Chemical characterization and multivariate analysis of atmospheric PM$_{2.5}$ particles

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Abstract The new European Council Directive (PE-CONS 3696/07) frames the inhalable (PM$_{10}$) and fine particles (PM$_{2.5}$) on priority to chemically characterize these fractions in order to understand their possible relation with health effects. Considering this, PM$_{2.5}$ was collected during four different seasons to evaluate the relative abundance of bulk elements (Cl, S, Si, Al, Br, Cu, Fe, Ti, Ca, K, Pb, Zn, Ni, Mn, Cr and V) and water soluble ions (F$^-$, Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, Ca^{2+} and Mg^{2+}) over Menen, a Belgian city near the French border. The air quality over Menen is influenced by industrialized regions on both sides of the border. The most abundant ionic species were NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$, and they showed distinct seasonal variation. The elevated levels of NO$_3^-$ during spring and summer were found to be related to the larger availability of the NO$_x$ precursor. The various elemental species analyzed were distinguished into crustal and anthropogenic source categories. The dominating elements were S and Cl in the PM$_{2.5}$ particles. The anthropogenic fraction (e.g. Zn, Pb, and Cu) shows a more scattered abundance. Furthermore, the ions and elemental data were also processed using principal component analysis and cluster analysis to identify their sources and chemistry. These approach identifies anthropogenic (traffic and industrial) emissions as a major source for fine particles. The variations in the natural/anthropogenic fractions of PM$_{2.5}$ were also found to be a function of meteorological conditions as well as of long-range transport of air masses from the industrialized regions of the continent.

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1 Introduction

The air quality in urban areas is of great concern nowadays; especially the connection between air pollution and human health has recently received increasing attention. Data on daily mortality show that, on a global scale, 4% to 8% of premature deaths may occur due to the exposure of suspended particulate matter (SPM) and especially of fine particles (PM$_{2.5}$) in the ambient and indoor environment (Ravindra et al. 2001; Kaushik et al. 2006; Pope and Dockery 2006). The studies of the size distribution of metals show that most of the toxic metals accumulate in the smallest particles (Fernandez et al. 2001; Wojas and Almquist 2007). This fraction predominantly deposits in the alveolar region of the lungs, where the adsorption efficiency for trace elements varies from 60–80% (Pope and Dockery 2006). These consequences demand to give priority to the chemical characterization of the fine and ultra fine (PM$_{0.1}$) fraction of airborne particles to understand their possible implication to health effects (Almeida et al. 2007; Kumar et al. 2008; Maenhaut 2008). Furthermore, these particles also play a significant role in global climate change and can be transported over long distances by prevailing winds (IPCC 2006).

However, several studies have investigated the sources and chemical composition of inhalable (PM$_{10}$) particles, e.g. Pakkanen et al. 2001; Querol et al. 2002; Ravindra et al. 2006; Jones and Harrison 2006; Ragosta et al. 2006, Harrison et al. 2008; but relatively few studies have made efforts to identify and chemically characterize the PM$_{2.5}$ particles in Europe (e.g. Putaud et al. 2004; Ariola et al. 2006, Qureshi et al. 2006; Viana et al. 2007; Kocak et al. 2007; Almeida et al. 2006a, 2008; Glavas et al. 2008) and across the world (e.g. Dutkiewicz et al. 2006; Zhang et al. 2007; Wojas and Almquist 2007). These studies also make use of various multivariate techniques such as principal component analysis (PCA), enrichment factors (EF), chemical mass balance (CMB), positive matrix factors (PMF) to understand the chemistry of PM$_{2.5}$ and to identify their origin/sources (Almeida et al. 2006a, b; Moreno et al. 2006; Rizzo and Scheff 2007; Lee et al. 2008). Some studies also investigate the influence of meteorological parameters and transboundary movement of air masses on PM$_{2.5}$ mass and chemical composition and reported a significant relation among them (Kocak et al. 2007; Ravindra et al. 2008a, b; Glavas et al. 2008).

In order to evaluate cross-border air pollution at the border of Belgium and France, an INTERREG project ('Interregional co-operation programme', supported by the European Community), called 'Exposition des Populations vivants au cœur de l'Euro-Région aux polluants atmosphériques: le cas des Poussières Fines' (EXPER/PF—Exposure of populations living in the heart of the Euro-region to atmospheric pollutants: the case of fine dust) has been organized in 2003. The Euro-region was defined by Nord-Pas-de-Calais for France and the province of West-Flanders for Belgium. The large industrial areas in the conurbations Lille and Dunkerque (North of France) and the city of Lille itself were considered as the main potential sources of air pollution in this region.

In agreement with the INTERREG objectives, the present study aimed to assess the relative abundance of heavy metals and the water-soluble ions in PM$_{2.5}$ particles including their relation with meteorological and seasonal variations. The influence of long-range air mass movement was also evaluated with respect to the masses and composition of fine particles. Further, some multivariate statistical methods were used to identify and characterize the origin/emission sources of these species. The study has a broad prospective as it also

covers the objective defined in the new European Council Directive (PE-CONS 3696/07) and leads to understand the nature, source and behavior of fine particles over Europe.

2 Experimental

2.1 Site specifications

The city of Menen is situated nearby the French border in Belgium (Fig. 1 and S1), and is influenced by emissions from the industrial activities in the conurbations Lille and Dunkerque. The city covers an area of 33 km^2 and has a population of 32,000 inhabitants. The sampling station in Menen (Wervikstraat) is situated outside the city centre, nearby the borderline with France. The site is located in an environment with few buildings, in order to permit a good circulation of the air and is 8 km from the French city of Tourcoing, in a northerly direction. The region between Tourcoing and Halluin can be classified as a suburban zone; the areas around Wervicq and Rollegem have a more rural character. However, the local air quality at this sampling site may also be influenced by the industrial activities at the conurbation Lille. Lille was earlier a leading textile centre, known for its lisle (a smooth cotton thread); major industries include nowadays metallurgy, chemicals, engineering, distilling, computer and food processing. In addition to this, open fires and incinerator activities have also been reported in Menen and in the North of France. The closest coke-oven industries in Belgium are situated in Zelzate, around 70 km to the north of Menen. The conurbation of Lille (including several cities on the French side and Kortrijk on the Belgian side) counts more than 1.7 million inhabitants.

Fig. 1 Location of Menen (source: Google Earth)

2.2 Sampling

The $PM_{2.5}$ samples were collected on cellulose nitrate filters (Sartorius Biotechnology, Germany) using a Sequential Sampler Leckel SEQ 47/50. The sampling was performed at a rate of 2.3 $m^3 h^{-1}$ and in total 55.2 m^3 of air passed through each filter. Every day the filters were changed automatically as the sampler was pre-programmed. The sampler may contain up to 15 filter holders. During each season, the $PM_{2.5}$ samples were collected for a month and Table 1 gives an overview of the sampling periods. Various meteorological parameters (e.g. temperature, pressure and wind direction) were also recorded using a mobile laboratory at Wervicq, a nearby station of Menen.

However, standard procedure was used for $PM_{2.5}$ sampling and precautions were taken to avoid contamination but several studies suggest that some volatilization losses may occur during storage and especially for halogens (Maenhaut et al. 1987; Salma et al. 1997; Viana et al. 2007). This may introduces an artifact bias in measurement, which also depends on the sampling device used, particle size fraction, the composition of aerosol, the chemical form of reactive species, duration of the sample storage and the analytical technique used (Almeida et al. 2006b; Viana et al. 2007). In case of nitrate, the evaporation losses were found negligible below 20°C (Schaap et al. 2004; Pathak and Chan 2005).

2.3 Analysis of chemical species

2.3.1 ED-XRF measurements

Collected filter samples were initially submitted for bulk elemental analysis by energy dispersive X-ray fluorescence (ED-XRF) spectrometry (Epsilon 5 from PANalytical, Almelo, The Netherlands). The ED-XRF has a powerful X-ray tube, 3D polarizing geometry, up to 15 secondary targets and a high-resolution Ge-detector. The homogeneous collection of particle allows ED-XRF analysis of the samples. The method has been calibrated with MicroMatter standards; these are thin polymer films with pure element deposition. The concentrations of the standards have been determined by a weighing procedure by the manufacturer. The method has been validated by NIST standards (SRM 2783—Nuclepore filter with deposited PM_{10}).

2.3.2 Ion chromatography

After ED-XRF analysis, the filters were leached ultrasonically in Milli-Q water and filtered to determine the water-soluble ion concentrations by ion chromatography (IC). The analysis of

Table 1 Overview of the sampling periods

Sampling period	Date	Season	Samples (n)[a]
SP1	16 April 2003 until 13 May 2003	Spring	28
SP2	20 August 2003 until 16 September 2003	Summer	28
SP3	01 October 2003 until 28 October 2003	Autumn	27
SP4	26 November 2003 until 20 December 2003	Winter	28

[a] For both ions and elements

aqueous extracts was performed on a dual column Dionex (Sunnyvale, CA, USA) DX-120 ion chromatograph equipped with a Dionex AS50 auto sampler, which performed isocratic ion analysis applications using conductivity detection. Electrochemical suppression of the background conductivity was achieved using Dionex Self-Regenerating Suppressors™, models ASRS-ULTRA (anions) and CSRS-ULTRA (cations). This suppression involved a neutralisation of the eluent by exchanging the eluent counter ions respectively with H^+ or OH^- (generated by the electrolysis of H_2O) respectively in anion and cation analysis.

The determination of the ions F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+} and Mg^{2+} were performed using the following setup: separation of the anionic analytes was attained on a AG14 guard column, preceded by a Dionex AS14 analytical column; the separation of the cationic analytes was attained on a CS12 cation separation column, preceded by a Dionex CG12A guard column. For anion separation, the eluent was composed of 3.5 mM Na_2CO_3/ 1.0 mM $NaHCO_3$ and the flow rate was set at 1.2 ml min^{-1}. For cation separation, the eluent was 20 mM H_2SO_4, with a flow rate of 1.0 ml min^{-1}.

Calibration was performed using certified standard multi-ion solutions (Combined Seven Anion Standard II, Combined Six Cation Standard II, Dionex), which were diluted to effective concentrations of 20, 10, 5, 2.5 and 1 ppm standard solutions. Data acquisition, construction of the calibration curve and peak integration was achieved with the aid of the Peaknet software package, version 6.11. The output in milligrams per liter from the instrument is converted to concentration in µg m^{-3}, by taking into account the applied dilutions, sampling or exposure time, and the sampling rate. Limit of detection (LOD) data were calculated from eleven independent determinations of blank filters, each of them subjected to the same chemical procedure as the sampled filters. The LODs were found to be 0.03, 0.02, 0.003, 0.004, 0.002, 0.01, 0.06, 0.1, and 0.1 µg m^{-3} for NH_4^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}, respectively. The precisions of the determinations were better than 3.6%.

2.4 Multivariate analysis

The PCA and hierarchical cluster analysis (HCA) are the most common multivariate statistical methods applied in environmental studies. The SPSS software package (version 13.0) was used for the multivariate analysis. The method of HCA helps to classify the various groups of ions and elements. As the variables have large differences in scaling, standardization was performed before computing proximities and can be done automatically by the HCA procedure. Further, the Ward's method of clustering was applied by the use of the squared Euclidean distance as a measure. The levels of various ions and elements vary by different orders of magnitude and hence the PCA was applied to the correlation matrix. Likewise, each variable was normalized to unit variance and thus contributed equally. In the present study, only factors having an Eigen value > 1 were retained for further analysis.

3 Results and discussions

3.1 ED-XRF and sample damage

ED-XRF is commonly considered to be a non-destructive technique, which makes it possible to perform this analysis prior to other analytical techniques. However, when

applying IC successive to ED-XRF, in order to analyze ions such as NO_3^- and SO_4^{2-}, significant artifact errors may occur due to beam damage, when applying an X-ray radiation (Laux et al. 1996; Spence and Howells 2002). Almeida et al. (2006b) also suggest some Cl volatilization losses during proton induced X-ray emission measurements. Considering this drawback, Van Meel et al. (2008) investigated the effect of the different parameters such as acceleration voltage, current, irradiation time and medium; on the concentration on these volatile inorganic compounds. The study indicates that these losses can be negligible with optimized beam conditions and irradiation time.

3.2 Influence of meteorological conditions

During the winter campaign, the daily average temperature ranged from −7.5°C to 12°C, whereas during summer it varied from 19°C to 32°C. The air pressure varied between 995 and 1035 hPa, which likely indicate the presence of depression and anticyclone. Supplementary Figure S2 shows the wind roses for the winter and the summer campaigns during 2003 at Menen. Interestingly, the wind roses for winter campaign looked like those obtained for a whole year. Most of the time winds blow from the south-west and the second most important direction was north-east. In summer, a significant part of wind blew from north-west.

The annual pollution roses of $PM_{2.5}$ masses are shown in Fig. 2. The figure depicts that the relatively higher levels of $PM_{2.5}$ were observed at Menen, when wind comes from north to the east and to the south. This suggests that the $PM_{2.5}$ masses are not only influenced by local sources but also by regional/global activities. Similar observations were also reported by Glavas et al. (2008) at a Mediterranean coastal site in Greece. The various pollutants can also be washed out during rainfall (Ravindra et al. 2003). The variation is $PM_{2.5}$ masses and their relative chemical compositions were also further investigated using backward trajectories in section 3.4.

3.3 $PM_{2.5}$ mass and relative ratio of water-soluble ions and metals

The level of $PM_{2.5}$ ranges from 3 to 74 µg m^{-3} at Menen during various seasons with an annual mean concentration of 17 µg m^{-3}. In comparison with other studies, these levels fall in the low to moderate range (Chaloulakou et al. 2003; Rodriguez et al. 2004; Putaud et al. 2004; Kocak et al. 2007; Glavas et al. 2008). On an annual average basis, the $PM_{2.5}$ mass accounts for 59% of total PM_{10} mass at Menen. Further, the difference between PM_{10} and $PM_{2.5}$ were found smaller during the winter season than summer. Karaca et al. (2005) have also reported a significant relationship between PM_{10} and $PM_{2.5}$. During 2003, the daily value of 50 µg m^{-3} exceeded 79 times at Menen, while only 35 exceedances of the daily value of 50 µg m^{-3} are permitted on a yearly basis for the protection of health as per European Directive (1998; PE-CONS 3696/07). Water-soluble ions form a major component of atmospheric aerosols and can comprise up to 60–70% of total particulate mass. Bencs et al. (submitted) found that water-soluble ions can constitute on average 40% of $PM_{2.5}$ mass and range from 10% to 90% during various seasons. The levels of elements were found to be highly fluctuating in Belgium and range from 0.1% to 24% with an average of 3.4%. In the present study, the $PM_{2.5}$ mass ratio of water-soluble ions and elements also seems in agreement with Bencs et al. (submitted) and follows a similar trend during different seasons.

Interestingly elemental composition shows more distinct seasonal behavior than water-soluble ions having relatively higher levels during cold seasons. The relatively
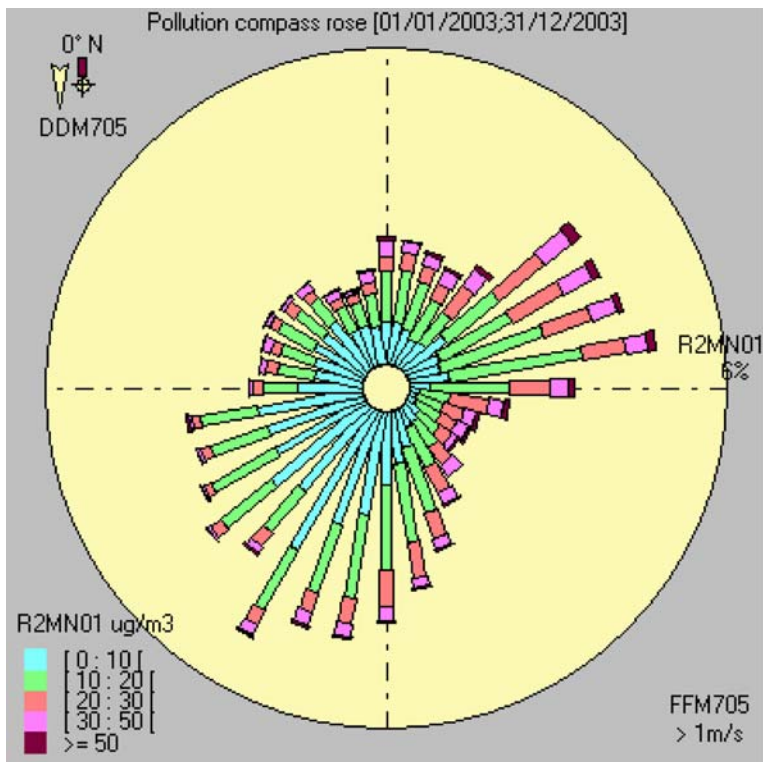
Fig. 2 Pollution roses for $PM_{2.5}$ at Menen during 2003

higher levels of water-soluble ions and elements during winter can be related to increased emission from vehicular sources, domestic heating and power plants. Further meteorological parameters may also play an important role. Yuan et al. (2006) has also shown more regional source contribution to $PM_{2.5}$ during winter months than summer.

3.4 Chemical composition of $PM_{2.5}$

3.4.1 Water-soluble ions in $PM_{2.5}$

The analytical results for the seasonal concentrations of the detected water-soluble ions or water soluble fractions are reported in Table 2. As can be seen, the most abundant ionic species in the $PM_{2.5}$ fraction were NO_3^-, SO_4^{2-} and NH_4^+ during all seasons, summed in order of decreasing concentration. The Cl^-, K^+, Mg^{2+} and Ca^{2+} showed a lower contribution to the total water-soluble ion content, with average concentrations smaller than 1 µg m^{-3}. The mean NO_3^- concentration was most elevated during spring, reaching maximum concentrations of 8.1 µg m^{-3}; the levels appeared in agreement with Schaap et al. (2002) for Europe. The seasonal difference in NO_3^- levels can be explained by the higher availability of the precursor NO_x (in particular NO_2) due to additional conversion of NO to NO_2, which benefits from increased ambient O_3 photochemical activity (Seinfeld and Pandis 1998).

Table 2 Mean ionic ($\mu g\ m^{-3}$) composition of $PM_{2.5}$ over Menen during various seasons

Ions	Conc. $\pm$ CL$_{0.95}$	Min	Max	Conc. $\pm$ CL$_{0.95}$	Min	Max
	Spring			Summer		
F^-	0.01±0.00	0.00	0.02	0.03±0.02	0.01	0.31
Cl^-	0.26±0.05	0.03	0.55	0.25±0.11	0.07	1.67
NO_3^-	8.12±3.31	0.39	37.3	4.17±1.94	0.94	28.1
SO_4^{2-}	4.76±1.39	0.31	14.1	3.23±0.52	1.01	6.82
NH_4^+	2.34±0.59	0.21	5.91	1.92±0.36	0.64	3.53
K^+	0.12±0.03	0.01	0.36	0.13±0.04	0.05	0.59
Mg^{2+}	0.02±0.01	0.01	0.04	0.02±0.00	0.01	0.04
Ca^{2+}	0.08±0.01	0.01	0.28	0.06±0.02	0.03	0.30
	Autumn			Winter		
F^-	0.02±0.01	0.01	0.15	0.10±0.03	0.01	0.26
Cl^-	0.37±0.11	0.11	1.26	0.89±0.30	0.03	3.52
NO_3^-	4.10±1.14	0.66	11.10	5.28±1.32	0.48	13.3
SO_4^{2-}	3.70±1.13	0.96	15.6	4.99±2.07	0.23	16.9
NH_4^+	1.74±0.45	0.48	4.33	1.88±0.66	0.12	6.05
K^+	0.21±0.08	0.05	1.14	0.25±0.08	0.04	0.84
Mg^{2+}	0.03±0.01	0.01	0.10	0.03±0.01	0.01	0.08
Ca^{2+}	0.05±0.01	0.01	0.14	0.07±0.02	0.02	0.18

CL confidence limit

The levels of SO_4^{2-} were found lower during summer/autumn campaigns than winter/ spring at Menen. The higher levels of SO_4^{2-} can be related to secondary sulfate formation associated with photochemical activities during summer (Morishita et al. 2006; Kim et al. 2007), however during winter this might be related to the reduced vertical dispersion due to inversion (Ravindra et al. 2008a, b) and increased thermal power emissions in Europe (Breivik et al. 2006). Further, the levels of NH_4^+ shows no significant variations over the year but have slightly higher levels during spring. Belgium is a known centre for animal keeping (especially for pig farming) and hence it can be expected that related activities emit significant NH_3 throughout the year (MIRA 2006). This also indicates that the above major species may occur in the form of $(NH_4)_2SO_4$ and/or NH_4NO_3 throughout the year over the studied area. However, during spring/winter months the formation of NH_4NO_3 is expected to be more due to larger availability of the related ions and their thermal stability.

Acid-forming constituents of the water soluble fraction (WSF e.g., SO_4^{2-}, NO_3^-), and other pollutants, related also to acidic rain, have severe effects on human health (Raizenne et al. 1996). Furthermore, some epidemiological data indicated possible seasonal effects of particulate matter composition (Ostro 1995; Michelozzi et al. 1998). In addition to the health concern, the WSF of atmospheric aerosols contains many important compounds, which can change the size, composition, particle density and lifetime of aerosols owing to their hygroscopic nature. On the other hand, water-soluble components may increase the solubility of toxic organic compounds, such as *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) by acting as surface active agents. Therefore, they may increase the toxicity of these compounds to human health (Jacobson et al. 2000; IPCC 2006; Ravindra et al. 2008a, b).

3.4.2 Bulk elements in $PM_{2.5}$

The seasonal elemental concentrations, obtained from the bulk analysis of filter samples, are summarized in Table 3, whereas annual averages are shown in supplementary Table S1. The main elements in fine particle were S and Cl with mean atmospheric concentrations of 715 and 227 ng m^{-3}, respectively. Furthermore, in decreasing order K, Fe, and Si, contributed to a large extent (ranging from 91 to 158 ng m^{-3}) to the total elemental concentration of $PM_{2.5}$. The levels of total Cl seem lower than the soluble Cl$^-$ measure by IC. A recent study by Almeida et al. (2006b) suggests that measured total Cl concentration

Table 3 Mean elements (ng m^{-3}) composition of $PM_{2.5}$ over Menen during different seasons

| Elements	Average ± $CL_{0.95}$	Min	Max	Average ± $CL_{0.95}$	Min	Max
	Spring			Summer		
V	5.5±1.5	2.3	14.6	4.8±0.9	1.8	9.6
Cr	1.0±0.3	0.0	3.2	0.7±0.4	0.0	4.3
Mn	7.3±2.4	0.9	32.4	4.7±1.1	1.6	13.2
Ni	2.7±0.7	0.5	8.4	2.5±0.4	0.7	4.3
Cu	4.8±1.1	0.9	11.4	11±8	1.1	70.2
Zn	45±14	7.5	148	35±13	8.2	145
Pb	24±7	4.1	90.9	21±6	4.6	61.3
K	117±33	27.3	293	102±21	34.0	279
Ca	58±17	10.7	173	39±16	0.2	190
Ti	5.1±1.8	1.1	22.6	4.2±2.3	0.7	26.4
Fe	112±30	23.7	363	92±31	14.8	339
Br	8.4±1.5	3.2	21.4	6.2±1.3	2.3	19.4
Rb	1.9±0.3	0.9	4.1	1.7±0.3	0.7	3.9
Al	66±15	14.4	168	34±7	7.5	87.5
Si	136±30	52.4	348	68±14.4	18.5	203
S	766±139	271	1,576	599±109	141	1,160
Cl	125±17	48.3	244	116±20	51	261
	Autumn			Winter		
V	4.3±1.0	1.4	14.6	5.1±1.2	1.1	15
Cr	1.8±0.6	0.0	5.9	2.3±0.8	0.0	7.3
Mn	7.9±2.2	1.8	32.6	12±5	1.1	50.3
Ni	3.1±0.7	0.7	8.2	3.4±0.9	0.9	10
Cu	6.8±1.9	1.4	21	10±4	1.1	45
Zn	60±15	17.1	163	99±35	8.2	364
Pb	34±11	7.1	112	54±20	5.2	219
K	202±48	53.5	551	206±64	31.9	718
Ca	43±9	2.7	82	38±15	0.5	149
Ti	6.5±2.5	0.5	25.3	5.3±1.5	0.2	13.7
Fe	163±70	22.8	1,011	174±60	12.8	626
Br	9.1±1.5	4.3	23	17±5	4.3	44.4
Rb	–	–	–	–	–	–
Al	48±10	9.8	105	59±17	1.8	166
Si	76±13	26.4	160	81±27	12.1	315
S	651±96	171	1,258	830±250	212	2,538
Cl	227±55	93.4	822	432±147	80	1817

CL confidence limit

may be lower than the soluble Cl⁻ concentration, partially due to volatilization losses. However, these losses can be minimized using optimum instrumental conditions (Van Meel et al. 2008). Zn, Al, Ca, and Pb occurred in moderate concentrations, ranging from 33 to 60 ng m⁻³. The elements Br, Mn, Cu, Ti, Ni, V and Cr were classified as trace elements with mean concentrations below 10 ng m⁻³. Table 3 also shows the variation in the atmospheric concentrations of the elements, with 95% confidence limits and the difference between the minimum and the maximum concentrations of each element.

The variability (or the concentrations as a function of time) of the observed atmospheric concentrations of the different elements is demonstrated in Fig. 3. According to the relative abundances of the different elements in the samples, two distinct groups of elements were identified. The first group of elements, characterized by a similar concentration pattern as a function of time (Fig. 3), included the elements Mn, K, Ca, Ti, Fe, Al and Si, which are mainly elements of crustal (natural) origin. The second group of elements consisted of Zn, Pb, S, V, Cr, Ni, Cu, Br, etc. which are mainly elements of anthropogenic origin. This anthropogenic group of elements occurred in more scattered relative abundances in the PM₂.₅ samples, as demonstrated in Fig. 3. This concentration pattern seems to be related to the changes in meteorological conditions, such as wind speed, wind direction, or, on a larger scale, long range transports, which can cause large differences in the amount of the different anthropogenic elements in PM₂.₅ (Glavas et al. 2008; Almeida et al. 2008).

However, different elements in Fig. 3 were distinct in two categories on their daily fluctuations and trends; some of elements can overlap in both categories, such as Cl, K, etc. K is considered a crustal element but it is also an important biomass burning tracer. Similarly Cl may also originate from sea salt; however, sea salt accounts only ~5% of PM₂.₅ mass in Belgium (Viana et al. 2007; Bencs et al., submitted). The Cl/Cl⁻ ratios towards unity in PM₂.₅ can be associated to the maritime air masses, where as lower values were associated with polluted continental air masses (Almeida et al. 2006). In the present case except for autumn (0.61), the remaining Cl/Cl⁻ ratios (~0.45), indicated towards continental

Fig. 3 Occurrence of the crustal elements (*above*) and anthropogenic elements (*below*) in PM₂.₅ over Menen (*Dotted lines* depicts the concentration on secondary y-axis)
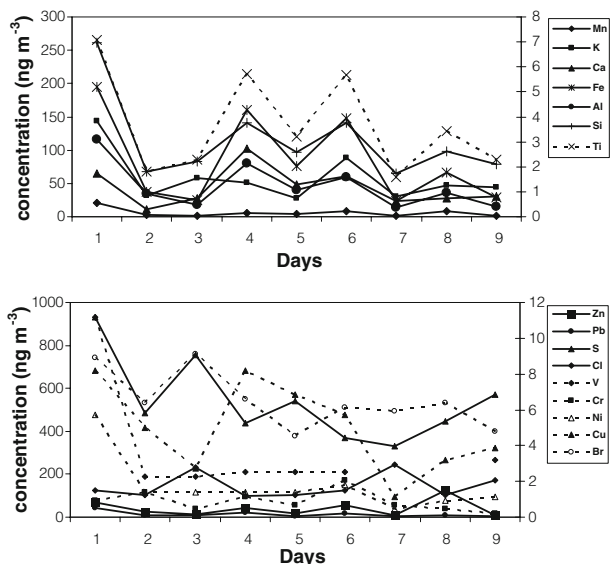
origin. The study also indicates a more limited transport of fine sea-salt particles from the marine environment to terrestrial areas, due to more intensive atmospheric removal processes (e.g., reaction of sea-salt with secondary aerosols). Other possibility for Cl loss is the conversion of fine sea-salt to coarse, "aged" particles with a short atmospheric life-time, due to rapid deposition (Bencs et al., submitted, and reference therein). To further investigate elemental categorization, the application of enrichment factors (EFs) was also applied.

The calculation of EFs also classifies the registered elements into two groups according to their origin in $PM_{2.5}$. The calculation of EFs is a commonly used tool, which is applied in studies involving elemental bulk analysis of atmospheric aerosols (Hoornaert et al. 2004; Lonati et al. 2005; Samara and Voutsa 2005; Manoli et al. 2002). EFs indicate whether the observed concentration of a specific element is enriched in comparison to the concentration which would be expected if the element would only originate from a particular source. A crustal EF of a specific element $EF_{crust}(X)$ is defined as follows:

$$EF_{crust}(X) = \frac{(C_x/C_{ref})_{aerosol}}{(C_x/C_{ref})_{crust}} \qquad (1)$$

where C_x is the concentration of a specific element in the aerosol or in the crust and C_{ref} the concentration of the reference element in the aerosol or in the crust (Seinfeld and Pandis 1998). Several elements, such as Si, Al, Fe, Ti and Sc, have been reported in literature as reference elements for the calculation of crustal enrichment factors (Hacisalihoglu et al. 1992; Van Malderen et al. 1996). In the majority of the studies, either Al or Fe has been selected as a reference element. In the area of Menen, both elements could be considered as having negligible anthropogenic sources. However, taking into account the average relative standard deviations of the detection of Fe and Al by means of ED-XRF, with respective values of 3.5% and 43%, Fe was selected in this study as the crustal reference element. For the average elemental concentrations in soil, the crustal averages reported by Mason et al. (1966) were applied.

According to the value of the EF, the nature of the source can be evaluated. If the EF of an element approaches unity, the predominant source of this element is crustal. Strictly following the definition of the EF, one would expect an element to be enriched in case the EF value is larger than 1. However, threshold values of 4 (Hacisalihoglu et al. 1992) and 5 (Voutsa et al. 2002) have been proposed in literature, in order to account for possible local variations in soil composition. In this study the threshold value is set at 4, consequently EF>4 suggest that a significant fraction of the element is contributed from non-crustal sources.

The statistical distribution of the EF values for $PM_{2.5}$ collected in Menen during four sampling periods is presented in Fig. 4. All elements, which were previously classified in the first group according to their relative abundance in each $PM_{2.5}$ sample (Fig. 3), are represented by EF values close to one (Al, Si, Ca, Ti, Fe) or smaller than 4 (K and Mn). It can be concluded that these elements mainly originated from natural (crustal) sources. However, all elements which were previously classified in the second group according to their scattered relative abundance in each sample (Zn, Pb, S, Cl, V, Cr, Ni, Cu, Br) were characterized by EF values ranging from 4 to 1,000 and are considered enriched. Moderate EFs, with median values ranging from 5 to 10, were determined for the elements V, Cr and Ni. The elements Cu and Zn were more enriched in $PM_{2.5}$ according to their EF with median values between 50 and 500. S, Cl and Pb, were the most enriched elements in $PM_{2.5}$, with median EF values ranging from 500 to 1,000. These elements probably

Fig. 4 Crustal EF for PM$_{2.5}$ samples collected in Menen: median (*black triangle*), minimum/maximum value and interquartile range (*white rectangle*)
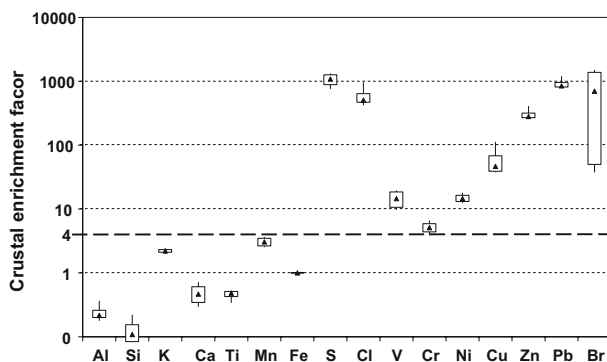
originated from nearby industrial activities. The interquartile ranges from the enriched elements showed some variation, which can probably be attributed to meteorological circumstances. The smallest interquartile ranges were observed for the elements Ni, Zn and Pb; the largest interquartile range was observed for Br.

3.5 Source apportionment

The PCA is a widely used technique to simplify large data and to extract small number factors to analyze relationship among the observed variables. Recently, several studies has applied PCA to identify and characterize the emission source of PM$_{2.5}$ (Almeida et al. 2006a, b; Moreno et al. 2006; Manoli et al. 2002). This proves continued wider acceptability of PCA in aerosol science. In addition to PCA; CMB and PMF also offer the possibility to recover directly unknown source profile from ambient data. Some of the example studies on CMB and PMF applications for source categorization of PM$_{2.5}$ include Pekney et al. (2006), Morishita et al. (2006); Hwang and Hopke (2007); Kim et al. (2007), Lee et al. (2008), Marmur et al. (2007), Rizzo and Scheff (2007) and Viana et al. (2008). However, these complex and powerful models/techniques are used with numerous underlying assumptions and limitations (Seinfeld and Pandis 1998). Hence, in the present study we only focus on the use of HCA and PCA for the multivariate analysis of PM$_{2.5}$ data.

3.5.1 Hierarchical cluster analysis (HCA)

The HCA was used to explore the relatively homogenous group of various ions and elements based on their average concentration during the different seasons. Figure 5 shows a visual representation of the hierarchical clustering solution. The connected vertical lines designate joined cases. The dendrogram rescales the actual distances to numbers between 0 and 25, preserving the ratio of the distances between steps.

As can be seen from the dendrogram of the ions, they can be categorized in three groups. The group #1 includes F$^-$, Mg^{2+}, Ca^{2+}, K$^+$, Cl$^-$, whereas groups #2 and #3 include NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$, respectively. Fine particles are formed primarily by combustion and/or secondary chemical reactions in the atmosphere. The observation in the ion dendrogram shows the likely existence of secondary chemical reactions over Menen i.e. the conversion of SO$_2$ to SO$_4^{2-}$ and from NO$_2$ to NO$_3^-$. These gaseous precursors are emitted from various anthropogenic activities, specifically by industrial and vehicular exhausts. Further it also indicates that NH$_4^+$ ion may neutralize the fine aerosol acidity and may appear in partially neutralized forms as (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and NH$_4$Cl over Menen. These results also seem

```
                        Rescaled Distance Cluster Combine

C A S E          0         5        10        15        20        25
Label     Num    +---------+---------+---------+---------+---------+

F          1     ─┐
Mg         7     ─┤
Ca         8     ─┤
K          6     ─┼─┐
Cl         3     ─┘ ├─────────────────────────────────────────┐
NH4        5     ───┘                                          │
NO3        2     ─┐                                            │
SO4        4     ─┘
```

```
                        Rescaled Distance Cluster Combine

C A S E          0         5        10        15        20        25
Label     Num    +---------+---------+---------+---------+---------+

V          1     ─┐
Ti        10     ─┤
Mn         3     ─┤
Br        12     ─┤
Cu         6     ─┤
Ni         4     ─┤
Rb        13     ─┤
Cr         2     ─┤
Pb         7     ─┼─┐
Ca         8     ─┤ │
Al        14     ─┤ │
Zn         5     ─┘ ├───────────────────────────────────────┐
K          9     ─┐ │                                        │
Fe        11     ─┤ │                                        │
Cl        17     ─┼─┘                                        │
Si        15     ─┘                                          │
S         16     ───────────────────────────────────────────┘
```
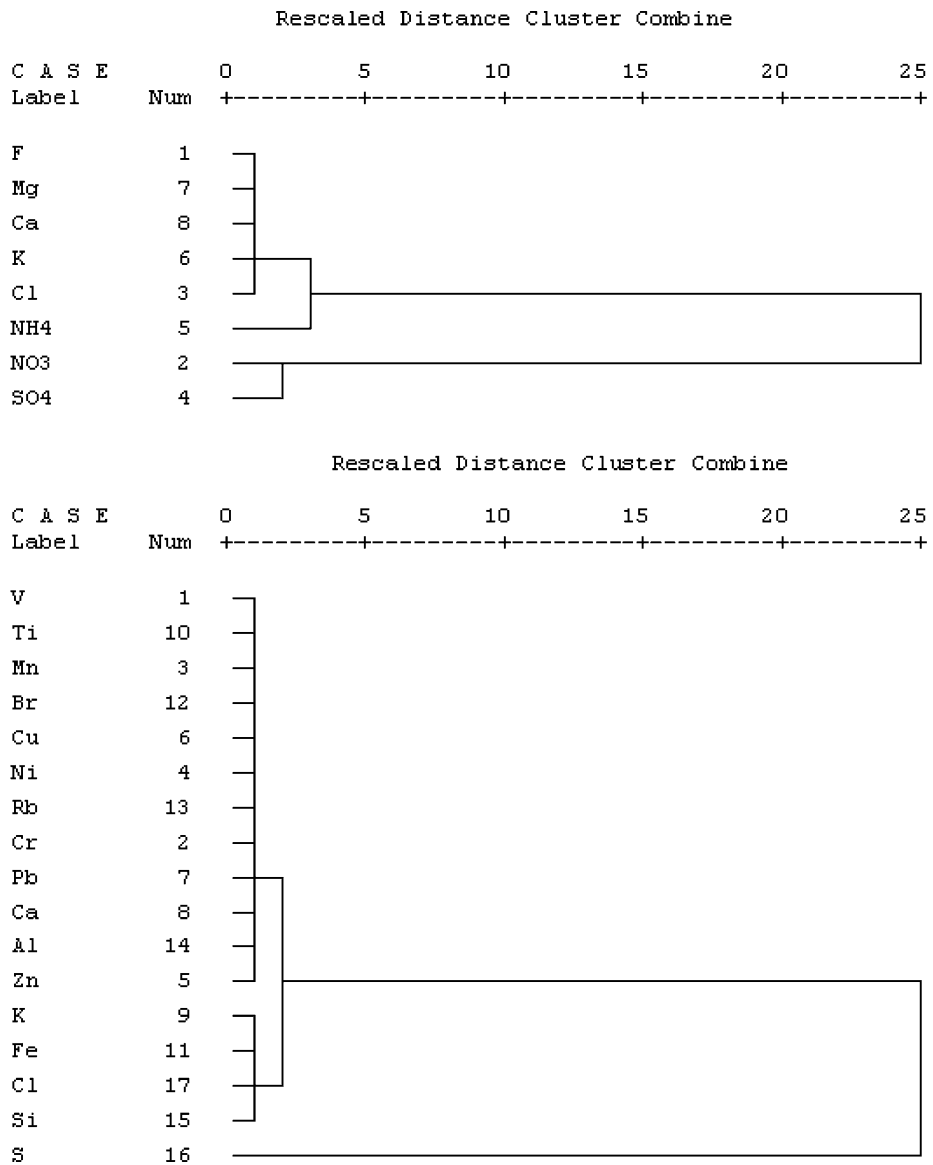
Fig. 5 Hierarchical cluster analysis of ions (*above*) and elements (*below*) using seasonal average levels at Menen

in accordance with a study of Bencs et al. (submitted), who studied the water-soluble fractions at 6 different places in Belgium. The dendrogam of various elements also classifies them in to three main categories (Fig. 5). Group #1 mainly consists of anthropogenic elements, while group #2 includes crustal elements. The S was distinctly placed in group #3. This shows the existence of S sources over Menen. The industrial area nearby Wervicq might be an important emission source of S, since it emitted 1,900 tons of SO_2 in 2003. Another industrial emission source, which emitted 340 tons of SO_2 in 2002, is situated 3 km north-westerly towards Rollegem (MIRA 2006).

3.5.2 Principal component analysis (PCA)

The PCA was used with varimax rotation and Kaiser normalization to study the relationships between the ions and elements. The application of varimax rotation can maximize the variance of the factor loading and hence make the results more easily interpretable. Tables 4 and 5 show the results of the factor analysis of daily concentrations of ions and elements at Menen. Factor loading determine the most representative species in each factor and a loading > 0.7 is typically regarded as excellent, whereas a loading < 0.3 as very poor. Each of these factors can be identified as either an emission source, or a chemical interaction. As can be seen from Table 4, factor #1 has a high loading for NH_4^+, SO_4^{2-} and NO_3^- species with a variance of 41%; which supports the dominance of these species over Menen and the existence of secondary aerosol formation reactions. Similar results were also suggested by HCA as explained there. The NO_3^- and SO_4^{2-} ions are generally found to be produced as secondary aerosol during combustion, biomass burning and vehicular emissions (Seinfeld and Pandis 1998) and by the neutralization of ammonia. Hence it can be concluded that these sources dominate over the border area near Menen.

The factor #2 has high factor loading of F^-, Cl^-, NO_3^- and K^+. These ions have been mainly assigned to coal/wood burning (Khalil and Rasmussen 2003; Yuan et al. 2006). Some open fires and incinerator activities have also been reported in the vicinity of Menen (Van Lieshout et al. 2001). Almeida et al. (2006b) suggest that a high K/K+ ratio (~4) indicate a high content of mineral aerosol transported from the North of Africa and South of Europe. In the present case the ratios vary from 0.78 to 0.98 during various seasons and hence the high loading of K^+ together with other high loading species indicate the influence of industrial and traffic related activities on the $PM_{2.5}$ composition. Only Cl^- and Mg^{2+} show high loading for factor #3. The Mg^{2+} is found to be related to exposed soil, unpaved roads and construction activities, where as Cl^- ions is mainly related to sea-salt particle contribution. Sea salt particles generally have a short atmospheric life-time due to their rather rapid deposition. This might be the reason for their appearance in factor #3, with only 15% variance.

Table 5 show the PCA results for various elements and groups them in 4 factors. Factor #1 has a high factor loading of mixed crustal and anthropogenic elements e.g. S, Si, Al, K, Ti, Ca, Fe, with moderate loading of Cl, Cr, Mn, Zn and Pb, and represents a variance of around 53%. High loading of Fe, Mn and Cr indicate towards road dust (Manoli et al.

Table 4 Factor analysis of daily ions levels over Menen

Ion Species	Factor 1	Factor 2	Factor 3
F^-	−0.09	0.90	−0.03
Cl^-	0.10	0.65	0.63
NO_3^-	0.58	0.68	−0.12
NH_4^+	0.93	0.05	−0.11
SO_4^{2-}	0.88	0.06	0.14
K^+	0.24	0.76	0.30
Mg^{2+}	0.07	0.02	0.95
Ca^{2+}	0.57	0.11	0.16
Eigen Values	3.25	1.73	1.16
Variance %	40.6	21.6	14.5
Cumulative %	40.6	62.2	76.7
Comments	Anthropogenic	Coal/Wood/Traffic	Natural

Table 5 Factor analysis of daily elements concentrations over Menen

Species	Factor 1	Factor 2	Factor 3	Factor 4
V	0.04	−0.07	0.93	0.12
Cr	0.41	0.83	−0.02	0.10
Mn	0.42	0.42	0.60	0.18
Ni	0.15	0.06	0.92	0.22
Cu	−0.20	0.86	0.00	−0.02
Zn	0.45	0.74	0.39	0.18
Pb	0.42	0.49	0.63	0.21
K	0.57	0.26	0.49	0.22
Ca	0.68	0.60	0.05	0.18
Ti	0.54	0.76	0.05	0.12
Fe	0.50	0.72	0.25	0.09
Br	0.17	0.07	0.11	0.91
Rb	0.29	0.18	0.35	0.80
Al	0.82	0.37	0.31	0.20
Si	0.84	0.39	0.18	0.18
S	0.73	0.02	0.41	0.14
Cl	−0.52	0.00	0.23	0.49
Eigen Values	9.1	2.6	1.4	1.1
Variance %	53.3	15.0	8.1	6.6
Cumulative %	53.3	68.5	76.4	83
Comments	Anthropogenic	Traffic	Gasoline	Industrial

2002). However, the loading of other metals also indicates a relation with more sources such as tire wear (Zn), and vehicular emission (Pb). Factor #2 has a relatively high factor loading for anthropogenic elements (Cr, Cu and Zn). The Zn is emitted from lubricant oil, brake linings and tires (Song et al. 2006) and Cu has been related with diesel engines (Samara and Voutsa 2005). Factor #3 has a significant loading for V, Mn, Ni and Pb. The Pb was used in the past as an important anti-detonator in gasoline. However, relative loading of other metals also suggest influence of industrial sources and it can be understood as there are various industries near the border area of Belgium and France. There are coke-ovens or steel industry in Zelzate, around 70 km to the north of Menen and depending on the meteorological conditions, these can influence the composition of $PM_{2.5}$. Furthermore, factor #4 is characterized by a high loading of Br and Rb and this cab be related to the natural as well as industrial sources.

The water-soluble ions and elements data was also processed together using PCA and results are shown in supplementary Table S2 with a brief discussion. In general, results seem in agreement with the above findings. However, as different methods were applied for ions and elemental measurements and both fractions have different physico-chemical properties; it seems realistic to assess their source/ origin separately.

3.6 $PM_{2.5}$ composition in relation to backward trajectories

In the above section it has been observed that the water-soluble ionic species and mainly the anthropogenic elements show considerable daily variation at Menen. These daily variations were a function of meteorological circumstances, local sources of air pollution and long-range transports. The long-range sources of air pollution can be tracked by combining information about the composition of particulate matter with backward

trajectory information. The parameters selected for the backward trajectories were chosen at a starting point of 20 m above sea level and a backward counting time of 120 h.

After combining each sample with its corresponding daily backward trajectory it could be concluded that the anthropogenic elements in $PM_{2.5}$ were strongly dependent on the origin and the track of the air masses before reaching the sampling site. According to the backward trajectories, the samples could be classified into three groups. Typical backward trajectories characterizing group #1, group #2 and group #3 are shown in Fig. 6. The group #1 includes samples which were characterized by the lowest concentrations of all anthropogenic elements and high concentrations of Cl. In these cases the backward trajectories indicated a track which originated in the Atlantic Ocean and solely passed over it before reaching the site. However, in these samples Cl originating from marine aerosols occurred in relatively elevated concentrations, reaching a mean value and a corresponding 95% confidence limit of 12 ± 40 ng m^{-3}.

Group #2 was categorized by moderately increased concentrations of various anthropogenic elements. In these cases the backward trajectories indicated tracks, which originated in the Atlantic Ocean and subsequently passed over continental areas before reaching the sampling site. Depending on the continental site over which it passed, different anthropogenic elements were enriched in $PM_{2.5}$. The most elevated concentrations in the group #2 were registered mainly for the elements V (5.2 ± 1.4 ng m^{-3}), Cr (2.5 ± 1.0 ng m^{-3}), Cu (9.6 ± 5.5 ng m^{-3}), Zn (106 ± 53 ng m^{-3}) and Pb (63 ± 31 ng m^{-3}) when the trajectories originated from the Atlantic Ocean, and moved over the United Kingdom before reaching the site. Backward trajectories also indicating that when trajectories spend most of their 5-day time over the United Kingdom relatively enriched concentrations of the elements V (5.2 ± 1.4 ng m^{-3}), Ni (2.8 ± 0.7 ng m^{-3}), Zn (35 ± 11 ng m^{-3}) and Pb (20 ± 5 ng m^{-3}) were observed in $PM_{2.5}$. Only moderately increased concentrations of the elements V, Cr, Cu, Zn and Pb were detected in case backward trajectories originated from the Atlantic Ocean passed over the North of France.

Group #3 included samples which were characterized by increased concentrations of the anthropogenic elements and low related 95% confidence limits: V (7.0 ± 2.5 ng m^{-3}), Cr (2.0 ± 0.8 ng m^{-3}), Ni (4.1 ± 1.4 ng m^{-3}), Cu (7.3 ± 2.0 ng m^{-3}), Zn (82 ± 20 ng m^{-3}), Pb (45 ± 13 ng m^{-3}), S (1160 ± 240 ng m^{-3}). These samples corresponded to backward trajectories originating in continental areas, such as Hungary, Poland or Germany, and air masses moving solely over continental areas, such as Germany, and France.
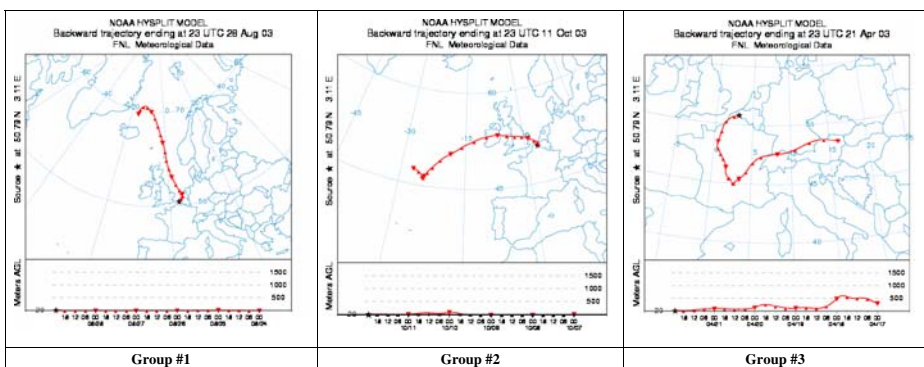

Fig. 6 Typical backward trajectories corresponding to the three groups

4 Conclusions

The ionic and elemental fractions of $PM_{2.5}$ were analyzed using IC and ED-XRF. The water-soluble ion fraction mostly contained the ions NO_3^-, SO_4^{2-} and NH_4^-; whereas all the other ions occurred at a concentration level below 1 μg m^{-3}. The elemental composition of $PM_{2.5}$ could be classified into two distinct groups according to their relative abundance in fine particles. Group #1 contained the natural elements, which occurred in proportional concentrations in each sample. Group #2 contained the anthropogenic elements, which occurred in more scattered relative abundances. The EF vs. soil calculations confirmed the respective natural and anthropogenic origin of the elements in both groups. Moreover, the EF indicated Pb and Cl, followed by Cu and Zn were the most enriched elements in $PM_{2.5}$ in Menen. Further the results also show that the aerosol composition in Menen varies considerably from day to day. The application of multivariate analysis shows the occurrence of secondary aerosol formation reactions and the existence of both natural (crustal) as well as anthropogenic sources (vehicular, industrial) of ions and elements. Combining the backward trajectory information with concentration levels of the anthropogenic elements indicates that the air masses having an origin and a track over the Atlantic Ocean contained the lowest levels of anthropogenic elements. Yet, air masses either originating from the Atlantic Ocean or from a continental area in combination with a track passing over continental areas, contained elevated concentrations of anthropogenic elements. The composition of the fine aerosol samples was a function of local, meteorological and seasonal circumstances at Menen. However a cross-border air pollution influence could be discerned, which mainly affected the anthropogenic elements in $PM_{2.5}$.

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