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# STATISTICAL EVALUATION OF XRF ELEMENTAL COMPOSITION DATA - A STEP TO SOURCE IDENTIFICATION OF $PM_{10}$ POLLUTION IN SOFIA

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**Abstract:** This study reviews the data for elemental composition of $PM_{10}$ obtained in four experimental campaigns run in February, July, October and December, 2012. The data, collected with TECORA low volume PM10 sampler, at the Central Meteorological Observatory of NIMH in Sofia were statistically evaluated. The ED-XRF technique was applied to determine more than 20 macro and micro elements in the $PM_{10}$ quartz fiber filter samples. The higher $PM_{10}$ daily concentrations were related to the higher concentrations for most of the elements, excluding Ag, K, Ca and Fe that show higher values in July. The concentrations from element to element expressed as ng.m-3 may vary in 3 orders of magnitude. HYSPLIT and FLEXTRA trajectory models were used to study the transport of air masses with higher silver concentrations observed in July 2012 in Sofia. Multivariate techniques as Factor analyses (FA) and Principle Components Analyses (PCA), were applied for source identification of the elemental composition data. The results show contribution of 3 or 4 factors depending on the chosen elements.

***Key words:*** *PM10, urban pollution, elemental concentration, EDXRF techniques*

## INTRODUCTION

Bulgaria is one of the European countries that does not comply with legally binding air quality limits and target concentration values, especially for particulate matter ($PM_{10}$, $PM_{2.5}$). The unfavorable meteorological conditions in Sofia, the most densely populated area in the country, placed in a closed valley surrounded by mountains up to 2 500m high, are combined with a number of different industrial, traffic and domestic emission sources of air pollutants which is a subject of different monitoring programs and investigations.

The national legislation following the EU Directive 2008/50/EC determines the $PM_{10}$ daily limit values of $50\mu g.m^{-3}$, not to be exceeded more than 35 times per calendar year. During 2012, the year of this experimental study, mean annual $PM_{10}$ concentration was about 10% above the limit value ($40\mu g.m^{-3}$) in all Sofia urban stations. The number of days with daily exceedances varies from 59 to 108 days for 5 Automatic Monitoring Stations (AMS), (Report RIEW, 2013). The air pollution with particulate matter in Sofia is characterized with distinguished seasonal pattern with peaks in the cold period of the year (Veleva, 2006; Ilieva, 2012; Hristova and Veleva, 2012). The investigation of elemental composition is important for identifying the source contribution to $PM_{10}$ concentration. Results from EDXRF analyses of macro and micro elements in $PM_{10}$, collected during several field campaigns are evaluated in the present study applying statistical methods.

## METHODS

$PM_{10}$ sampling was carried out with certified $PM_{10}$ samplers at the site of NIMH Central Meteorological Observatory (CMO) in Sofia during February, July, October and December 2012. 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. 24-hour $PM_{10}$ samples were collected with TECORA low volume air sampler on 47mm quartz fiber filters. The filters were changed at 8:00 LST and mass concentration was measured gravimetrically according to EN-12341 standard. 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 $PM_{10}$ filter samples. Synoptic

data from CMO-Sofia and data from the NIMH Monthly bulletin were used to describe the local meteorological conditions. The methodology of sampling and analyses is described in details in (Veleva et al., 2014a).

**RESULTS**

The data of $PM_{10}$ concentration and its elemental composition from four experimental campaigns in February, July, October and December, 2012 are summarized and discussed. The seasonal variations of the air particulate are characterized with high $PM_{10}$ values in winter (exceeding often daily limit value) and much lower mass concentrations in summer (Veleva et al., 2013). There are no days with $PM_{10}$ concentration above 50 $\mu g.m^{-3}$ in July, while in February in 9 out of 20 days the $PM_{10}$ concentration exceeded the limit value. Periods with $PM_{10}$>60 $\mu g.m^{-3}$ in several consecutive days are 13-15, 19-23 of February, and 23-25 of December characterized with anticyclonic weather and calm conditions. In October there are 2 out of 10 days with exceedance of the 50 $\mu g.m^{-3}$ at calm weather conditions. In December $PM_{10}$ is above daily limit value in 8 out of 14 days, because of the stagnant meteorological conditions determined by calm wind, low temperatures and cloudy and foggy weather. The highest $PM_{10}$ concentrations were measured on 23, 24 and 25 December in 2012 with maximum of 232.6 $\mu g.m^{-3}$.

The higher $PM_{10}$ daily concentrations are related to the higher concentrations for most of the elements. The elements calcium, iron and silver higher values were only measured in July compared to the other periods. The average concentrations of Ca and Fe in July and October are about 2 times higher compared to February and December, because of the soil dust resuspension. The Pb concentrations were measured in most of the samples in February and December, in one sample in July, and in 3 samples in October. The maximum concentrations of Ti, V, Cr, Mn, Ni, Cu, Zn, Sr, Sn, Pb are observed during the periods with calm conditions in February; maximum of Ca - in October; S, Cl, K, Br, Sb, I, Ba - in December. Similar are the maximum and average concentrations of Cd in February and December. Cadmium was below detection limit in the summer samples (Veleva et al., 2014b).

Plotted on Figure 1 and Figure 2 are chosen periods with consecutive days from February and July that illustrate the variations in the elemental concentration during the winter and the summer. The periods are characterized with different $PM_{10}$ daily concentrations and different meteorological conditions. The concentrations of elements vary in 3 orders of magnitude, while the $PM_{10}$ mass concentration changes from minimum to maximum from 2 to 8 times.

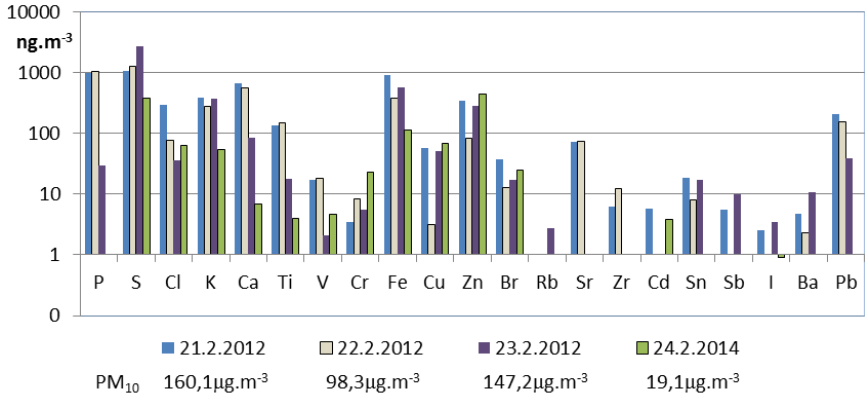


Figure 1. Elemental concentrations in $PM_{10}$ in four consecutive days in February 2012.

The macro elements are found in the majority of the $PM_{10}$ samples. The number of elements with concentrations below Detection Limit (DL) is higher in summer (Fig. 2). For example, Cd, I, Br, Zr and Ba are not detected in the July samples and Pb, Rb and Ni were detected once. The As was detected only in 3

days in the summer samples with maximum on 13 of July. Sn and Sb are below DL approximately in half of the winter samples. Ni is measured in a few samples in February and in one in July.

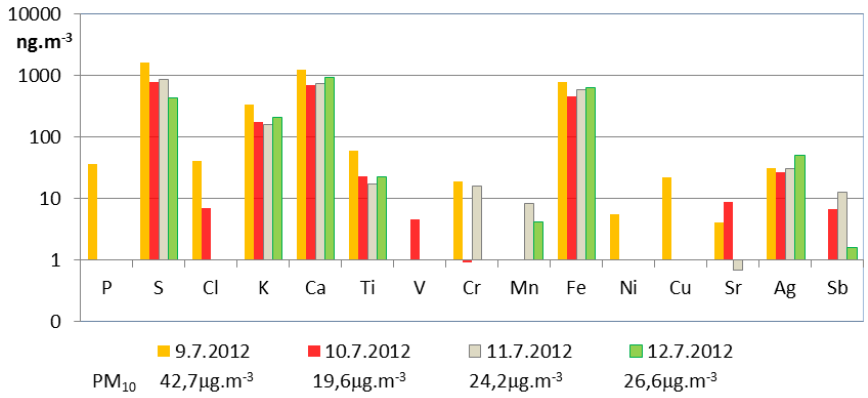


Figure 2. Elemental concentrations in $PM_{10}$ in four consecutive days in July 2012.

The macro elements K, Ca, Fe are in the range from less than 50 to 1000 ng.m$^{-3}$ in winter and from 100 to 1600 ng.m$^{-3}$ in summer. In July, the daily Cu concentrations are several times lower than in February, when the Cu concentrations are above 100 ng.m$^{-3}$ for certain days. Similar are the variations of Ti, Zn, Mn. The Ag was measured in all $PM_{10}$ summer samples, while in February it was not detected. Phosphorous shows high winter concentration, with average value of 534.1 ng.m$^{-3}$ in February, and of 30.6 ng.m$^{-3}$in July. The high P concentrations can be explained with the biomass and coal burning from domestic heating.

Silver is one of the interesting trace elements, rarely measured in the atmosphere. Atmospheric Ag can originate from mineral aerosols or industrial emissions. The global cycling of Ag is dominated by human activity, and includes releases in the environment from smelting, mining, industry, and wastewater treatment plants (Ranville et al., 2010). Silver is considered as a long range tracer of industrial activity in Arctic (Yli-Tuomi et al., 2003), and as geochemical tracers together with Se in the North Pacific from Asian fossil fuel combustion (Ranville et al., 2010).

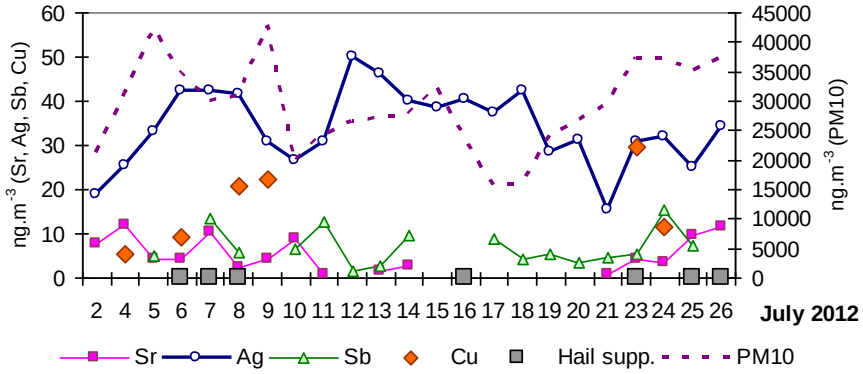


Figure 3. Variations of Ag, Sr, Sb, Cu and $PM_{10}$ concentrations in July 2012.
The days with hail suppression action are marked.

The Ag concentrations in Sofia were below detection limits during cold winter conditions in all February samples. Low concentrations of few ng.m$^{-3}$ were detected in 5 out of 9 days in October and in 5 out of 13 days in December. Maximum daily concentrations with average value of 34 ng.m$^{-3}$ were measured in July

2012 (Figure 3). The preliminary results from the winter and summer campaigns in 2013 show a presence of Ag in $PM_{10}$ reaching concentration of about 10 ng.m$^{-3}$ in some of the days. The day to day changes of Ag concentrations in July 2012 differs from the $PM_{10}$ variations as well as from the variations of elements like S, Cu, As, Sr, Sb, Zn, which can be explained with the different origin of silver in air particulate matter (Fig. 3). The variations of Ag differ from Cu concentration, from the Sr (as soil related element) and from the Sb, (microelement not measured in the soil from CMO, Sofia). The Cu may originate not only from the soil but also from the regional atmospheric transport from Pirdop copper smelter and refinery (the biggest facility for smelting and refining of copper in Eastern Europe, 60 km from Sofia, 740 m asl, main chimney of 325m height) one potential source of Cu, S and other trace elements.

Five-day backward air trajectories arriving daily at Sofia at 12:00 and 18:00 UTC were analyzed using HYSPLIT 4 model (Draxler and Rolph, 2013) and FLEXTRA back trajectories (*www.nilu.no/trajectories*; Stohl et al., 2005 ) with the purpose of determining the potential regional source of atmospheric silver. The prevailing transport of air masses when Ag concentrations >30 ng.m$^{-3}$ are observed, is from NE, N and NW directions to Sofia, coming from Central Europe, passing over different regions of Romania and Serbia and Northwestern Bulgaria. In this part of Bulgaria there are 4 rocket launching sites of the Hail Suppression Agency. The method of delivery of reagent - artificial ice-forming nucleus (AgI) in clouds by rockets is applied in Bulgaria. It enables the direct and continuous dispersion of AgI reagent in seeding cloud areas. Similar technology is used in the regions near to the Bulgarian western boarder in Serbia *(http://www.weathermod-bg.eu/pages/tech_en.php)*.

The statistical analyses of the data with elemental composition (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) from 65 samples were done in several stages: distribution fitting, calculation of correlation coefficients and regression equations, FA and PCA multivariate methods. There are days with missing data for one or several elements because of technical problems. In this case it is possible to use the geometric mean for the corresponding month for data reconstruction of missing values (Ti for example). For K, Ca and S the multiple regression equations are used based on the $PM_{10}$ and Fe concentrations ($R^2$=65%, 69% and 87% correspondingly). The type of distribution to be fitted to the data histograms constructed with non-overlapping intervals was evaluated applying STATGRAPHICS Plus 5.0 software (Figure 4).

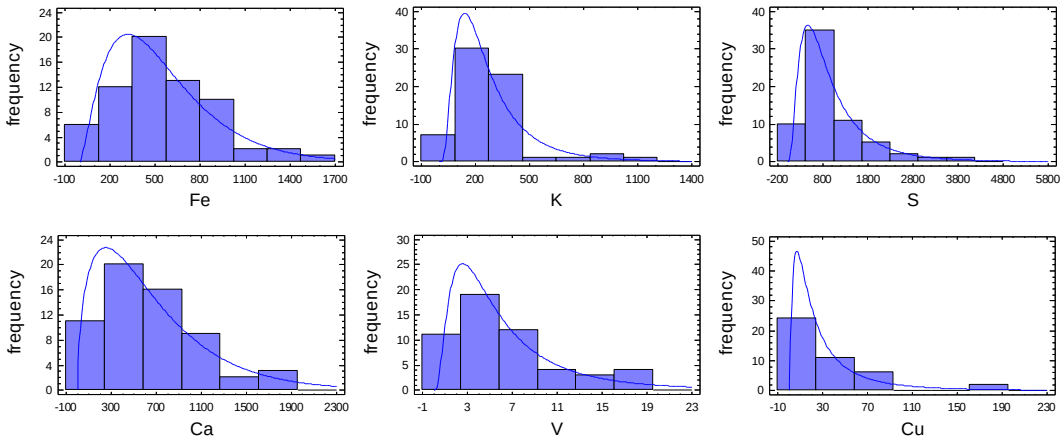


Figure 4. Histogram and fitted distribution function for Fe, K, S, Ca, V and Cu in all $PM_{10}$ samples in 2012.

The elements Fe, K, V, S, Ni, Ti, Cu, Zn, Sr, can be fitted to lognormal or gamma-distribution with 90% or higher confidence. There is no simple distribution function to be fitted to P, Mn, Ag histograms. For these elements bimodal distributions could be more appropriate.

The identification of pollution sources is required in many tasks concerning the air quality legislation (air quality assessment, development of action plans, identification of natural sources, etc.). Receptor models (RMs) are used to accomplish source apportionment by analysing chemical and physical parameters measured at one or more specific sites (EU Guide, 2014). Factor analyses and Principle Components Analyses can be applied in order to group the main potential sources. A first attempt to identify the $PM_{10}$ pollution sources in Sofia, based on the results for elemental composition, was performed in the present work by using multivariate techniques. Factor analyses (FA) and Principle Components Analyses (PCA) with STATGRAPHICS Plus 5.0 software were applied. The results show contribution of 4 factors if FA of P, S, Cl, K, Ca, Ti, V, Fe, Cu, Zn data is applied. The factors derived by PCA after varimax rotation are 3 or 4 depending of the selection of the set of elements and should be considered as preliminary, because of non sufficient number of data. The list of factors is as follows:

*Factor 1* – dominated by Fe and Ca, typical crustal elements;

*Factor 2* – fossil fuel and biomass burning – about 50% of $PM_{10}$, S, K;

*Factor 3* – industrial sources Cu, Br, Cl, Ti;

*Factor 4* – not well defined, the impact of road transport and resuspension from contaminated industrial areas around Sofia – Pb, Ni, Mn, Cd.

## CONCLUSIONS

The ED-XRF technique was applied to determine more than 20 macro and micro elements in the $PM_{10}$ filter samples. The higher $PM_{10}$ daily concentrations are related to the higher concentrations for most of the elements, excluding Ag, Ca and Fe higher values in July compared to February.

The Receptor models and FA and PCA in particular are recognized as useful tools for Air quality management. Their implementation in air quality studies of $PM_{10}$ pollution for Sofia region requires enlarged data set and more results from the next experimental campaigns.

## ACKNOWLEDGEMENTS

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## REFERENCES

Draxler, R.R. and Rolph, G.D., 2013: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD.

EU Guide, 2014: European Guide on Air Pollution Source Apportionment with Receptor Models. Luxembourg: Publications Office of the European Union, 2014. http://www.jrc.ec.europa.eu.

Hristova E., B. Veleva, 2013: Variation of air particulate concentration in Sofia, 2005-2012. *Bulgarian J.of Meteorology and Hydroogy.*, **18**, 1-2, 47-56.

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

Ranville M. A., G. A. Cutter, C. S. Buck, W. M. Landing, L. S. Cutter, J. A. Resing, A. R. Flegal. 2010: Aeolian contamination of Se and Ag in the North Pacific from Asian fossil fuel combustion. *Environmental Science and Technology*, **44** (5), 1587-1593.

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

Stohl, A., C. Forster, A. Frank, P. Seibert, and G. Wotawa, 2005: Technical Note : The Lagrangian particle dispersion model FLEXPART version 6.2. *Atmos. Chem. Phys.* **5**, 2461-2474.

Veleva, B. 2006: Time Variation of the Dust Concentration and Deposition in Sofia During the Period 1981-2002, Proc. of BALWOIS 2006 Conf., 23-26 May 2006, Ohrid, http://balwois.com/conference/balwois-2006/.

Veleva, B., E. Hristova, E. Nikolova, M. Kolarova, R. Valcheva, 2013: PM10 concentration and elemental composition by EDXRF techniques in Sofia. J. Internat. Sci. Publ., Ecology & Safety 2013**,** Vol.**7**, part 1, 83-96. *http://www.scientific-publications.net.*

Veleva, B., E. Hristova, E. Nikolova, M. Kolarova, R. Valcheva, 2014a: Elemental composition of air particulate ($PM_{10}$) in Sofia by EDXRF techniques. *J. Chem. Technol. Metall.*, **49**, 2, 2014, 163-169.

Veleva, B., E. Hristova, E. Nikolova, M. Kolarova, R. Valcheva, 2014b: Seasonal variation of PM10 elemental composition in urban environment. J. Intern. Sci. Publ., Ecology and Safety 2014, Vol. **8**, 2014, 265-275, *http://www.scientific-publications.net*

Yli-Tuomi T., L.Venditte, P.K. Hopke, M. Shamsuzzoha Basunia, S. Landsberger, Y. Viisanen, J. Paatero.et al. 2003: Composition of the Finnish Arctic aerosol: collection and analysis of historic filter samples. *Atmospheric Environment,* **37**, 2355–2364.