Application of PCA and FA models for source apportionment of PM_{10} in Sofia

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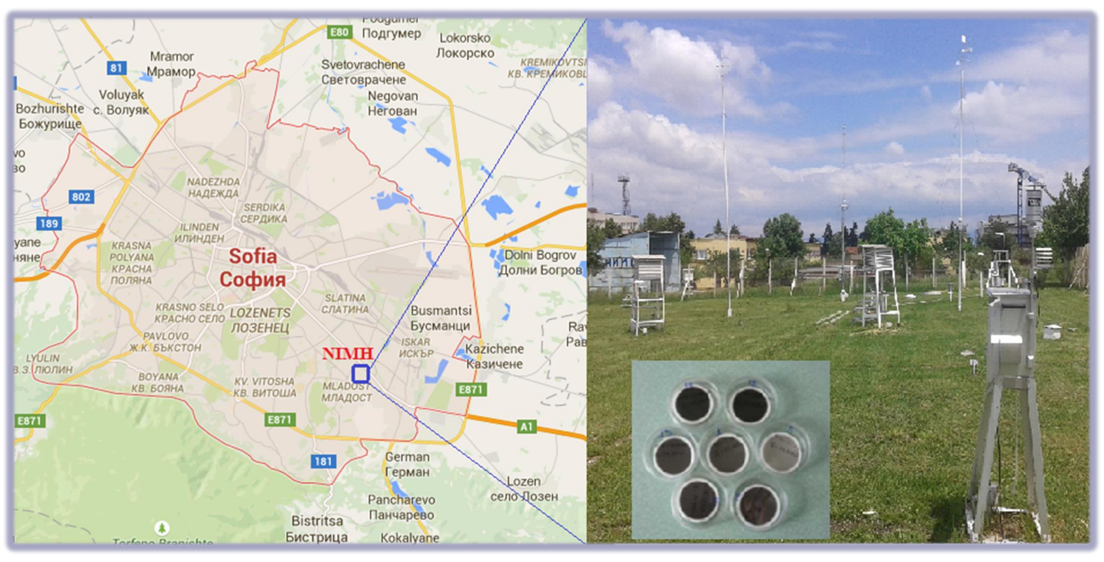
INTRODUCTION

Particulate matter, PM_{10} and $PM_{2.5}$ is a serious problem for the urban air pollution in many Bulgarian cities [1,2]. PM10 harmful health effect is well known and depends on the concentration, size and chemical composition.

In this study air particulate PM_{10} mass concentration and more than 20 elements, measured by EDXRF technique, in the daily quartz filter samples are obtained during winter and summer experimental campaigns at NIMH observatory in Sofia. These data and SO_2 and NO_2 concentrations from air quality urban background stations are used to perform source apportionment study. Multivariate techniques as Factor analyses (FA) and Principle Components Analyses (PCA) by STATISTICA.6 software are applied to identify sources of PM_{10}.

Map of Sofia and sampling site

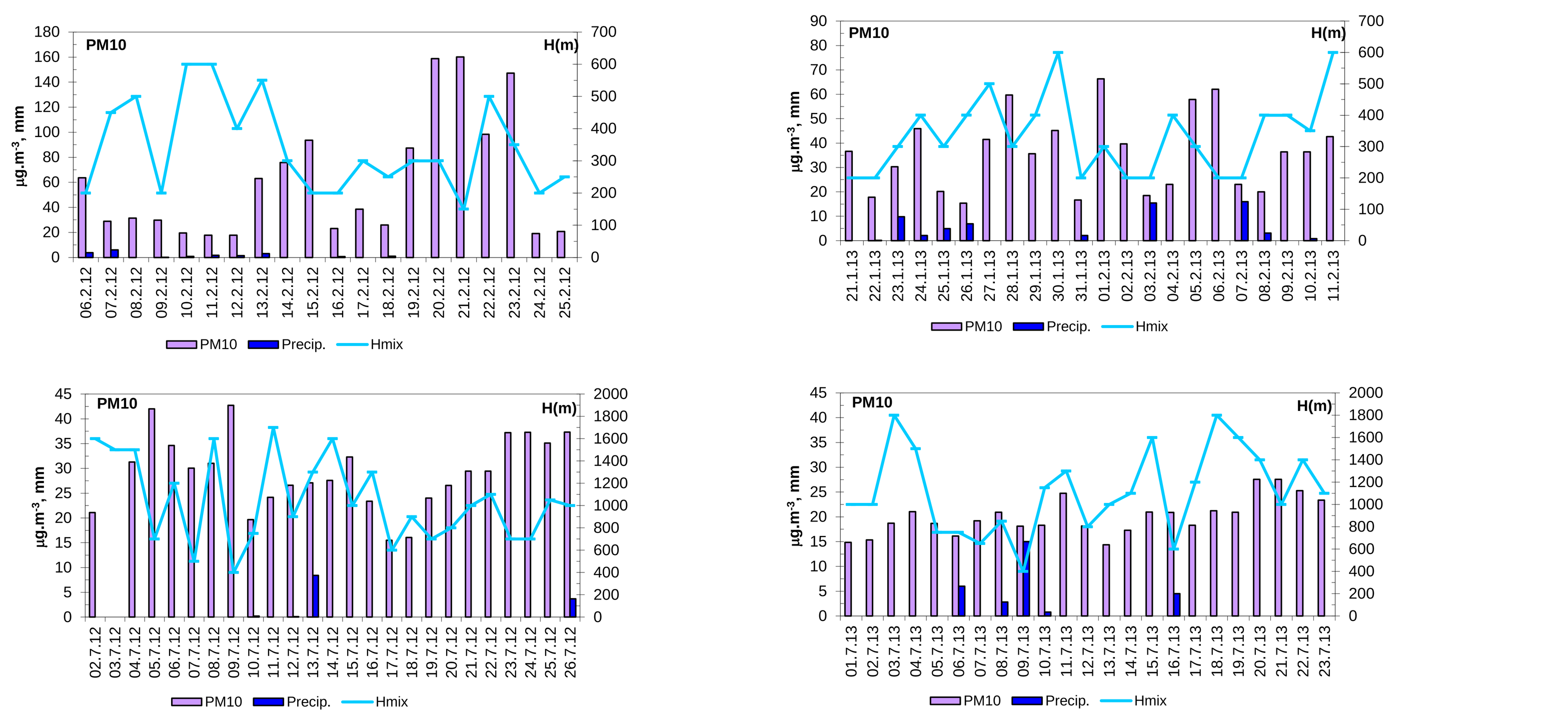


SAMPLING AND METHODS

- *PM_{10} sampling was carried out at the site of Central Meteorological Station (CMS) of NIMH*
- *Sampling periods – 6.02–25.02.2012, 2.07-26.07.2012, 21.01-11.02.2013, 1-23.07.2013.*
- *Certified PM10 sampler TECORA Echo PM is used.*
- *Sampling duration is 24h (at 8:00 LST).*
- *47mm quartz fiber filters (Whatman). Filters were conditioned for 48h before and after sampling in a temperature and humidity controlled room (T= 20±2° C, RH=50±5%).*
- *Energy Dispersive X-Ray Fluorescence (EDXRF) technic in INRNE is used .*

PM_{10} mass concentration

Stagnant weather conditions and inversions are the major factor for the high PM10 values, registered during the cold period. Higher PM10 daily concentrations correlate with higher concentrations of the S, K, Ti, Sr. The PM10 mass concentration, the daily sum of precipitation and mixing height determined from 12 UTC aerological soundings is presented below.



Factor analyses

The whole data set (85 daily values) is divided in summer and winter subsets. The contribution of 5 factors for each group with different elemental components is derived. 85% of the PM_{10} concentration in summer is due to the impact of K, Ca, Ti, Fe source. In separate group with no significant contribution are Zn and Cu.

When we use the entire data set, 51% of the contribution to PM_{10} is from sources related to the traffic and road dust resuspension (NO_2, Zn, Sr, Ti). The source of S and Mn (grouped in one factor) contribute with 18% to the PM_{10} and the crustal elements source (K, Ca, Fe) with about 4.5%.

Factor Loadings (Varimax normalized) _winter data set (Marked loadings are >,700)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
PM_{10}	0,316	0,362	0,342	0,629	0,013	0,362
NO_2	0,296	0,120	0,007	0,747	-0,079	0,433
SO_2	-0,064	0,478	0,467	0,027	-0,180	0,505
P	-0,042	0,113	-0,310	0,038	0,768	0,424
S	0,035	0,188	0,903	0,219	0,117	0,062
Cl	0,908	-0,007	-0,216	0,202	0,042	-0,031
K	0,781	0,112	0,528	0,131	0,117	0,086
Ca	0,883	-0,032	-0,033	0,046	0,201	0,018
Ti	0,324	0,252	0,097	0,029	0,065	0,866
Mn	0,028	-0,338	0,881	-0,082	-0,071	0,141
Fe	0,830	0,147	0,121	0,423	-0,012	0,049
Cu	0,354	0,686	-0,189	0,271	0,017	0,058
Zn	0,086	0,011	-0,043	0,856	0,073	0,071
Rb	-0,161	-0,075	-0,391	0,042	-0,813	0,126
Sr	-0,102	-0,005	0,136	0,464	0,255	0,839
Sn	-0,067	-0,134	0,295	0,635	-0,477	-0,258
Sb	0,305	-0,758	-0,056	0,125	-0,298	-0,256
Ba	0,741	-0,067	0,096	-0,143	-0,167	0,175

Factor Loadings (Varimax normalized) summer data set, (Marked loadings are >,700)

	Factor 1	Factor 2	Factor 3	Factor 4
PM_{10}	0,958	0,064	0,000	-0,173
NO_2	-0,230	-0,447	0,595	-0,126
SO_2	0,254	0,191	0,650	0,332
S	0,640	-0,243	-0,160	-0,381
K	0,925	0,198	0,105	0,025
Ca	0,856	0,047	0,329	0,097
Ti	0,897	0,200	0,032	0,078
Mn	0,026	-0,257	-0,111	0,823
Fe	0,905	0,102	0,203	0,113
Cu	-0,054	-0,822	0,133	0,026
Zn	-0,144	-0,827	-0,146	0,250
Rb	-0,292	0,038	-0,851	0,323

Factor Loadings (Varimax normalized)_All Data set (Marked loadings are >,700)

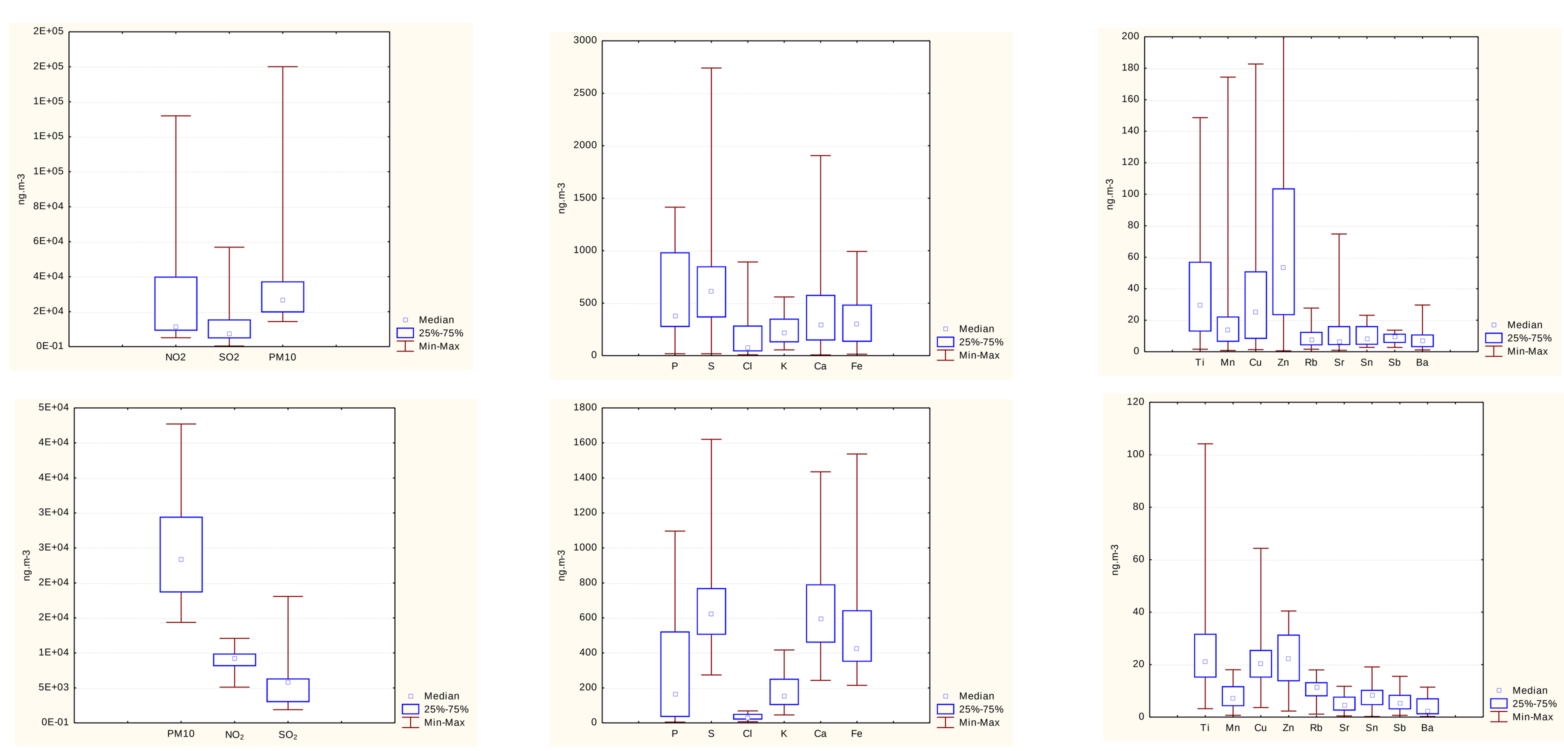
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
PM10	0,771	0,262	0,400	0,096	0,070
NO2	0,852	0,005	0,177	0,378	0,078
SO2	0,523	-0,096	0,563	0,171	-0,164
P	0,491	-0,224	-0,157	0,086	-0,630
S	0,142	0,156	0,844	-0,123	0,081
Cl	0,402	0,602	-0,231	0,504	-0,009
K	0,262	0,720	0,478	0,280	-0,006
Ca	-0,055	0,915	-0,067	-0,011	-0,047
Ti	0,570	0,435	0,346	-0,083	-0,371
Mn	-0,049	-0,036	0,792	0,236	0,234
Fe	0,103	0,909	0,048	-0,096	0,152
Cu	0,584	0,279	-0,197	0,017	-0,077
Zn	0,753	0,044	-0,009	0,129	0,384
Rb	-0,120	-0,059	-0,258	-0,694	0,205
Sr	0,761	0,016	0,218	-0,419	-0,117
Sn	0,256	-0,058	0,153	0,095	0,822
Sb	-0,016	0,091	-0,037	0,778	0,384
Ba	0,113	0,606	0,122	0,415	-0,019

Element concentrations

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. For example, Cd, I, Br, Zr and Ba are not detected in the July 2012 samples when Pb, Rb and Ni were detected once. The As was detected only in 3 days in the summer of 2012 with maximum on 13 of July. Sn and Sb are below DL approximately in half of the winter samples. Ni is detected in about 25% of total samples: measured once in July 2012 and in ~ 50% of days in July 2013 . The macro elements K and Fe are in the range from less than 50 to 1000 $ng.m^{-3}$ in winter and from 100 to 1500 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. Phosphorous shows high winter concentration, with average value of 534.1 - 590 $ng.m^{-3}$ in 2012 and 2013 correspondingly, and of 31 – 500 $ng.m^{-3}$ in July 2012 - 2013.

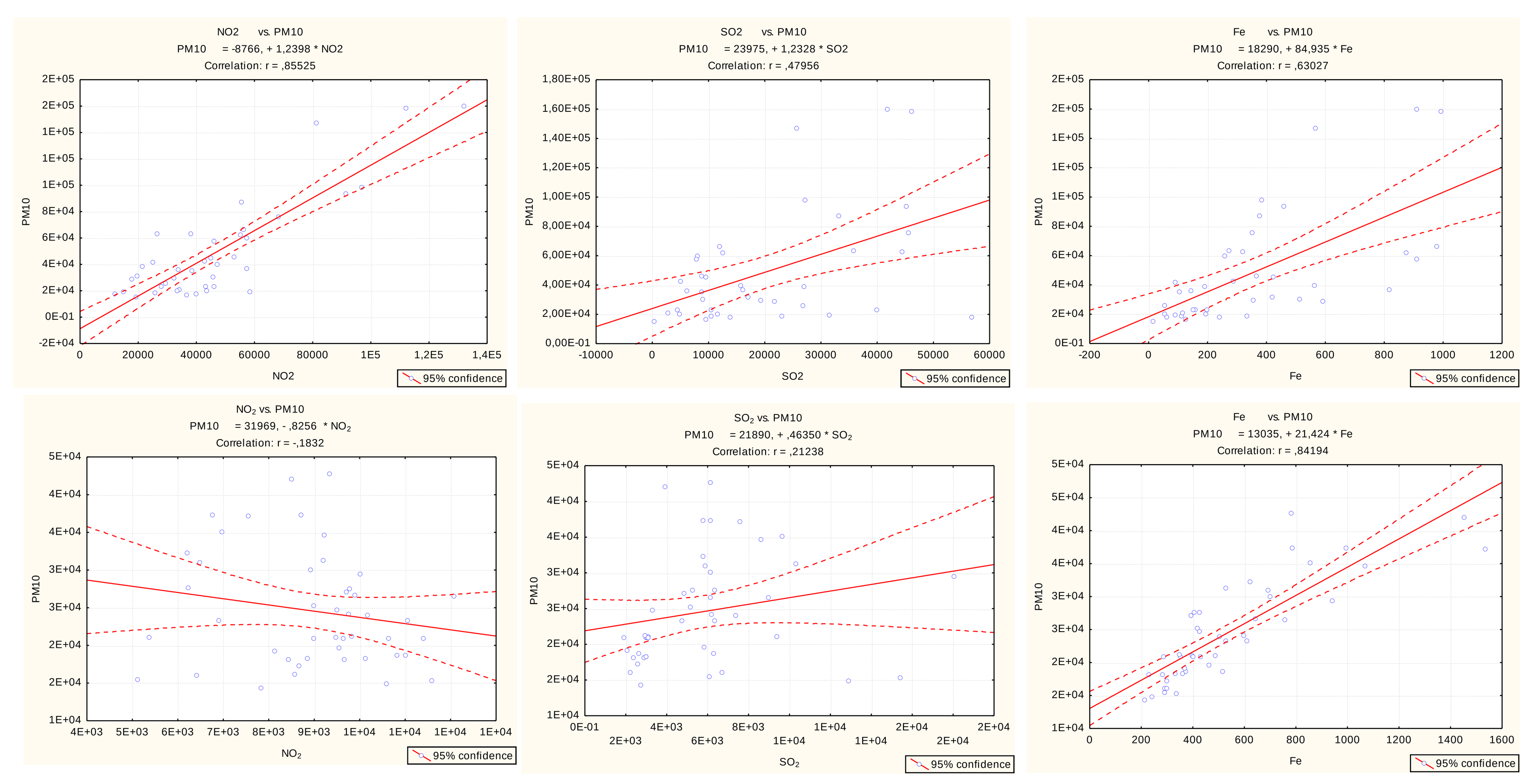
Winter

Summer



Statistical analysis

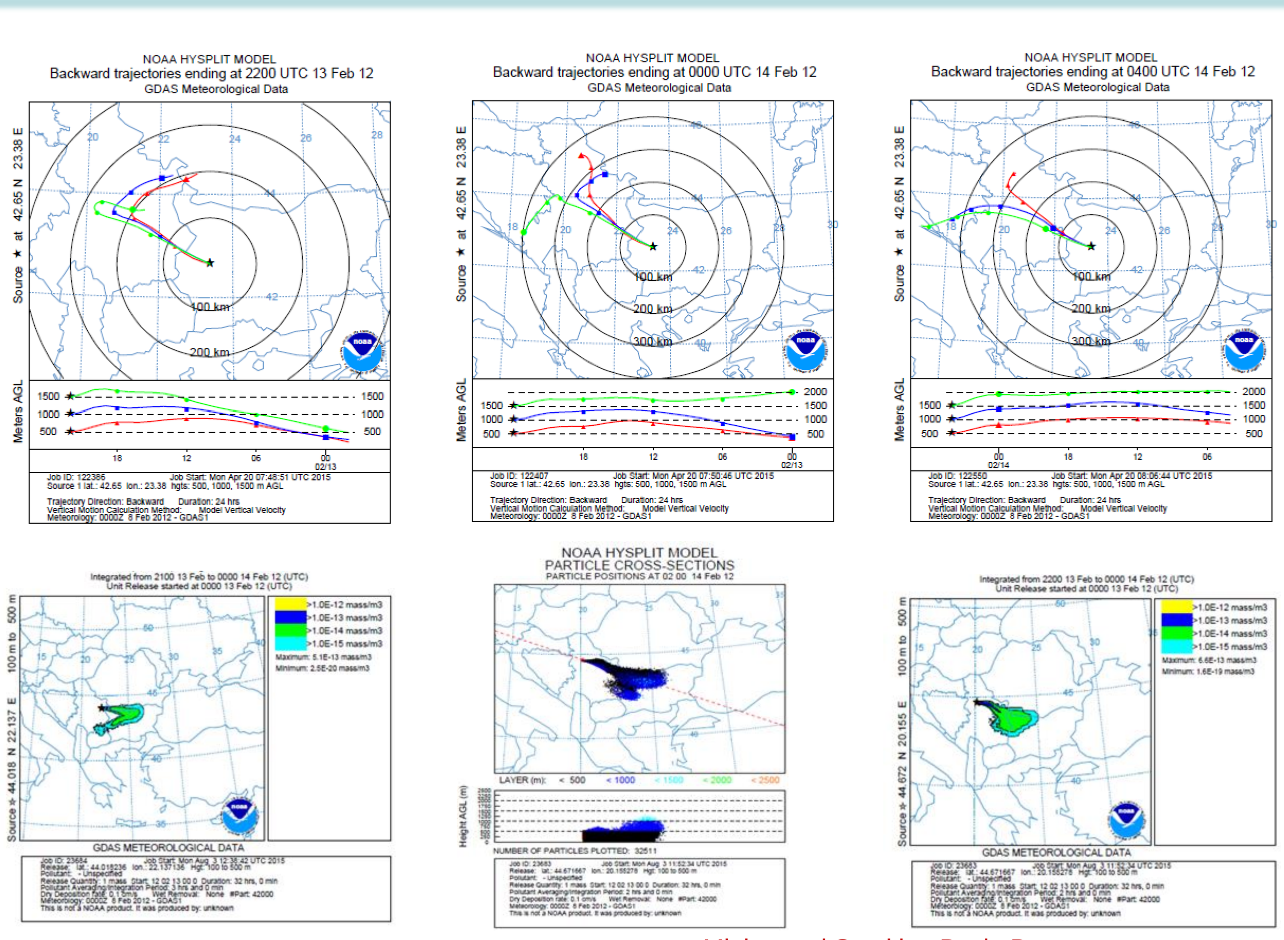
The correlations between some elements and PM_{10} mass concentration are presented in scatter plot figures for winter and summer experiments. Weak correlation between PM_{10} and Fe, K and Ti is observed in winter periods. No correlation (r<0.3) is found between PM10and P, Ca, Mn, Sb and Ba. Correlation coefficient > 0.6 is obtained between PM_{10} and NO_2, Ti and Sr. The temporal variations of these elements are influenced probably by different sources contribution and source profiles. High seasonal variability of PM_{10}/NO_2 correlation coefficient is registered (0.85 in winter versus 0.18 in summer). Significant correlation (r>0.57) is obtained between elements pairs: K-Fe, K-Ca, K-Ba, K-Ti, K-Cl, Ca-Fe, Ca-Ba, Sr-Ti, S-Mn.



Winter

Summer

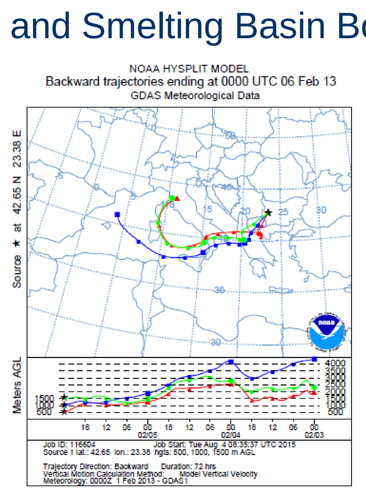
Sulfur content in PM_{10} in winter is related to the same factor as Mn. It does not correlate significantly with most of the other elements in PM_{10} and NO_2 and SO_2 24-average concentrations. High S concentrations and high S to PM_{10} ratio is registered in the PM_{10} samples of 6, 13, 21,22, 23 February 2012 and in 5 and 6 February 2013. HYSPLIT Trajectory Model [3] is applied in cases with high sulfur concentration to trace back the origin of air masses. HYSPLIT dispersion model is run in case when back trajectories indicate the regional transport from major industrial SO_2 sources. In winter there is a local sulfur background because of the domestic heating.



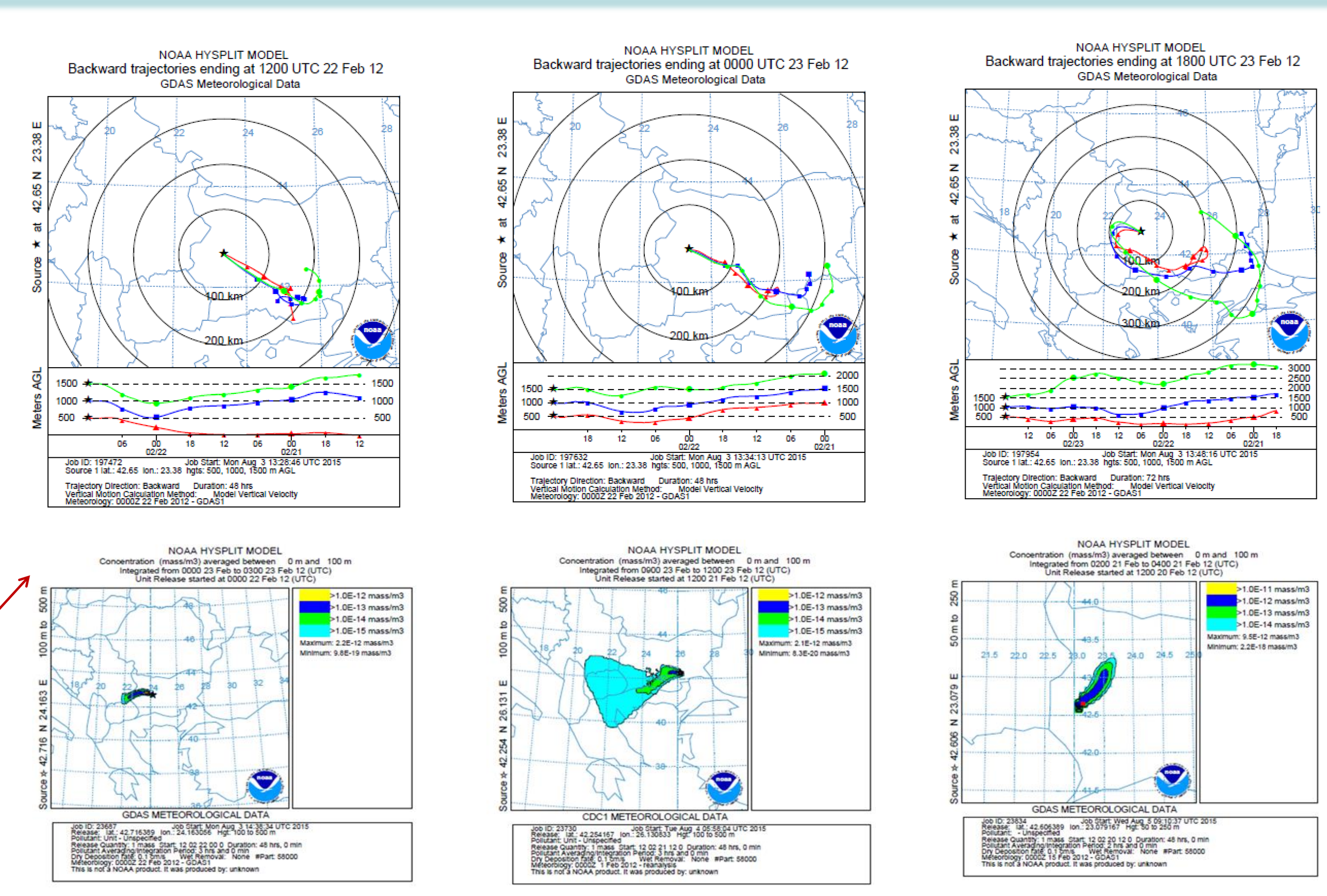
TPP “Nikola Tesla A”

Mining and Smelting Basin Bor

Backward trajectories for 13.02.2012 sources from Serbia could contribute to the elevated S concentration. Dispersion model is run for TPP “Nikola Tesla A” and Mining and Smelting Basin Bor



High S concentration in PM10 during the period 21-23 February 2012 most probably is due to Bulgarian sources (TPP Maritza Iztok, Arubis and TPP Republika, Pernik)



Aurubis - Copper and Copper Recycling

TPP “Maritza Iztok”

TPP “Republika”, Pernik

SUMMARY

The ED-XRF technique was applied to determine more than 20 macro and micro elements in the PM_{10} filter samples in Sofia. 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.

The factors derived by PCA after varimax rotation are 3 to 6 depending of the selection of the set of elements and should be considered as preliminary. More and enlarged data set is needed.

Further work is planned to determine water soluble ions in PM_{10} samples. EDXRF data from next sampling campaigns will be utilized in further source apportionment study.

ACKNOWLEDGEMENTS

European Union

This presentation was supported by the Project BG051PO001-3.3.06-0063 funded by European Operational Program “Human Resources Development”.

European Social Fund

References:

[1] Nat. Rep. of MoEW, (2013) National Report on the State and Protection of The Environment, MoEW, Sofia, http://eea.government.bg/bg/soer/2013 ;

[2] Hristova, E., Veleva, B. (2013) 'Variation of air particulate concentration in Sofia, 2005-2012', Bulgarian J. of Met. and Hydr., Vol. 18, No1-2, pp 47-56.;

[3] 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.