Proceedings of the XI International Conference on PIXE and its Analytical Applications
Puebla, Mexico, May 25-29,2007

Comparison Of Debrecen Fine Fraction Aerosol Data With Others Collected In A European Collaboration

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Abstract. Fine (PM2.5) atmospheric aerosol samples were collected with a two-stage "GENT" SFU sampler. Airborne particulate masses were measured. Elemental concentrations of Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Pb elements were obtained by PIXE method. The black carbon (BC) content of fine aerosol was determined, too. Our data of the time interval from June 2000 to June 2001 were compared with others collected in some western and middle European laboratories. Similarities and differences were found in the regional features, in the yearly average concentrations for silicon and sulphur elemental constituents and PM2.5. Silicon, black carbon and sulphur are considered as main representatives of the crustal material, traffic and long-range background pollution components, respectively.

Keywords: urban aerosol, fine fraction, PM2.5, BC

INTRODUCTION

Recently a number of papers have been published by European groups [1], [2], [3], [4], [5] organized mainly by western and middle European laboratories, in which comparative data have been presented from co-ordinated research programs based on joint evaluation of elemental compositions and reflectance of ambient fine aerosol particles for air qualification in a number of urban sites. Methodical papers [6], [7] serve as a basis for a correct comparability of data measured by separate groups.

In this work, a comparison is given on atmospheric aerosol data collected by European groups and in the Hungarian city, Debrecen, June 2000 to June 2001.

SAMPLING AND ANALYSIS

The sampling was made in Debrecen in the garden of the Institute of Nuclear Research, 1.5 km away from the downtown, at a height of 2 m from the ground.

A GENT-type two-stage stacked filter sampler [8] was used for collecting size fractioned aerosol samples. This sampler operated in the first once and next twice a week at a flow rate of 16 l/min, for 24 hours.

PM2.5 mass concentrations were measured with a Sartorius microbalance. Black carbon data were determined by a smoke stain reflectometer in $\mu g/m^3$ units, contrary to reflectance data given as absorption coefficients in 10^5 units in other papers.

Elemental composition were analysed by proton-induced X ray emission method (PIXE) and the concentrations of Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe Ni, Cu Zn, Br, Ba, and Pb elements were calculated by the computer package PIXYKLM [10]. Details of sampling and analytical technics are given in paper [9].

Results in this work are mainly based on analytical data for PM2.5, BC mass and Si, S elements.

COMPARISON OF DATA

From June 2000 to December 2001, scanned in the co-ordinated program of *Götschi et al* [1] is fully covered by a part of our long-term data set collected in Debrecen. Altogether, data of 63 sampling days were used in our work from June 2000 to June 2001.

Due to the analogy between the observation periods, sampling durations and the similarity of the analytical methods used in paper [1] and our work, we found it plausible to find out how much the air quality characteristics observed at our location fit in the general European trends. With information from our data set the borders of the blank areas on the map of Europe given in [1] can be shifted to the eastward by a

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couple of hundred more kilometres. The importance of such an extension is shown on the one hand by earlier budget calculations of aerosol particles over Hungary [11], which indicate, that Hungary in many cases is a net sink of aerosol arriving with the prevailing north-western wind in the form of interregional transport. On the other hand, the importance of Mediterranean and even Saharan aerosol influence has been also demonstrated in our earlier paper [12].

TABLE 1. List of numbering of the sampling sites and their subdivision into geographic regions taken from paper [1]. Hungary, Debrecen site is referred as site 22.

Region	No	Site
West And Central Europe	1	Antwerp South
	2	Antwerp City
	3	Paris
	4	Erfurt
	5	Basel
Spain	6	Barcelona
	7	Caldakao
	8	Albacete
	9	Oviedo
	10	Huelva
Alpine France	11	Grenoble
Northern Italy	12	Pavia
	13	Turin
	14	Verona
England	15	Ipswich
	16	Norwich
Scandinavia	17	Reykjavik
	18	Gothenburg
	19	Umea
	20	Uppsala
Estonia	21	Tartu
Hungary	**22**	**Debrecen**

In the following presentation the comparison of our data with those from [1] in *Table 2* and the discussion of the results will be facilitated by using the numbering and assignment of the sites to selected geographic regions following the scheme in *Table 1* which shows the sites of the European collaboration named above. Hungary, Debrecen is referred as site 22.

In *Table 2,* the fine fraction PM2.5 and elemental concentrations are presented together with BC in the following groups

- Yearly mean PM2.5 mass and elemental concentration data were averaged for 21 European sites based on the paper [1]
- The same sort of Debrecen data averaged for the annual (01.06.00-31.05.01), winter (01.12.00-28.02.01), summer (01.06.00-31.08.00) periods. The durations of the above periods are the same as in [1]
- Debrecen <Winter>/<Summer> concentrations ratios
- Seasonal variations in average monthly concentration data in Debrecen for the above defined year.

RESULTS AND DISCUSSION

Many-sided effects of geographical environment, atmospheric chemistry, meteorology and methodology at the different locations of the sampling sites play an important role in the variation of the measured total mass concentration, optical characteristics, size distribution and absolute elemental concentrations of the regional constituents of the aerosol. The influence of time and local variation in the profiles and emission rates of the natural and anthropogenic sources are of primary importance in determining air quality and its environmental effects.

The seasonal variation of the elemental concentrations and their behavior in building up the regional aerosol profiles are influenced by actual conditions for the separate seasonal effects and site locations pertinent both to natural and anthropogenic sources in different parts of a year. Variation of meteorological parameters and their consequences on the snow-covered and frozen area of the soil surfaces during winter and increased soil erosion in warm and dry periods are strongly dependent on the geographical location of the observation sites. Furthermore, the role of air mass transport processes is determining both on interregional and global scales. As for anthropogenic seasonal influences, the winter aerosol load is increased by extensive heating with various fuels, salt and sand spreading on the greasy roads, and the resuspension of road dust caused by traffic. Another periodicity appears with the increased agricultural activities and forest burning in the summer periods. Therefore the separate deduction of data aiming at the determination winter/summer average ratios, even distributions of monthly average concentration are of special importance.

The regional subdivision of the European sampling sites shown in *Table 1* aims at finding similarities in the aerosol characteristics typical for regions of similar conditions in emission sources, geographic surface structure, and meteorological behavior. For a first orientation about the existence of similarities and differences within and among the regional features, respectively, yearly average concentrations are presented in *Figure 1* for silicon, and sulfur elemental constituents and PM2.5 mass concentrations for sites 1-22. Silicon, black carbon, and sulfur are considered as main representatives of the crustal material, traffic and long-range background pollution components, respectively, while PM2.5 is a parameter accepted for measuring overall air quality from the point of view of human health conditions in a site. For a qualitative evaluation of air conditions in Debrecen site named as 22, yearly values for sites 1-21 are shown with respective columns augmented with Debrecen value shown as columns in site 22. The straight lines denoted as <1-21> represent yearly average data given

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TABLE 2. Debrecen data on PM2.5, fine fraction BC and elemental concentrations averaged for annual (01.06.00-31.05.01), monthly, winter (01.12.00-28.02.01), summer (01.06.00-31.08.00) periods compared with yearly average data taken by Götschi et al [1] over European sites listed in Table 1.

Average Data	No. of sample	PM2.5 μg/m^3	BC μg/m^3	Al ng/m^3	Si ng/m^3	S ng/m^3	Cl ng/m^3	K ng/m^3	Ca ng/m^3	Ti ng/m^3	Mn ng/m^3	Fe ng/m^3	Cu ng/m^3	Zn ng/m^3	Br ng/m^3	Pb ng/m^3
21 EU Sites Data [1]																
Yearly (01.06.00-31.05.01)	84	19.1		216.5	501.5	1172	701.8	240.6	115.3	5.8	7.0	99.8	10.1	50.9	6.1	24.4
Present Data																
Yearly (01.06.00-31.05.01)	63	18.2	3.0	137.4	215.2	1071	21.08	218.2	78.6	5.4	4.6	114.5	6.2	20.4	6.1	21.1
Winter (01.12.00-28.02.01)	22	21.4	4.4	153.7	154.2	1083	22.5	298.1	51.1	2.9	5.1	91.3	8.9	28.5	8.6	31.6
Summer (01.06.00-31.08.00)	12	15.1	1.9	105.6	225.0	1203	17.9	127.3	78.6	6.5	3.1	111.0	3.6	13.6	2.3	13.0
<Winter>/<Summer>		*1.4*	*2.3*	*1.5*	*0.7*	*0.9*	*1.3*	*2.3*	*0.7*	*0.5*	*1.7*	*0.8*	*2.5*	*2.1*	*3.7*	*2.4*
Monthly distribution																
June 00	4	16.2	1.7	104.7	216.6	1289	19.3	98.9	76.8	5.8	3.9	109.1	4.7	16.5	2.6	15.2
July 00	3	13.9	2.1	92.1	197.2	914	14.5	106.7	66.3	7.4	3.3	104.5	3.0	11.9	1.9	11.5
August 00	4	14.9	2.0	116.8	254.2	1124	19.2	171.1	89.6	6.6	3.9	118.2	2.8	12.1		12.1
September 00	4	16.5	2.2	115.3	132	905	17.1	136.4	41.7	3.3	3.3	83.5	4.4	16.3	2.8	9.1
October 00	3	28.8	4.4	260.2	457.2	1536	35.8	516.0	168.8	11.3	7.1	210.0	6.5	20.8	4.7	37.0
November 00	4	26.2	6.7	180.6	182.8	983	22,0	260.5	79.5	4.4	5.6	116.9	3.7	25.9	9.3	24.7
December 00	3	17.4	3.6	125.3	125.3	812	19.8	289.7	31.7	1.3	6.2	77.6	23.2	26.6	8.3	25.0
January 01	7	26.1	4.3	173.9	173.9	1370	27.5	411.2	34.0	2.8	4.5	85.3	4.9	38.4	9.5	62.3
February 01	8	15.7	3.0	134.8	134.8	898	20.9	230.8	59.5	3.0	3.9	85.3	4.0	23.1	7.3	14.2
March 01	8	14.1	2.5	125.3	125.3	970	17.6	156.5	59.5	3.4	4.2	97.6	5.1	21.2	6.7	20.2
April 01	7	14.3	2.0	129.8	187.5	999	18.2	120.8	81.6	5.1	4.5	104.1	7.3	18.6	7.4	13.3
May 01	8	14.3	1.5	89.8	396.0	1054		119.8	154.0	10.7	4.9	180.1	4.6	12.8		8.8

for all sites in [1]. It is clearly seen from the figure, that yearly average silicon concentration here is much below the European average, nearly equaling with English and Scandinavian levels, in contrast to elevated values is Spain and Northern Italy. The local levels of sulfur are more uniformly distributed over the part of Europe considered, with local peaks at Spain and Northern Italy again. The Hungarian average value remains however below the <1-21> European average. <PM2.5> exhibits high values in Northern Italy and well expressed lowering at Scandinavian location. Our result remains near the European average.

In *Figure 2a*, following the presentation in [1] of seasonal variations in other European sites, shown are Debrecen monthly average elemental concentrations of sulfur and silicon denoted with *, relative to yearly average <> values of the respective elements, as well as similar BC ratios for the period June 2000 – May 2001. All three curves shown are multiplied by the absolute value of yearly average <PM2.5> in Debrecen. Such a presentation gives an absolute scale of <PM2.5> in showing the seasonal variation of the respective constituents. Because of the abrupt month-to-month fluctuation between neighboring maxima and minima appearing on the curves, mainly due to the poor statistic, we added in *Figure 2b* similar curves obtained from our respective data set averaged over a ten years period. In 2 (b) curves we received well expressed winter maxima for S and BC, while a winter minimum can be observed on the Si curve. These behaviors are in full accordance with the expectations outlined above.

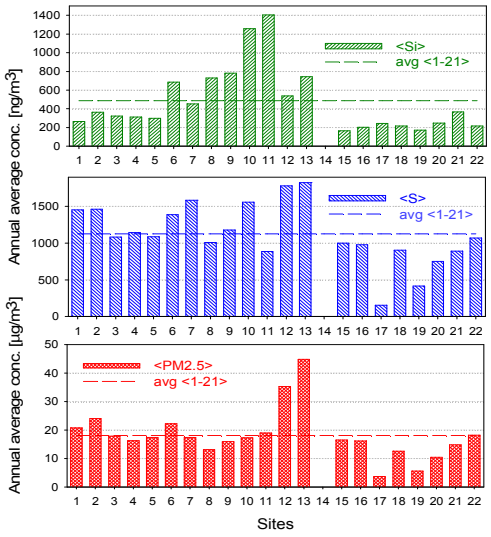

Figure 1. Yearly average elemental concentrations of Si, PM2.5 and S in sampling sites defined in Table 1, for the period June 2000-June 2001.

The concentrations of sulfur as well as their seasonal variation show considerable spread over Europe. Sulfur represents an intensive contribution to the PM2.5 in most sites. As shown in Table 2, yearly average values <S> and <PM2.5> amount to 1071 ng/m^3 and 18.2 μg/m^3 in Debrecen, respectively. The strong correlation of PM2.5 mass concentration and sulfur found in 21 European sampling sites is also

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present in the Debrecen measurements. The value of the Pearson correlation coefficient calculated for the pairs of yearly average values and found to be 0.8402 shows a slight decrease to 0.8393 only when the respective Debrecen data are added to data from the other sites considered.

As indicated in the paper [1] in most observation sites within cities located close to roads of intense traffic the concentration of sulfur is strongly correlated with PM2.5 values. Under such conditions PM2.5 concentrations can be considered as highly over-sampled with respect to average exposure of inhabitants in the city. In our site located in a green area in a distance over 100 meter from a street of moderate traffic the seasonal trend of the time series of PM2.5 and S still show up close similarities. The Pearson correlation coefficient calculated over a whole year period amounts to 0.633. As for the maximum concentrations appearing on both curves over the same period, they are located between October and February as shown in the monthly distribution data of Table 2.

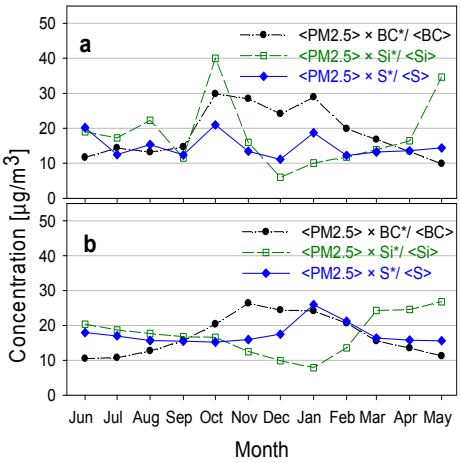

Figure 2. Monthly average elemental concentrations of sulfur and silicon denoted with *, relative to yearly average <> values of the respective elements, as well as similar BC ratios, in Debrecen site. All three curves are shown multiplied by the value of yearly average <PM2.5> here as in paper [1]. In (a) and (b) part data are averaged for the periods June 2000 – June 2001 and 1997-2007, respectively.

As for the long-term variations in levels of aerosol pollutants in the regional areas of the atmosphere around sampling sites in the named collaboration, paper [1] gave a hint on possible effects of the reorganization of economy going on in former socialist countries in the last two decades. The most characteristic feature of these processes is a general recession hitting energy intensive heavy-industry sectors, which led to a positive effect of gradually improving energy-intensities of the countries. From the sites active in the collaboration air quality in Erfurt (located in the territory of former German Democratic Republic) may have been influenced. Similar effects appear in Hungary, as well. It should be mentioned, however, that air quality since 1990 has further been improved here by building up a network of electrostatic aerosol filters and desulfuration plants on flue gas channels of existing fossil fuel based power stations in Hungary.

ACKNOWLEDGMENTS

This work was supported by the National Research and Development Program (NRDP 3A/089/2004) and the Hungarian National Research Foundation (OTKA F603777).

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