Some Review for Identification of Air Pollution Sources of Ulaanbaatar City Using ED-XRF Analysis

D. Shagjjamba[1], S. Lodoysamba[2], G. Gerelmaa[1], P. Zuzaan[1]

[1]Nuclear Research Center, National University of Mongolia, Ulaanbaatar, Mongolia
[2]School of Applied Science and Engineering of the National University of Mongolia, Ulaanbaatar, Mongolia.

The conventional XRF analysis is wide used and suitable analytical method for various fields, especially environmental studies. Air pollution associated with atmospheric particulate matter (PM) is a serious problem in Ulaanbaatar city, the capital of Mongolia. According to World Bank estimation Ulaanbaatar is one of most polluted city. In this paper, we have done XRF analysis on Air Particulate Matters for determining to identification sources and its contributions which was the first time in Mongolia. Main pollution sources for $PM_{2.5}$ particles of Ulaanbaatar by the result of XRF analysis are soil, combustion and vehicles.

Уламжлалт Рентген-флюоресценцийн шинжилгээ нь төрөл бүрийн салбарт ялангуяа хүрээлэн байгаа орчны судалгаанд өргөн хэрэглэгддэг, тохиромжтой аналитик арга юм. Атмосферийн тоосонцороос (PM) үүдэлтэй агаарын бохирдол бол Монгол улсын нийслэл Улаанбаатар хотын хувьд онцгой асуудал юм. Дэлхийн банкны үнэлгээгээр Улаанбаатар нь дэлхийн хамгийн их бохирдолтой хотын нэг болж байна. Агаарын тоосонцорт хийсэн Рентген-флюоресценцийн шинжилгээний дүнг бохирдлын үүсгүүрүүдийг тогтоож тэдний хувь хэмжээг тодорхойлох Монголд анх удаа хийгдэж буй ажлыг бидний энэхүү өгүүлэлд тусгав. Рентген-флюоресценцийн шинжилгээний дүнгээр хөрс, түлшний шаталт болон тээврийн хэрэгслэл нь Улаанбаатарын PM2.5 тоосонцрын үндсэн үүсгүүрүүд болж байна.

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I. INTRODUCTION

The conventional XRF analysis is wide used and suitable analytical method for various fields, especially environmental studies. In this paper, we have done XRF analysis on Air Particulate Matters for determining to identification sources and its contributions which was the first time in Mongolia**.** Air pollution associated with atmospheric particulate matter (PM) is a serious problem in Ulaanbaatar city, the capital of Mongolia. According to World Bank estimation [2], Ulaanbaatar is one of most polluted city and 90 percent of $PM_{2.5}$ pollution has anthropogenic origin [3]. In this paper presenting the $PM_{2.5}$ pollution source identification based on ED-XRF elemental analysis and study carried out at Nuclear Research Center (NRC) National University of Mongolia (NUM). The five main factors were identified using dataset of contents of 18 elements determined by XRF analysis.

II. EXPERIMENTAL

GENT sampler was used to collect sample of PM in the air , where particles are collected on two filters in series, the top filter (Nuclepore filter, pore size 8 μm) collects the coarse ($PM_{10-2.5}$) particle fraction and the bottom one (Nuclepore filter, pore size 0.4 μm) collects the fine ($PM_{2.5}$) particle fraction. The samples were collected for 24 hours, but in some days particularly in the winter it was not possible to collect the sample over the entire 24 hours because the high particulate matter concentrations lead to filter clogging. Thus, the sampler was operated alternating time on and time off (e.g., 1 h on followed by 1 h off) over the course of the 24 hours period to provide a representative sample for that day. $PM_{2.5}$ and $PM_{10-2.5}$ samples were collected on two day in a week (Monday and Thursday) from 2009 to 2014 at the National University of Mongolia air quality monitoring site 4 kilometers east of the center of Ulaanbaatar (latitude $47^{o}.55^{'}$, longitude $106^{o}.55^{'}$, 1300 m above sea level). Samples were analyzed by the SPECTRO XEPOS ED-XRF Analytical Instruments GmbH (Germany) equipped with a Pd anode X-ray tube operated at maximal values of 50 kV and 2 mA, the target changer with up to 8 polarization and secondary targets, Si-Drift Detector (SDD) spectral resolution (FWHM) at Mn Ka $\leq$ 150 eV with Peltier cooling and automatic system for changing samples. Software package for quantitative and qualitative analysis was used X-LabPro.

Minimum Detection Limit (MDL) has been calculated as following formula and results were shown in Table 1.

$$LOD = \frac{3 * \sqrt{Background} * C_i}{N_i}$$

Where, Ci is concentration of sample (near.LOD), Ni is net pulse count.

Table 1. Minimum Detection Limits for elemental concentration of both $PM_{2.5}$ and $PM_{10-2.5}$ sample

Elements	$PM_{2.5}$, ng/ m^3	$PM_{10-2.5}$, ng/ m^3
Na	497.0	260.0
Mg	290.1	138.9
Al	26.4	50.1
Si	4.0	14.7
P	32.8	27.8
S	5.5	6.0
Cl	7.9	6.9
K	106.5	38.5
Ca	6.2	16.0
Ti	75.5	5.2
V	5.0	1.1
Cr	5.1	19.2
Mn	1.5	63.3
Fe	5.8	10.7
Co	17.1	5.0
Ni	1.9	1.1
Cu	3.6	0.5
Zn	6.5	4.2
Br	5.0	5.0
Pb	9.5	4.7
BC	719.6	401.3
As	2.0	0.6
Ta	91.0	11.5

MDL for the SPECTRO XEPOSED-XRF spectrometer were experimentally found using results of elemental analysis.

Black carbon (BC) concentrations on filters were determined by light reflection using a M43D Digital Smoke Stain Reflectometer. For atmospheric particles, BC is the most highly absorbing component in the visible light spectrum and with small absorption coming from soils, sulfates and nitrate [7,8]. Hence, to the first order it is assumed for the purposes of this study that all the absorption by particles on filters is due to BC. Output from elemental analysis, Factorization method (PMF), identifies a number of "factors" which are defined by their specific and separate element composition, or profile. From this elemental profile, it is often possible to allocate the "factor" to a certain pollution source, based upon knowledge of tracer elements or the elemental composition of the emissions from the source type.

III. RESULTS AND DISCUSSION

Identification of pollution sources and its apportionment was done at the NRC,NUM. A total of 391 pairs of $PM_{2.5}$ and $PM_{10-2.5}$ samples were collected and analyzed. More than 20 elements contents from Na to U such as Na , Mg, Al, Si, P, S,Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Mo, Pb, Th and U were determined in the air particulate samples by the ED-XRF analyses. Analyses of the fine samples are almost the same contents of elements except V and Cr was not identified in the fine particles. In the Table 2 statistical average maximum, minimum., and median contents of elements of 391 $PM_{2.5}$ samples were shown.

Elemental analysis of the air filters were based on the use of MICROMATTER-XRF Calibration Standards. However contents of Th and U are not verified due to unavailability of standards. Higher contents of those elements into the air samples are fitting with results of other studies as high content of U in the soil surrounded Ulaanbaatar area [1], and higher specific activity of Uranium was noted in the studies of coal and coal ash used for Thermal Power Plants and households of Ulaanbaatar city by Gamma-spectrometry measurements [6].

Soil elements as Al, Si, Ca, Ti and Fe are main contribution of both fine and coarse particles samples. For the coarse particles are main contributions of the soil. But for fine particles, main component is Volatile Organic

Table 2.Results of XRF analysis for $PM_{2.5}$ samples and summary statistics at the site NRC of NUM. (ng/m^3). 2009-2014

Species	Average	Max	Min	Median	StdDev	Cnts.
$PM_{2.5}$	79399	699654	2721	58730	71065	389
BC	5957	30503	1003	3827	5067	391
Na	2079	8481	111	1656	1437	391
Mg	930	4794	221	819	580	386

Al	270	2051	27	205	224	391
Si	656	5582	30	502	575	391
P	278	3196	87	191	220	391
S	2908	23801	46	1071	3850	391
Cl	218	1454	30	179	171	391
K	402	3294	30	322	308	391
Ca	717	6886	28	567	622	391
Ti	166	1622	50	140	113	391
Mn	63	589	11	52	42	391
Fe	538	4748	71	435	421	391
Ni	44	367	6	36	34	344
Cu	14	133	5	10	14	296
Zn	46	281	8	33	37	391
Pb	46	558	11	34	54	147

Components but cannot be determined by XRF. Those elements Al, Si, Ca, Ti and Fe not exactly can be soil origin but it can be anthropogenic origin for the $PM_{2.5}$. Elements V, Cr in the coarse particles can be considered as origin of soil. Content of Na is roughly 3 times hight in the coarse particles compared with content of fine particles and it does not depend on the season. Existance of Ni, Cu, Zn, Pb in all samples was observed and presence of Ni ,Cu, Zn into most of samples. Those are mainly origin of vehicles engine, breaks, and tires but they could be from the soil and from waste combustion also.

Receptor modeling is used for identification of pollution sources, at the receptor site and apportionment of the pollution sources was used Positive Matrix Factorization (PMF). PMF analysis is carried out using the PMF2 program [4,5]. The main five factors were identified in the result of dataset of contents of 18 elements determined by XRF analysis. Following pollution sources were identified by the each factor profiles Figure 1. In the Table 3 shows mass contributions of pollution sources of $PM_{2.5}$.

Table 3. Contributions of sources identified by PMF to mass of fine and course aerosol particles (%).

	Sources	**$PM_{2.5}$**	
		Mass	**error**
1	Soil-2	6.52	2.17
2	Soil-1	28.44	3.87
3	Combustion-1	22.71	2.30
4	Combustion-2	32.33	5.72
5	Vehicles	10.01	2.60

Soil-2(factor1): This factor is fugitive dust increasing in last years but is probably more construction and waste origin as it has higher content of Al, Si and Al /Si ratio is not typical as soil. The Al/Si ratio was obtained 0.64.

Soil-1(factor2): This factor contains key elements of Al, Si, Ca, Ti and Fe commonly associated with natural mineral soil fugitive dust of surrounding of the city. It increases spring and autumn and has low concentration in summer and winter. Summer soil has more moisture and covered by grasses resulting less fugitive dust and winter less fugitive dust because of snow cover. The Al/Si ratio was obtained as 0.32.

Combustion: Factor 3 and Factor 4 are combustion origin increasing in winter and have different profiles, namely, combustion -1(Factor-3) has much BC and some soil elements, that volatiles from the short chimney are condensed on the particles from the soil. Combustion-2(Factor-4) is mainly from the high temperature combustion, high content of Sulfur and also low content of soil elements.

Vehicle (Factor 5): This is from auto vehicles, has more BC and trace elements as Cu, Ni, Fe, Zn associated with vehicle combustion, breaks and fugitive dust by vehicles.

This is made by only XRF analysis and it should note that pollution source apportionment result can be different as we do not analyze Volatile organic components and ions.

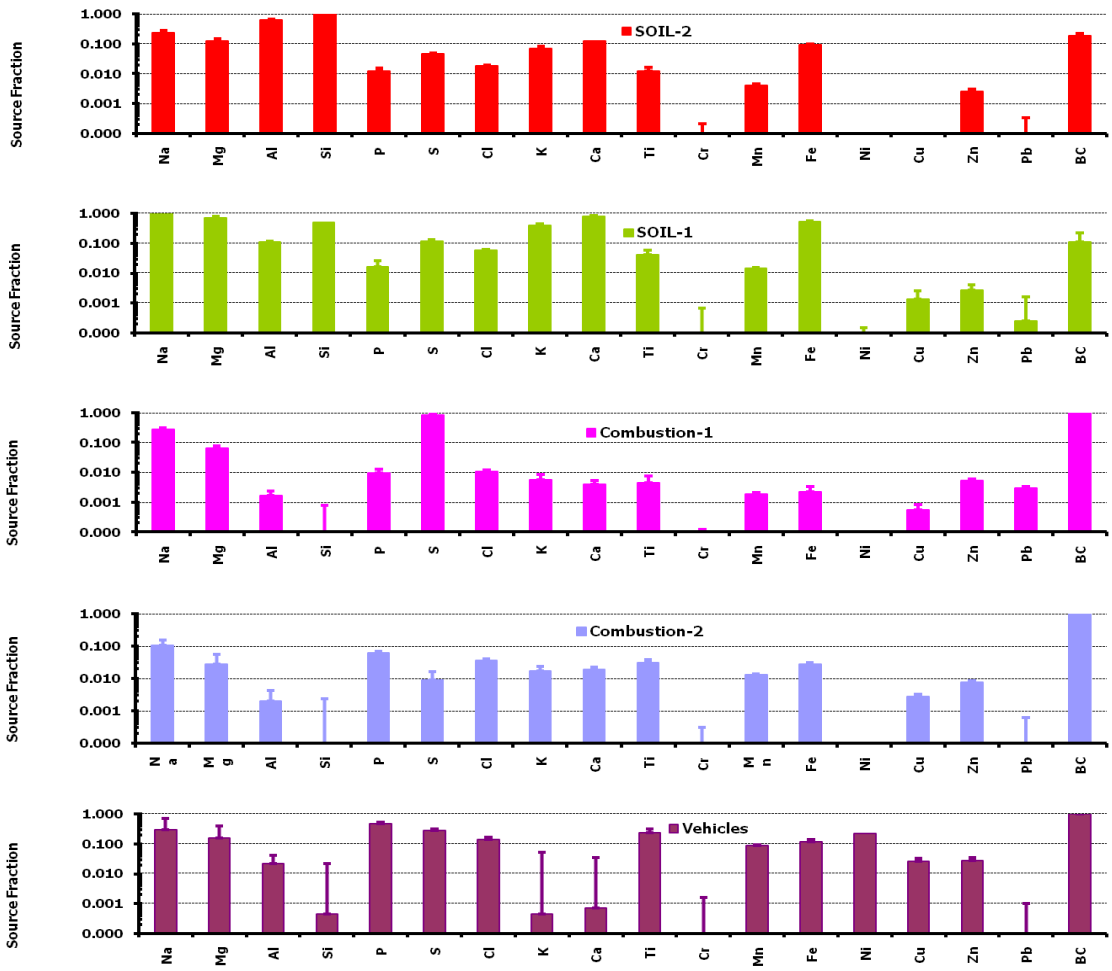

Figure 1: Factor profiles for the resolved factors of fine fraction by PMF

IV. CONCLUSIONS

Main pollution sources for $PM_{2.5}$ particles of Ulaanbaatar by the result of XRF analysis are soil, combustion and vehicles. But detailed pollution source apportionment of Ulaanbaatar city should be combined with organics, ion and other analysis, rather than XRF analysis only.

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