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Chemical composition, impact from biomass burning, and mass closure for PM(2.5) and PM(10) aerosols at Hyytiälä, Finland, in

Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

Original Citation:

Chemical composition, impact from biomass burning, and mass closure for PM(2.5) and PM(10) aerosols at Hyytiälä, Finland, in summer 2007 / W. Maenhaut; S. Nava; F. Lucarelli; W. Wang; X. Chi; M. Kulmala. - In: X-RAY SPECTROMETRY. - ISSN 0049-8246. - STAMPA. - 40:(2011), pp. 168-171. [10.1002/xrs.1302]

Availability:

This version is available at: 2158/495659 since: 2017-10-16T17:40:18Z

Published version:

DOI: 10.1002/xrs.1302

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Chemical composition, impact from biomass burning, and mass closure for PM_{2.5} and PM₁₀ aerosols at Hyytiälä, Finland, in summer 2007

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A comprehensive chemical aerosol characterisation was carried out at the forested site of Hyytiälä, Finland, from 2 to 30 August 2007. PM_{2.5} and PM₁₀ Nuclepore polycarbonate and quartz fibre filter samples were taken in parallel, typically for separate day-time and night-time periods. All samples were analysed for the particulate mass by weighing. The Nuclepore filters were analysed for over 20 elements by particle-induced X-ray emission (PIXE) spectrometry and for major anions and cations by ion chromatography. The quartz fibre filters were analysed for organic and elemental carbon by a thermal-optical transmission technique. A number of samples exhibited high K, Zn, and oxalate levels, indicating an impact from biomass burning. A noteworthy episode occurred on 12–13 August, when air masses were advected from the southern part of European Russia where extensive biomass burning had occurred. In the aerosol chemical mass closure calculations, eight aerosol types were considered. Organic matter (OM) contributed by far the most to the PM_{2.5} and PM₁₀ mass; it accounted for about 70% of the average PM_{2.5} and PM₁₀ mass and 48% of the coarse (PM_{10–2.5}) aerosol. Crustal matter, deduced from the PIXE data, provided a rather small contribution; only 3% in PM_{2.5}, 13% in PM₁₀, and 32% in the coarse aerosol. The mean PM_{2.5} and PM₁₀ mass concentrations and their attribution to the eight aerosol types for the 2007 campaign at Hyytiälä were similar to those for the cold period of a 2006 summer campaign at the forested site of K-pusztá, Hungary. OM was more important and nitrate was clearly less important at Hyytiälä, though. Copyright © 2011 John Wiley & Sons, Ltd.

Introduction

Within the EU-funded project European Supersites for Atmospheric Aerosol Research (EUSAAR)^[1] 20 high-quality ground-based stations are available. The stations were identified based on the high level of implemented instrumentation for the study of atmospheric aerosols (chemical, physical, and optical properties) and on their atmospheric probing capacity in an identified environment. One of the 20 stations is the Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II) in Hyytiälä, Finland. This station is a boreal coniferous forest station and is a good site for studying the formation and characteristics of biogenic secondary organic aerosol (SOA) that is formed from biogenic volatile organic compounds, such as isoprene and monoterpenes, that are emitted by the forest.^[2,3] It was therefore selected as a field study site for a 2007 summer campaign within the Belgian-funded project ‘Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols’ (BIOSOL). Although the emphasis in the campaign was thus on the organic aerosol, and in particular on biogenic SOA, it was felt that a complete chemical aerosol characterisation (including measurement of inorganic compounds, elements, and aerosol types) was also needed in order to be able to interpret the organic aerosol data. This article focuses on the elemental composition of the aerosol and on the aerosol chemical mass closure. Similar studies as presented here were performed at the forested EUSAAR station of K-pusztá, Hungary, during 2003 and 2006 summer campaigns.^[4] Therefore, the results of the 2007 campaign at SMEAR II are compared with those from the campaigns at K-pusztá.

Experimental

The SMEAR II station is located at 61°51′N, 24°17′E, 181 m above sea level. The largest city near the station is Tampere, ca 60 km S-SW of the measurement site. A detailed description of the SMEAR II station is given in Ref [5]. The aerosol samplings during our 2007 summer campaign took place from 2 to 30 August. Overall, the weather was nice during this period. The mean daily temperature rose from 15 °C on 2 August to around 20 °C in the period of 6–13 August and decreased to 6.5 °C on 30 August, with a secondary maximum of 17 °C on 22–24 August.

Several filter samplers were deployed in parallel, typically for separate day and night collections, and a total of 51 parallel collections were made. Among the samplers were two PM_{2.5} samplers [one (PM_{2.5}N) with a 0.4-µm pore-size Nuclepore polycarbonate filter, the other (PM_{2.5}Q) with two pre-fired Whatman QM-A quartz fibre filters in series] and two PM₁₀ samplers [(PM₁₀N) and (PM₁₀Q) with the same filter types as the PM_{2.5} samplers]. All filters in these four samplers had a diameter of 47 mm, and the four samplers operated at a flow rate of 17 l/min.

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Besides these low-volume filter samplers, also a high-volume dichotomous sampler (HVDS)^[6] was used; this device provided two size fractions [fine, <2.5 µm aerodynamic diameter (AD) and coarse, >2.5 µm AD] and pre-fired double Gelman Pall quartz fibre filters were used for each of the two size fractions. The purpose of the second (back) quartz fibre filter in the low-volume samplers and the HVDS was to assess artefacts (i.e. adsorption of volatile organic compounds and losses of semi-volatile organic compounds) in the collection of carbonaceous aerosols.^[7,8]

All low-volume filters were weighed with a microbalance to obtain the particulate mass (PM). The weighings were done at 20 °C and 50% relative humidity and the filters were pre-equilibrated at these conditions for at least 24 h. All quartz fibre filters were analysed for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission (TOT) technique.^[9] Particulate OC data were obtained as the difference between the OC on the front and back quartz fibre filters.^[10] The Nuclepore filters were analysed for over 20 elements (from Na to Pb) by particle-induced X-ray emission (PIXE) spectrometry,^[11] and for major inorganic anionic and cationic species by ion chromatography (IC).^[12] The fine size fraction filters of the HVDS samples were analysed for organic anionic species by IC as described in Ref [13].

Results and Discussion

Median concentrations

Table 1 presents the median concentrations and interquartile ranges in PM_{2.5} and PM₁₀ for the PM, several aerosol species, and 17 elements during the 2007 sampling campaign at Hyytiälä. When comparing the PM₁₀ data from SMEAR II with those from the campaigns at K-pusztá,^[4] it appears that the levels for the crustal elements (Al, Si, Ti, and Fe) are similar to those during the cold period of the 2006 campaign at K-pusztá, but substantially lower than in the warm period of this campaign or in the 2003 campaign at this site (it was continuously hot and dry during the latter campaign). The same is noted for S, the PM, OC, ammonium, and sulphate. For P, which has mineral aerosols, primary biogenic particles, and combustion as important sources on the global scale,^[14] and for Cu, Pb, and nitrate, which are anthropogenic elements and species, lower concentrations are noted at SMEAR II than at K-pusztá. In contrast, for Zn, also typically from anthropogenic sources, larger levels are seen at SMEAR II; this element is further discussed below. For the seasalt element Na, somewhat higher levels are noted at SMEAR II than at K-pusztá.

It further appears from Table 1 that most of the PM₁₀ mass is present in the PM_{2.5} size fraction for the PM and several species and elements. For nitrate, Na, Mg, Al, Si, P, Cl, K, Ca, Ti, Mn, and Fe, however, less than half of the PM₁₀ mass is in the PM_{2.5} size fraction. These findings show great resemblance to those obtained in the K-pusztá campaigns.^[4]

Time series for selected species and impact from biomass burning

Figure 1 shows the time series for the PM, OC, oxalate, K, and Zn (all in PM_{2.5}) during the 2007 summer campaign at SMEAR II. It is clear that the time series for K substantially differs from that for the PM and OC. The time series for Zn shows good resemblance to that of K and also oxalate has a tendency to be elevated in the samples where K is high. Fine K, Zn, and

Table 1. Medians (and interquartile ranges) of the PM_{2.5} and PM₁₀ mass concentrations for the PM, several aerosol species, and 17 elements for the 2007 summer campaign (2–30 August) at Hyytiälä, Finland

Species	PM _{2.5}		PM ₁₀	
	Median	25–75%	Median	25–75%
PM(N) ^a	7200	4300–9100	10 200	7300–12 400
PM(Q) ^a	8900	6500–12 900	14 700	9100–17 300
OC(Q)	2800	1590–3900	3400	2100–4700
EC(Q)	72	34–107	49	12.4–104
NH ₄ ⁺	580	360–920	570	350–790
NO ₃ ⁻	37	13.1–95	187	92–480
SO ₄ ²⁻	1520	910–2300	1690	1070–2500
Na ^b	49	33–85	116	57–270
Mg	2.0	DL-5.1	25	12.4–39
Al	15.6	5.6–25	81	40–135
Si	28	14.4–48	210	114–340
P	2.0	DL-4.0	9.3	5.5–13.4
S	580	350–870	590	360–880
Cl	2.4	0.62–10.2	5.5	2.7–44
K	45	25–68	90	59–127
Ca	10.9	6.2–16.6	50	33–100
Ti	0.92	DL-2.8	5.7	2.4–8.4
Mn	0.52	0.11–1.04	2.0	1.22–2.9
Fe	17.1	9.4–25	67	46–98
Ni	0.50	0.35–0.71	0.44	0.28–0.61
Cu	0.34	0.15–0.55	0.67	0.38–0.99
Zn	6.0	3.5–9.0	6.7	2.8–10.3
Br	2.0	1.49–2.4	2.1	1.47–2.6
Pb	1.59	0.73–2.8	1.45	0.65–3.0

DL, detection limit; IC, ion chromatography; PM, particulate mass.

^a PM(N) stands for PM data, derived from the PM_{2.5}N and PM₁₀N samplers, and PM(Q) for PM data, derived from the PM_{2.5}Q and PM₁₀Q samplers.

^b The data for Na, Mg, and Cl were obtained from IC, those for the other 14 elements from PIXE.

oxalate are all indicators for biomass burning.^[15–17] Particularly striking is that there are three samples in a row (i.e. the day-time samples of 12 and 13 August and the night-time sample of 12 August) that exhibit high K, Zn, and oxalate levels. Inspection of the 5-day, three-dimensional air mass back trajectories, calculated with Hysplit^[18] for every 6 h of the campaign and for an arrival level of 100 m above ground at SMEAR II, indicated that the air masses, which arrived on 13 and 14 August, came from the south and had passed over the southern part of European Russia. Furthermore, the MODIS fire maps (obtained from the University of Maryland^[19]) and the Navy Aerosol Analysis and Prediction System surface smoke concentration data (obtained from the NRL/Monterey Aerosol Page^[20]) both indicated that there was extensive biomass burning in that part of Russia on 11 August. Considering the air mass transport, this biomass burning very likely affected our measurements at SMEAR II.

Consistent with the attribution of fine K in the three samples in a row to biomass burning was that it was fully water soluble as could be concluded from the excellent agreement between the PIXE and IC data for fine K in these samples; in the remaining samples typically only about 50% of the PM_{2.5} K was water soluble. Furthermore, the PM_{2.5}/PM₁₀ ratio for K in the three samples was around 0.8, whereas in the other samples the ratio was typically

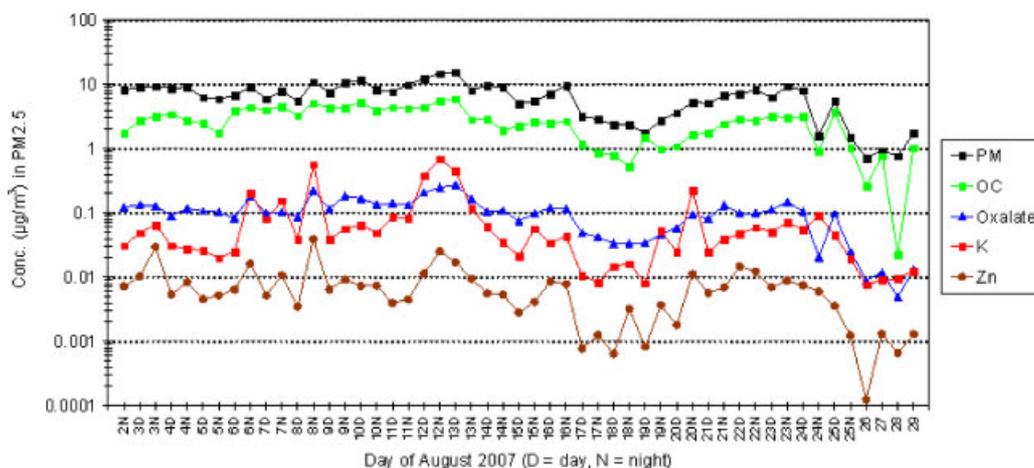


Figure 1. Time series for the PM, OC, oxalate, K, and Zn (all in PM_{2.5}) during the 2007 summer campaign at Hyytiälä, Finland.

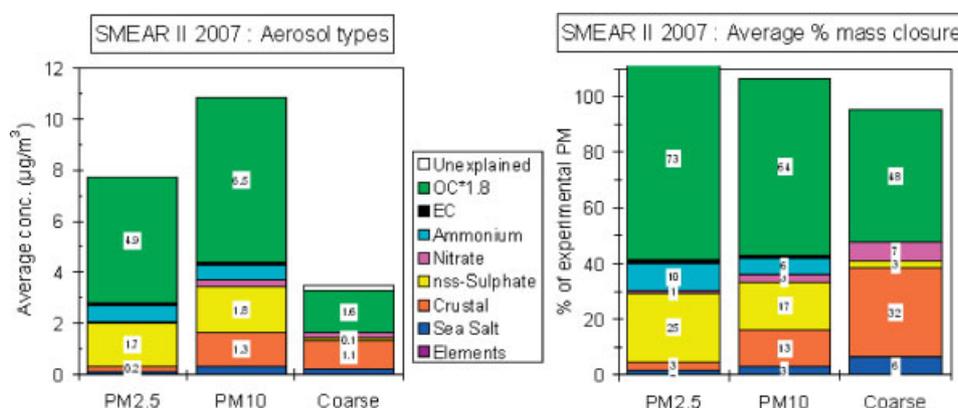


Figure 2. Average concentrations of eight aerosol types and of the unexplained gravimetric PM (left part) and percentage contributions of the various components to the average gravimetric PM (right part) for the 2007 summer campaign at SMEAR II, and this separately for the PM_{2.5}, PM₁₀, and coarse (PM_{10-2.5}) aerosol. The average concentrations of three aerosol types [i.e. organic matter (OC × 1.8), nss-sulphate, and crustal matter] and the percentage contributions of six components are also given in numeric form.

only around 0.5. This emphasises the large impact from fine biomass burning K, which was presumably present as KCl in those three samples.

Aerosol chemical mass closure

Aerosol chemical mass closure calculations were done for the PM_{2.5} and PM₁₀ aerosol, and also for the coarse (PM_{10-2.5}) size fraction, and this for each individual sampling. As gravimetric PM data we used the data from the Nuclepore polycarbonate filters. For reconstituting this PM, eight aerosol types (or components) were considered, i.e. (1) organic aerosol (or organic matter, OM), which was estimated as 1.8 OC (the same OC-to-OM conversion factor of 1.8 was used in the K-pusztá summer campaigns^[4]), (2) EC, (3) ammonium, (4) nitrate, (5) non-seasalt (nss) sulphate, (6) seasalt, estimated as Cl + 1.4486 Na, whereby 1.4486 is the ratio of the concentration of all elements except Cl in sea water to the Na concentration in sea water (with Na and Cl obtained from IC), (7) crustal matter, derived from five elements measured by PIXE (i.e. Al, Si, Ca, Ti, and Fe), and (8) elements, which is the sum of the mass of all non-crustal/non-seasalt elements measured by PIXE (S and K were excluded from this sum).^[21] The average concentrations of the various aerosol types (and of the unexplained gravimetric PM) are shown in the left part of Fig. 2, whereas the right part

of the figure shows the percentage contributions of the various components to the average gravimetric PM. OM contributes by far the most to the PM_{2.5} and PM₁₀ mass; it is responsible for about 70% of the average PM_{2.5} and PM₁₀ mass and 48% of the coarse aerosol. Crustal matter provides a rather small contribution to the PM; it accounts for only 3% in PM_{2.5}, 13% in PM₁₀, and 32% in the coarse size fraction.

The percentage contributions of the various components to the average gravimetric PM_{2.5} and PM₁₀ mass for the 2007 campaign at SMEAR II are compared to the data obtained for the 2003 and 2006 campaigns at K-pusztá^[4] in Table 2. For the 2006 campaign at K-pusztá, separate averages are given for the cold and warm periods. The mean PM data and associated standard deviations are also included in Table 2. It appears that the mean PM mass data for the 2007 Hyytiälä campaign are quite similar to those for the cold period of the 2006 campaign at K-pusztá. Also the percentage contributions are similar for most components. The main differences are noted for OM, which is about 1.5 times more important at Hyytiälä than for the cold period of the 2006 campaign at K-pusztá, and for nitrate, which is ten and three times less important in PM_{2.5} and PM₁₀, respectively, at Hyytiälä. Incidentally, the meteorological conditions were rather similar in the 2007 campaign at Hyytiälä and in the cold period of the 2006 campaign at K-pusztá; for example, when excluding the last 2 days,

Table 2. Percentage attribution of the mean gravimetric PM_{2.5} and PM₁₀ mass to eight aerosol types (components)

Component	PM _{2.5} K-pusztá, 2006 summer, cold period	PM _{2.5} K-pusztá, 2006 summer, warm period	PM _{2.5} Hyttiälä, 2007 summer	PM ₁₀ K-pusztá, 2006 summer, cold period	PM ₁₀ K-pusztá, 2006 summer, warm period	PM ₁₀ K-pusztá, 2003 summer campaign	PM ₁₀ Hyttiälä, 2007 summer
Organic matter	49	45	73	48	40	45	64
Elemental carbon	3.3	2.3	1.2	2.7	1.8	0.6	0.6
Ammonium	13	9.5	9.7	8.3	5.6	7.9	5.9
Nitrate	9.9	2.1	0.9	10	3.0	3.5	2.9
nss-Sulphate	24	22	25	17	15	17	17
Seasalt	2.0	0.4	1.5	2.2	0.4	0.9	3.1
Crustal matter	3.1	17	3.2	10	28	25	13
Other elements	0.2	0.2	0.2	0.2	0.2	0.2	0.1
Sum	104	98	114	99	94	99	107
PM mean ± SD (µg/m ³)	7.7 ± 2.8	17.9 ± 6.1	6.8 ± 3.5	11.3 ± 3.4	26 ± 10	23 ± 6	10.2 ± 5.1

Comparison of the attributions for the 2007 summer campaign at Hyttiälä, Finland, with those for the 2003 and 2006 summer campaigns at K-pusztá, Hungary. Separate data are given for the cold and warm periods of the 2006 summer campaign at K-pusztá. The average PM data and associated standard deviations (SD) for each campaign are also included.

the daily maximum temperatures ranged from 15 to 27 °C in the Hyttiälä campaign, whereas they ranged from 12 to 23 °C in the cold period of the 2006 campaign at K-pusztá.

Conclusions

It may be concluded that the Hyttiälä site is like the K-pusztá site, a good site for studying biogenic aerosols in summer. It is very little influenced by anthropogenic activities. It exhibited lower levels of typical anthropogenic indicators, such as nitrate and EC, than K-pusztá, and OM made up for about 70% of the average PM_{2.5} and PM₁₀ mass and even for 48% of the coarse aerosol. Nonetheless, long-range transport of anthropogenic aerosols may occur and the impact of this should be taken into account. During our 2007 campaign there was clearly an episode of long-range transport of biomass burning aerosols from the southern part of European Russia. This led to increased levels of fine K, Zn, and oxalate. It is quite likely that the composition of the OM was substantially affected by pyrogenic organic compounds in the three samples, which were clearly impacted by biomass burning. This should be considered when interpreting the organic speciation data.

Acknowledgements

We gratefully acknowledge the financial support from the Belgian Federal Science Policy Office (contract no. SD/AT/02B), the Fonds voor Wetenschappelijk Onderzoek-Vlaanderen, the Special Research Fund of Ghent University, and the EU projects ACCENT and EUSAAR. We are indebted to several members of the team from the University of Helsinki for assistance in the field campaign and for providing meteorological and atmospheric trace gas data. We are also indebted to Jan Cafmeyer and Sheila Dunphy from Ghent University for their technical assistance.

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