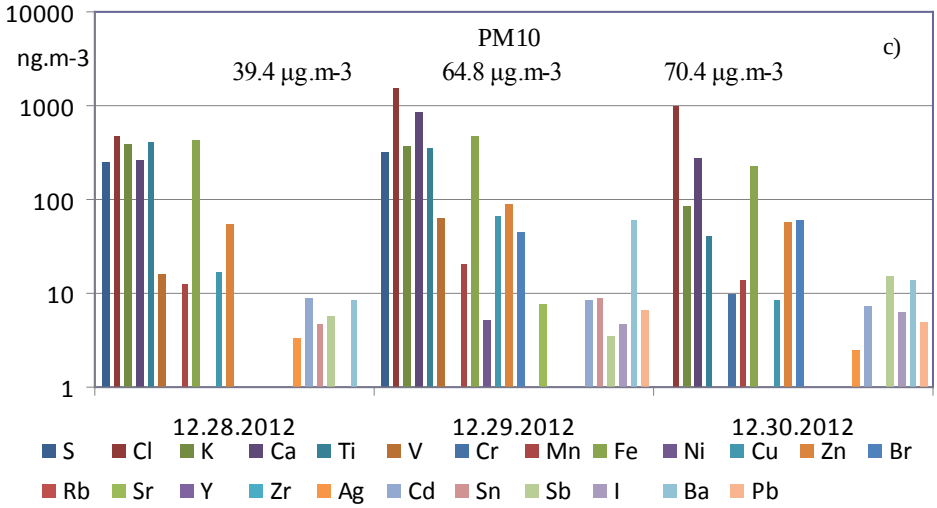


Fig.4. Concentration of elements in 3 consecutive days in December: a) period with variable PM10 concentration; b) high pollution episode; c) low PM10 concentrations after clean up by precipitation

The decrease in PM10 and elements concentrations dropped sharply in the first 3 days of the December experiment (Fig. 4a), due to rain on 18 and snow precipitation on 19. The period 21-24.12 is characterized with calm weather and anticyclonic conditions forming unfavorable situation for air pollutants dispersion, Fig.4b. In the end of the month foggy weather was observed which caused increase of PM10 concentrations and respectively the concentrations of the macro elements as S, Cl, K, and microelements as Zn, Cu, Ba, Cd, Pb.

During the period 28-30 December, the PM10 concentrations are 3 to 4 times lower but the concentrations of the elements Cu, Mn, Ba and Br are higher than during the period of high air pollution episode (Fig.4b,c). High concentrations of Zn, Mn, Cu are measured on 17 and 29 of December, when weak winds with eastern component were prevailing.

3.4. Summary results of the field campaigns in 2012

The statistics for the measured elemental concentrations from 4 field campaigns are presented in Table 1. The concentrations of most of the analyzed elements are lower in summer, excluding calcium, iron and silver. The average concentrations of Ca and Fe in July and October are about two times higher in respect to the winter months (Table 1). This can be explained with the relatively higher impact of soil dust in the warm period, in comparison to the specific conditions with permanent snow cover in February 2012. The Pb concentration was measured only in one sample in July and in 3 samples in October, in opposite to more regular Pb presence in the February and December PM10 samples. The Ag was not detected in February. The highest concentrations were measured in PM10 summer samples and was found in lower concentration in some days in October and December. The source of Ag is not yet identified and these results need further clarification.

The maximum concentrations of the elements are observed during the periods with calm conditions: in February for the elements Ti, V, Cr, Mn, Ni, Cu, Zn, Sr, Sn, Pb; in October – Ca; in December - S, Cl, K, Br, Sb, I, Ba. Similar are the maximum and average concentrations of Cd in February and December. Cadmium was below detection limit in summer samples. The range of measured elemental concentrations in urban air is wider in comparison to the background values reported for mountain stations in Bulgaria (Wiman et al., 2007).

Mean concentrations of crustal elements like Fe, K, and Ti, in Sofia in 2012, given in Table 1, are comparable with the corresponding values for other cities, summarized in our previous work (Veleva et al. 2013). The iron concentration in PM10 is higher for Budapest and Athens as reported in Muranszky et al., 2011, Tecer et al., 2012. The elemental sulfur concentration, measured in Sofia in December is the highest one compared to the values given for Turin and Milan (Malandrino et al, 2013). The lead concentrations in PM10 in February in Sofia are not exceptional high, similar to Budapest and Athens and about 2 times lower than in regions, where leaded gasoline is still used (as in Izmir, Tecer et al., 2012).

Volume 8, ISSN 1314-7234 (Online), Published at: http://www.scientific-publications.net

Table 1. Average, minimum and maximum values (ng.m^{-3}) for the elements, measured by EDXRF during field campaigns in 2012.

Element	February			July			October			December		
	Aver.	Min	Max	Aver.	Min	Max	Aver.	Min	Max	Aver.	Min	Max
P	534	18	1052	31	5	97	423	170	793	246	164	320
S	976	288	2740	742	274	1620	953	50	1719	1441	313	4034
Cl	117	8	868	31	7	55	57	13	120	606	62	2089
K	260	55	495	236	114	417	271	53	365	402	25	1187
Ca	338	7	751	854	514	1435	1214	116	1886	370	41	705
Ti	69	2	149	38	9	104	37	1	51	19	2	66
V	9	1	19	4	1	8	8	2	14	6	3	10
Cr	8	1	23	7	1	20	2	1	4			
Mn	60	2	174	8	1	18	8	2	16	9	1	22
Fe	357	53	993	714	290	1537	747	135	1127	514	89	1329
Ni	38	21	62			5	7	3	10	4	1	5
Cu	43	2	183	17	5	30	39	10	83	29	3	80
Zn	102	1	440	14	2	32	71	3	195	114	24	297
Br	24	8	51	5	3	7	22	1	45	27	2	63
Rb	8	3	13				8	5	12	8	6	10
Sr	23	1	75	6	1	12				5	1	14
Zr	7	3	12				4	2	6	4	1	11
Ag				34	16	50	4	2	5	4	3	5
Cd	6	2	14				4	2	7	7	1	15
Sn	9	3	19				8	5	11	8	2	16
Sb	6	3	11	7	2	16	5	2	9	8	2	18
I	3	1	8							11	2	21
Ba	10	1	26				11	2	21	17	8	61
Pb	75	5	209				9	3	18	13	5	25

4. CONCLUSIONS

In the present study EDXRF techniques, used to characterize the PM10 elemental composition proved to be reliable technique to measure the variations in the elemental composition of PM10 for the analyzed elements. The reported results for some important microelements (As, Cd, Pb, Ni) do not present a significant level of attention from a toxicological point of view. The concentrations of most of the analyzed elements are lower in warmer months, July and October, than in February and December, in correspondence to the lower PM10 mass concentration.

The results from parallel sampling in October show that the measured concentrations at the Central Meteorological Observatory of NIMH (site 1) of the most of the elements can be considered as representative for the background air pollution in Sofia. The concentrations of elements like Fe, Zn, P show that additional study for their variability in other parts of Sofia could be useful to clarify their origin.

The results obtained for seasonal variation of macro and microelements in 2012 could be further used in source apportionment studies.

ACKNOWLEDGEMENTS

The results reported in the present work are in the frame of project activities of IAEA TC Project RER 1/008. The intercomparison measurements were performed under the same project by Dr. Lucyna Samek, AGH University of Science and Technology (AGH-UST) Krakow, Dr. Kresimir Sega, Institute for Medical Research and Occupational Health (IMI), Zagreb and Dr. Nikolla Civici, Centre of Applied Nuclear Physics, Tirana.

REFERENCES

AQMP of Sofia, 2011. Air Quality Management Program for emission reduction to reach the standards for PM10 and NO2 of Sofia Municipality for the period 2011-2014., HTMU, Sofia, June 2011.

Argyropoulos G., Manoli E., Kouras A., Samara C., 2012, Concentrations and source apportionment of PM10 and associated major and trace elements in the Rhodes Island, Greece, Science of the Total Environment, 432, 12–22.

Gugamsetty B., Wei1 H., Liu C., Awasthi A., Hsu S., Tsai C., Roam G., Wu Y., Chen C., 2012, Source characterization and apportionment of PM10, PM2.5 and PM0.1 by using Positive Matrix Factorization, Aerosol Air Qual. Res., 12, 476–491.

Hristova E., Veleva B., 2013, Variation of air particulate concentration in Sofia, 2005-2012. Bulgarian Journal of Meteorology and Hydrology, 18/1-2, 47-56.

Ilieva N., 2012. PhD Thesis. Analyses and management of the atmospheric air quality in Sofia. HTMU. Sofia.

Kukkonen J., Pohjola M., Sokhib R. S., Luhanab L., Kitwiroonb N., Fragkoub L., Rantama M, Bergec E., Ødegaardd V., Slørdale L. H., Denbye B., Finardif S., 2005, Analysis and evaluation of selected local-scale PM10 air pollution episodes in four European cities: Helsinki, London,Milan and Oslo, Atmospheric Environment, 39, 2759–2773.

Malandrino M,, M, Martino, G, Ghiotti, et al, 2013, Inter-annual and seasonal variability in PM10 samples monitored in the city of Turin (Italy) from 2002 to 2005, Microchemical Journal, 107, 76–85,

Misaelides P., C. Samara, F. Noli, Th. Kouimtzis, I. Anou, 1993, Toxic element concentrations in airborne particulate matter in the area of Thessaloniki, Greece, The Science of Total Environment, 130, 139–146.

Monthly Bulletin of NIMH, February 2012, July 2012, October 2012, December 2012. Sofia.

Muránszky G., Óvári M., Virág I., Csiba P., Roland Dobai R., Záray G., 2011, Chemical characterization of PM10 fractions of urban aerosol, Microchemical Journal, 98, 1–10.

Nikolova E., R.Valcheva, 2006, " 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.

Pierrou, U., 1976, The global phosphorus cycle. In, Svensson and Soderlund (eds.), Nitrogen, Phosphorus and Sulphur – Global Cycles. SCOPE Report 7. Ecol. Bull. (Stockholm) 22:75-88.

Rep. RIEW. 2013. Regional Rep. for the state of the environment in 2012, MoEW, RIEW, Sofia, 2013, http://www. riew-sofia.org

Seinfeld J.H. and Pandis N.S., 2006, Atmospheric Chemistry and Physics. From Air Pollution to Climate Change, 2-nd Ed. John Wiley & Sons, Inc.USA. 1225p.

Srinivas B. and Sarin M. M., 2012, Atmospheric pathways of phosphorous to the Bay of Bengal: contribution from anthropogenic sources and mineral dust Tellus B 2012.2813-2821.

Tecer L.H., Tuncel G., Karaca, F., Alagha O., Süren P., Zararsız A., Kırmaz R., 2012, Metallic composition and source apportionment of fine and coarse particles using positive matrix factorization in the southern Black Sea atmosphere, Atmospheric Research, 118, 153–169.

Vicars W., J. Sickman, P. Ziemann, 2010, Atmospheric phosphorus deposition at a montane site: Size distribution, effects of wild fire, and ecological implications .Atmospheric Environment 44, 2813-2821

Veleva B. S., E. Hristova, E. Nikolova, M. P. Kolarova, R. Valcheva, 2013, PM10 concentration and elemental composition by EDXRF techniques in Sofia, 22 Intern. Symp. Ecology & Safety, 7-11 June 2013, Sunny Beach.

Veleva B., E. Hristova, E. Nikolova, M. Kolarova, R. Valcheva, 2014. Elemental composition of air particulate (pm10) in Sofia by EDXRF techniques. J. of Chemical Technology and Metallurgy, 49, 2 (in press).

Wang Q., Bi X., Wu J., Zhang Y., Feng Y., 2013, Heavy metals in urban ambient PM10 and soil background in eight cities around China, Environ Monit Assess, 185, 2, 1473-1482.

WHO, 2000, Air Quality Guidelines for Europe. WHO Regional Publications Eur. Ser. No. 91, Regional Office for Europe, Copenhagen, Denmark.

Wiman B., E.Donev, P.Nikolova, L. Yurukova, 2007, Aerosol-borne trace elements in Bulgaria: concentration levels in coastal and mountain regions. Bulgarian Geophysical Journal, Vol. 33, 3-19.