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.

Keywords: Fine particles (PM$_{2.5}$), ions, heavy metals, chemical composition, sources, multivariate analysis and trajectories.

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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 (Kacak et al., 2007; Ravindra et al., 2008; Glavas et al., 2008).

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

87   In agreement with the INTERREG objectives, the present study aimed to assess
88   the relative abundance of heavy metals and the water-soluble ions in $PM_{2.5}$ particles
89   including their relation with meteorological and seasonal variations. The influence of
90   long-range air mass movement was also evaluated with respect to the masses and
91   composition of fine particles. Further, some multivariate statistical methods were used to
92   identify and characterize the origin/emission sources of these species. The study has a
93   broad prospective as it also covers the objective defined in the new European Council
94   Directive (PE-CONS 3696/07) and leads to understand the nature, source and behavior of
95   fine particles over Europe.

96
97   **2. Experimental**
98
99   **2. 1 Site specifications**

100   The city of Menen is situated nearby the French border in Belgium (Figure 1 and
101   S1), and is influenced by emissions from the industrial activities in the conurbations Lille
102   and Dunkerque. The city covers an area of 33 km^2 and has a population of 32,000
103   inhabitants. The sampling station in Menen (Wervikstraat) is situated outside the city
104   centre, nearby the borderline with France. The site is located in an environment with few
105   buildings, in order to permit a good circulation of the air and is 8 km from the French city
106   of Tourcoing, in a northerly direction. The region between Tourcoing and Halluin can be
107   classified as a suburban zone; the areas around Wervicq and Rollegem have a more rural
108   character. However, the local air quality at this sampling site may also be influenced by
109   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.

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 ^{o}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 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 mg L^{-1} from the

172 instrument is converted to concentration in µg m^{-3}, by taking into account the applied

173 dilutions, sampling or exposure time, and the sampling rate. Limit of detection (LOD)

174 data were calculated from eleven independent determinations of blank filters, each of

175 them subjected to the same chemical procedure as the sampled filters. The LODs were

176 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^+,

177 Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}, respectively. The precisions of the

178 determinations were better than 3.6 %.

179

180 **2.4 Multivariate analysis**

181 The PCA and hierarchical cluster analysis (HCA) are the most common

182 multivariate statistical methods applied in environmental studies. The SPSS software

183 package (version 13.0) was used for the multivariate analysis. The method of HCA helps

184 to classify the various groups of ions and elements. As the variables have large

185 differences in scaling, standardization was performed before computing proximities and

186 can be done automatically by the HCA procedure. Further, the Ward's method of

187 clustering was applied by the use of the squared Euclidean distance as a measure. The

188 levels of various ions and elements vary by different orders of magnitude and hence the

189 PCA was applied to the correlation matrix. Likewise, each variable was normalized to

190 unit variance and thus contributed equally. In the present study, only factors having an

191 Eigen value > 1 were retained for further analysis.

192

193 **3. Results and discussions**

194 **3.1 ED-XRF and sample damage**

195 ED-XRF is commonly considered to be a non-destructive technique, which makes

196 it possible to perform this analysis prior to other analytical techniques. However, when

197 applying IC successive to ED-XRF, in order to analyze ions such as NO_3^- and SO_4^{2-},

198 significant artifact errors may occur due to beam damage, when applying an X-ray

199 radiation (Laux et al., 1996; Spence and Howells, 2002). Almeida et al. (2006b) also

200 suggest some Cl volatilization losses during proton induced X-ray emission

201 measurements. Considering this drawback, Van Meel et al. (2008) investigated the effect

202 of the different parameters such as acceleration voltage, current, irradiation time and

203 medium; on the concentration on these volatile inorganic compounds. The study indicates

204 that these losses can be negligible with the used beam conditions and irradiation time.

205

206 **3.2 Influence of meteorological conditions**

207 During the winter campaign, the daily average temperature ranged from -7.5 $^{\circ}$C to

208 12 $^{\circ}$C, whereas during summer it varied from 19 $^{\circ}$C to 32 $^{\circ}$C. The air pressure varied

209 between 995 and 1035 hPa, which likely indicate the presence of depression and

210 anticyclone. Supplementary Figure S2 shows the wind roses for the winter and the

211 summer campaigns during 2003 at Menen. Interestingly, the wind roses for winter

212 campaign looked like those obtained for a whole year. Most of the time winds blow from

213 the South-West and the second most important direction was North-East. In summer, a

214 significant part of wind blew from North-West.

215 The annual pollution roses of $PM_{2.5}$ masses are shown in Figure 2. The figure

216 depicts that the relatively higher levels of $PM_{2.5}$ were observed at Menen, when wind

217 comes from north to the east and to the south. This suggests that the $PM_{2.5}$ masses are not

218 only influenced by local sources but also by regional/global activities. Similar

219 observations were also reported by Glavas et al. (2008) at a Mediterranean coastal site in

220 Greece. The various pollutants can also be washed out during rainfall (Ravindra et al.,

221 2003). The variation is $PM_{2.5}$ masses and their relative chemical compositions were also

222 further investigated using backward trajectories in section 3.4.

223

224 **3.3 $PM_{2.5}$ mass and relative ratio of water-soluble ions and metals**

225 The level of $PM2_{.5}$ ranges from 3 to 74 µg m^{-3} at Menen during various seasons

226 with an annual mean concentration of 17 µg m^{-3}. In comparison with other studies, these

227 levels fall in the low to moderate range (Chaloulakou et al.; 2003; Rodriguez et al.; 2004;

228 Putaud et al., 2004; Kocak et al., 2007; Glavas et al., 2008). On an annual average basis,

229 the $PM_{2.5}$ mass accounts for 59% of total PM_{10} mass at Menen. Further, the difference

230 between PM_{10} and $PM_{2.5}$ were found smaller during the winter season than summer.

231 Karaca et al. (2005) have also reported a significant relationship between PM_{10} and

232 $PM_{2.5}$. During 2003, the daily value of 50 µg m^{-3} exceeded 79 times at Menen, while only

233 35 exceedances of the daily value of 50 µg m^{-3} are permitted on a yearly basis for the

234   protection of health as per European Directive (PE-CONS 3696/07). Water-soluble ions

235   form a major component of atmospheric aerosols and can comprise up to 60-70 % of total

236   particulate mass. Bencs et al. (2008) found that water-soluble ions can constitute on

237   average 40% of $PM_{2.5}$ mass and range from 10 to 90% during various seasons. The levels

238   of elements were found to be highly fluctuating in Belgium and range from 0.1 to 24%

239   with an average of 3.4%. In the present study, the $PM_{2.5}$ mass ratio of water-soluble ions

240   and elements also seems in agreement with Bencs et al. (2008) and follows a similar

241   trend during different seasons.

242   Interestingly elemental composition shows more distinct seasonal behavior than

243   water-soluble ions having relatively higher levels during cold seasons. The relatively

244   higher levels of water-soluble ions and elements during winter can be related to increased

245   emission from vehicular sources, domestic heating and power plants. Further

246   meteorological parameters may also play an important role. Yuan et al. (2006) has also

247   shown more regional source contribution to $PM_{2.5}$ during winter months than summer.

248

249   **3.4 Chemical composition of $PM_{2.5}$**

250   *3.4.1 Water-soluble ions in $PM_{2.5}$*

251   The analytical results for the seasonal concentrations of the detected water-soluble

252   ions or water soluble fractions are reported in Table 2. As can be seen, the most abundant

253   ionic species in the $PM_{2.5}$ fraction were NO_3^-, SO_4^{2-} and NH_4^+ during all seasons, summed

254   in order of decreasing concentration. The Cl^-, K^+, Mg^{2+} and Ca^{2+} showed a lower

255   contribution to the total water-soluble ion content, with average concentrations smaller

256   than 1 µg m^{-3}. The mean NO_3^- concentration was most elevated during spring, reaching

257   maximum concentrations of 8.1 µg m^{-3}; the levels appeared in agreement with Schaap et

258   al. (2002) for Europe. The seasonal difference in NO_3^- levels can be explained by the

259   higher availability of the precursor NO_x (in particular NO_2) due to additional conversion

260   of NO to NO_2, which benefits from increased ambient O_3 photochemical activity

261   (Seinfeld and Pandis, 1998).

262   The levels of SO_4^{2-} were found lower during summer/autumn campaigns than

263   winter/spring at Menen. The higher levels of SO_4^{2-} can be related to secondary sulfate

264   formation associated with photochemical activities during summer (Morishita et al.,

265   2006; Kim et al., 2007), however during winter this might be related to the reduced
266   vertical dispersion due to inversion (Ravindra et al., 2008) and increased thermal power
267   emissions in Europe (Breivek et al., 2006). Further, the levels of NH_4^+ shows no
268   significant variations over the year but have slightly higher levels during spring. Belgium
269   is a known centre for animal keeping (especially for pig farming) and hence it can be
270   expected that related activities emit significant NH_3 throughout the year (MIRA, 2006).
271   This also indicates that the above major species may occur in the form of $(NH_4)_2SO_4$
272   and/or NH_4NO_3 throughout the year over the studied area. However, during spring /
273   winter months the formation of NH_4NO_3 is expected to be more due to larger availability
274   of the related ions and their thermal stability.

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

286

287   *3.4.2 Bulk elements in PM$_{2.5}$*

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

296   due to volatilization losses. However, these losses can be minimized using optimum

297   instrumental conditions (Van Meel et al., 2008). Zn, Al, Ca, and Pb occurred in moderate

298   concentrations, ranging from 33 to 60 ng m^{-3}. The elements Br, Mn, Cu, Ti, Ni, V and Cr

299   were classified as trace elements with mean concentrations below 10 ng.m^{-3}. Table 3 also

300   shows the variation in the atmospheric concentrations of the elements, with 95%

301   confidence limits and the difference between the minimum and the maximum

302   concentrations of each element.

303   The variability (or the concentrations as a function of time) of the observed

304   atmospheric concentrations of the different elements is demonstrated in Figure 3a and 3b.

305   According to the relative abundances of the different elements in the samples, two

306   distinct groups of elements were identified. The first group of elements, characterized by

307   a similar concentration pattern as a function of time (Figure 3a), included the elements

308   Mn, K, Ca, Ti, Fe, Al and Si, which are mainly elements of crustal (natural) origin. The

309   second group of elements consisted of Zn, Pb, S, V, Cr, Ni, Cu, Br, etc. which are mainly

310   elements of anthropogenic origin. This anthropogenic group of elements occurred in

311   more scattered relative abundances in the PM$_{2.5}$ samples, as demonstrated in Figure 3b.

312   This concentration pattern seems to be related to the changes in meteorological

313   conditions, such as wind speed, wind direction, or, on a larger scale, long range

314   transports, which can cause large differences in the amount of the different anthropogenic

315   elements in PM$_{2.5}$ (Glavas et al., 2008; Almeida et al., 2008).

316   However, different elements in Figure 3 were distinct in two categories on their

317   daily fluctuations and trends; some of elements can overlap in both categories, such as Cl,

318   K, etc. K is considered a crustal element but it is also an important biomass burning

319   tracer. Similarly Cl may also originate from sea salt; however, sea salt accounts only ~5%

320   of PM$_{2.5}$ mass in Belgium (Viana et al., 2007; Bencs et al., 2008). The Cl/Cl^{-} ratios

321   towards unity in PM$_{2.5}$ can be associated to the maritime air masses, where as lower

322   values were associated with polluted continental air masses (Almeida et al., 2006). In the

323   present case except for autumn (0.61), the remaining Cl/Cl^{-} ratios (~0.45), indicated

324   towards continental origin. The study also indicates a more limited transport of fine sea-

325   salt particles from the marine environment to terrestrial areas, due to more intensive

326   atmospheric removal processes (e.g., reaction of sea-salt with secondary aerosols). Other

327 possibility for Cl loss is the conversion of fine sea-salt to coarse, "aged" particles with a

328 short atmospheric life-time, due to rapid deposition (Bencs et al., 2008 and reference

329 therein). To further investigate elemental categorization, the application of enrichment

330 factors (EFs) was also applied.

331   The calculation of EFs also classifies the registered elements into two groups

332 according to their origin in $PM_{2.5}$. The calculation of EFs is a commonly used tool, which

333 is applied in studies involving elemental bulk analysis of atmospheric aerosols (Hoornaert

334 et al., 2004; Lonati et al., 2005; Samara and Voutsa, 2005; Manoli et al., 2006). EFs

335 indicate whether the observed concentration of a specific element is enriched in

336 comparison to the concentration which would be expected if the element would only

337 originate from a particular source. A crustal EF of a specific element $EF_{crust}(X)$ is defined

338 as follows:

339 $$EF_{crust}(X) = \frac{\left(C_x / C_{ref}\right)_{aerosol}}{\left(C_x / C_{ref}\right)_{crust}} \quad\quad [1]$$

340 Where C_x is the concentration of a specific element in the aerosol or in the crust and C_{ref}

341 the concentration of the reference element in the aerosol or in the crust (Seinfeld and

342 Pandis, 1998). Several elements, such as Si, Al, Fe, Ti and Sc, have been reported in

343 literature as reference elements for the calculation of crustal enrichment factors

344 (Hacisalihoglu et al., 1992; Van Malderen et al., 1996). In the majority of the studies,

345 either Al or Fe has been selected as a reference element. In the area of Menen, both

346 elements could be considered as having negligible anthropogenic sources. However,

347 taking into account the average relative standard deviations of the detection of Fe and Al

348 by means of ED-XRF, with respective values of 3.5% and 43%, Fe was selected in this

349 study as the crustal reference element. For the average elemental concentrations in soil,

350 the crustal averages reported by Mason et al. (1966) were applied.

351   According to the value of the EF, the nature of the source can be evaluated. If the

352 EF of an element approaches unity, the predominant source of this element is crustal.

353 Strictly following the definition of the EF, one would expect an element to be enriched in

354 case the EF value is larger than 1. However, threshold values of 4 (Hacisalihoglu et al.,

355 1992) and 5 (Voutsa et al., 2002) have been proposed in literature, in order to account for

356 possible local variations in soil composition. In this study the threshold value is set at 4,
357 consequently EF>4 suggest that a significant fraction of the element is contributed from
358 non-crustal sources.

359   The statistical distribution of the EF values for $PM_{2.5}$ collected in Menen during 4
360 sampling periods is presented in Figure 4. All elements, which were previously classified
361 in the first group according to their relative abundance in each $PM_{2.5}$ sample (Figure 3),
362 are represented by EF values close to one (Al, Si, Ca, Ti, Fe) or smaller than 4 (K and
363 Mn). It can be concluded that these elements mainly originated from natural (crustal)
364 sources. However, all elements which were previously classified in the second group
365 according to their scattered relative abundance in each sample (Zn, Pb, S, Cl, V, Cr, Ni,
366 Cu, Br) were characterized by EF values ranging from 4 to 1000 and are considered
367 enriched. Moderate EFs, with median values ranging from 5 to 10, were determined for
368 the elements V, Cr and Ni. The elements Cu and Zn were more enriched in $PM_{2.5}$
369 according to their EF with median values between 50 and 500. S, Cl and Pb, were the
370 most enriched elements in $PM_{2.5}$, with median EF values ranging from 500 to 1000.
371 These elements probably originated from nearby industrial activities. The interquartile
372 ranges from the enriched elements showed some variation, which can probably be
373 attributed to meteorological circumstances. The smallest interquartile ranges were
374 observed for the elements Ni, Zn and Pb; the largest interquartile range was observed for
375 Br.

376

377 **3.5 Source apportionment**

378   The PCA is a widely used technique to simplify large data and to extract small
379 number factors to analyze relationship among the observed variables. Recently, several
380 studies has applied PCA to identify and characterize the emission source of $PM_{2.5}$
381 (Almeida et al., 2006a,b; Moreno et al., 2006; Manoli et al., 2006). This proves continued
382 wider acceptability of PCA in aerosol science. In addition to PCA; CMB and PMF also
383 offer the possibility to recover directly unknown source profile from ambient data. Some
384 of the example studies on CMB and PMF applications for source categorization of $PM_{2.5}$
385 include Pekney et al. (2006), Morishita et al. (2006); Hwang et al. (2007); Kim et
386 al.(2007), Lee et al. (2008), Marmur et al. (2007), Rizzo and Scheff (2007) and Viana et

387 al. (2008). However, these complex and powerful models/techniques are used with
388 numerous underlying assumptions and limitations (Seinfeld and Pandis, 1998). Hence, in
389 the present study we only focus on the use of HCA and PCA for the multivariate analysis
390 of $PM_{2.5}$ data.

391

392 *3.5.1 Hierarchical cluster analysis (HCA)*

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

398   As can be seen from the dendrogram of the ions, they can be categorized in 3
399 groups. The group #1 includes F^-, Mg^{2+}, Ca^{2+}, K^+, Cl^-, whereas groups #2 and #3 include
400 NH_4^+, NO_3^-, and SO_4^{2-}, respectively. Fine particles are formed primarily by combustion
401 and/or secondary chemical reactions in the atmosphere. The observation in the ion
402 dendrogram shows the likely existence of secondary chemical reactions over Menen i.e.
403 the conversion of SO_2 to SO_4^{2-} and from NO_2 to NO_3^-. These gaseous precursors are
404 emitted from various anthropogenic activities, specifically by industrial and vehicular
405 exhausts. Further it also indicates that NH_4^+ ion may neutralize the fine aerosol acidity
406 and may appear in partially neutralized forms as $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl over
407 Menen. These results also seem in accordance with a study of Bencs et al. (2008), who
408 studied the water-soluble fractions at 6 different places in Belgium. The dendrogam of
409 various elements also classifies them in to three main categories (Figure 5). Group #1
410 mainly consists of anthropogenic elements, while group #2 includes crustal elements. The
411 S was distinctly placed in group #3. This shows the existence of S sources over Menen.
412 The industrial area nearby Wervicq might be an important emission source of S, since it
413 emitted 1900 ton of SO_2 in 2003. Another industrial emission source, which emitted 340
414 tons of SO_2 in 2002, is situated 3 km north-westerly towards Rollegem (MIRA, 2006).

415

416 *3.5.2 Principal component analysis (PCA)*

417   The PCA was used with varimax rotation and Kaiser normalization to study the

418   relationships between the ions and elements. The application of varimax rotation can

419   maximize the variance of the factor loading and hence make the results more easily

420   interpretable. Tables 4 and 5 show the results of the factor analysis of daily

421   concentrations of ions and elements at Menen. Factor loading determine the most

422   representative species in each factor and a loading > 0.7 is typically regarded as excellent,

423   whereas a loading <0.3 as very poor. Each of these factors can be identified as either an

424   emission source, or a chemical interaction. As can be seen from Table 4, factor #1 has a

425   high loading for NH_4^+, SO_4^{2-} and NO_3^- species with a variance of 41%; which supports

426   the dominance of these species over Menen and the existence of secondary aerosol

427   formation reactions. Similar results were also suggested by HCA as explained there. The

428   NO_3^- and SO_4^{2-} ions are generally found to be produced as secondary aerosol during

429   combustion, biomass burning and vehicular emissions (Seinfeld and Pandis, 1998) and by

430   the neutralization of ammonia. Hence it can be concluded that these sources dominate

431   over the border area near Menen.

432   The factor #2 has high factor loading of F^-, Cl^-, NO_3^- and K^+. These ions have

433   been mainly assigned to coal/wood burning (Khalil and Rasmussen, 2003; Yuan et al.,

434   2006). Some open fires and incinerator activities have also been reported in the vicinity

435   of Menen (Van Lieshout et al., 2001). Almeida et al. (2006b) suggest that a high K/K+

436   ratio (~ 4) indicate a high content of mineral aerosol transported from the North of Africa

437   and South of Europe. In the present case the ratios vary from 0.78 to 0.98 during various

438   seasons and hence the high loading of K^+ together with other high loading species

439   indicate the influence of industrial and traffic related activities on the $PM_{2.5}$ composition.

440   Only Cl^- and Mg^{2+} show high loading for factor #3. The Mg^{2+} is found to be related to

441   exposed soil, unpaved roads and construction activities, where as Cl^- ions is mainly

442   related to sea-salt particle contribution. Sea salt particles generally have a short

443   atmospheric life-time due to their rather rapid deposition. This might be the reason for

444   their appearance in factor #3, with only 15% variance.

445   Table 5 show the PCA results for various elements and groups them in 4 factors.

446   Factor #1 has a high factor loading of mixed crustal and anthropogenic elements e.g. S,

447   Si, Al, K, Ti, Ca, Fe, with moderate loading of Cl, Cr, Mn, Zn and Pb, and represents a

448 variance of around 53%. High loading of Fe, Mn and Cr indicate towards road dust
449 (Manoli et al., 2006). However, the loading of other metals also indicates a relation with
450 more sources such as tire wear (Zn), and vehicular emission (Pb). Factor #2 has a
451 relatively high factor loading for anthropogenic elements (Cr, Cu and Zn). The Zn is
452 emitted from lubricant oil, brake linings and tires (Song et al., 2006) and Cu has been
453 related with diesel engines (Samara et al., 2005). Factor #3 has a significant loading for
454 V, Mn, Ni and Pb. The Pb was used in the past as an important anti-detonator in gasoline.
455 However, relative loading of other metals also suggest influence of industrial sources and
456 it can be understood as there are various industries near the border area of Belgium and
457 France. There are coke-ovens or steel industry in Zelzate, around 70 km to the north of
458 Menen and depending on the meteorological conditions, these can influence the
459 composition of $PM_{2.5}$. Furthermore, factor #4 is characterized by a high loading of Br and
460 Rb and this cab be related to the natural as well as industrial sources.

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

466

467 **3.6 $PM_{2.5}$ composition in relation to backward trajectories**

468 In the above section it has been observed that the water-soluble ionic species and
469 mainly the anthropogenic elements show considerable daily variation at Menen. These
470 daily variations were a function of meteorological circumstances, local sources of air
471 pollution and long-range transports. The long-range sources of air pollution can be
472 tracked by combining information about the composition of particulate matter with
473 backward trajectory information. The parameters selected for the backward trajectories
474 were chosen at a starting point of 20 meters above sea level and a backward counting
475 time of 120 h.

476 After combining each sample with its corresponding daily backward trajectory it
477 could be concluded that the anthropogenic elements in $PM_{2.5}$ were strongly dependent on
478 the origin and the track of the air masses before reaching the sampling site. According to

479   the backward trajectories, the samples could be classified into 3 groups. Typical

480   backward trajectories characterizing group #1, group #2 and group #3 are shown in

481   Figure 6. The group #1 includes samples which were characterized by the lowest

482   concentrations of all anthropogenic elements and high concentrations of Cl. In these cases

483   the backward trajectories indicated a track which originated in the Atlantic Ocean and

484   solely passed over it before reaching the site. However, in these samples Cl originating

485   from marine aerosols occurred in relatively elevated concentrations, reaching a mean

486   value and a corresponding 95% confidence limit of 125 ± 40 ng m^{-3}.

487   Group #2 was categorized by moderately increased concentrations of various

488   anthropogenic elements. In these cases the backward trajectories indicated tracks, which

489   originated in the Atlantic Ocean and subsequently passed over continental areas before

490   reaching the sampling site. Depending on the continental site over which it passed,

491   different anthropogenic elements were enriched in PM$_{2.5}$. The most elevated

492   concentrations in the group #2 were registered mainly for the elements V (5.2 ± 1.4 ng m^{-}

493   ^{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

494   m^{-3}) when the trajectories originated from the Atlantic Ocean, and moved over the United

495   Kingdom before reaching the site. Backward trajectories also indicating that when

496   trajectories spend most of their 5-day time over the United Kingdom relatively enriched

497   concentrations of the elements V (5.2 ± 1.4 ng m^{-3}), Ni (2.8 ± 0.7 ng m^{-3}), Zn (35 ± 11 ng

498   m^{-3}) and Pb (20 ± 5 ng m^{-3}) were observed in PM$_{2.5}$. Only moderately increased

499   concentrations of the elements V, Cr, Cu, Zn and Pb were detected in case backward

500   trajectories originated from the Atlantic Ocean passed over the North of France.

501   Group #3 included samples which were characterized by increased concentrations

502   of the anthropogenic elements and low related 95% confidence limits: V (7.0 ± 2.5 ng m^{-}

503   ^{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}),

504   Pb (45 ± 13 ng m^{-3}), S (1160 ± 240 ng m^{-3}). These samples corresponded to backward

505   trajectories originating in continental areas, such as Hungary, Poland or Germany, and air

506   masses moving solely over continental areas, such as Germany, and France.

507

508   **4. Conclusions**

509   The ionic and elemental fractions of $PM_{2.5}$ were analyzed using IC and ED-XRF.

510   The water-soluble ion fraction mostly contained the ions NO_3^-, SO_4^{2-} and NH_4^-; whereas

511   all the other ions occurred at a concentration level below 1 µg m^{-3}. The elemental

512   composition of $PM_{2.5}$ could be classified into two distinct groups according to their

513   relative abundance in fine particles. Group #1 contained the natural elements, which

514   occurred in proportional concentrations in each sample. Group #2 contained the

515   anthropogenic elements, which occurred in more scattered relative abundances. The EF

516   vs. soil calculations confirmed the respective natural and anthropogenic origin of the

517   elements in both groups. Moreover, the EF indicated Pb and Cl, followed by Cu and Zn

518   were the most enriched elements in $PM_{2.5}$ in Menen. Further the results also show that the

519   aerosol composition in Menen varies considerably from day to day. The application of

520   multivariate analysis shows the occurrence of secondary aerosol formation reactions and

521   the existence of both natural (crustal) as well as anthropogenic sources (vehicular,

522   industrial) of ions and elements. Combining the backward trajectory information with

523   concentration levels of the anthropogenic elements indicates that the air masses having an

524   origin and a track over the Atlantic Ocean contained the lowest levels of anthropogenic

525   elements. Yet, air masses either originating from the Atlantic Ocean or from a continental

526   area in combination with a track passing over continental areas, contained elevated

527   concentrations of anthropogenic elements. The composition of the fine aerosol samples

528   was a function of local, meteorological and seasonal circumstances at Menen. However a

529   cross-border air pollution influence could be discerned, which mainly affected the

530   anthropogenic elements in $PM_{2.5}$.

531

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802

Table 1: Overview of the sampling periods

804

Sampling period	Date	Season	Samples (n)*
SP1	16-04-03 until 13-05-03	Spring	28
SP2	20-08-03 until 16-09-03	Summer	28
SP3	01-10-03 until 28-10-03	Autumn	27
SP4	26-11-03 until 20-12-03	Winter	28

805 * for both ions and elements.

806
807
808
809 **Table 2: Mean ionic (µg m^{-3}) composition of PM$_{2.5}$ over Menen during various seasons**
810
811

Ions	Spring			Summer		
	Conc. $\pm$ CL$_{0.95}$	Min	Max	Conc. $\pm$ CL$_{0.95}$	Min	Max
F$^-$	0.01 $\pm$ 0.00	0.00	0.02	0.03 $\pm$ 0.02	0.01	0.31
Cl$^-$	0.26 $\pm$ 0.05	0.03	0.55	0.25 $\pm$ 0.11	0.07	1.67
NO$_3^-$	8.12 $\pm$ 3.31	0.39	37.3	4.17 $\pm$ 1.94	0.94	28.1
SO$_4^{2-}$	4.76 $\pm$ 1.39	0.31	14.1	3.23 $\pm$ 0.52	1.01	6.82
NH$_4^+$	2.34 $\pm$ 0.59	0.21	5.91	1.92 $\pm$ 0.36	0.64	3.53
K$^+$	0.12 $\pm$ 0.03	0.01	0.36	0.13 $\pm$0.04	0.05	0.59
Mg^{2+}	0.02 $\pm$ 0.01	0.01	0.04	0.02 $\pm$ 0.00	0.01	0.04
Ca^{2+}	0.08 $\pm$ 0.01	0.01	0.28	0.06 $\pm$ 0.02	0.03	0.30

Ions	Autumn			Winter		
	Conc. $\pm$ CL$_{0.95}$	Min	Max	Conc. $\pm$ CL$_{0.95}$	Min	Max
F$^-$	0.02 $\pm$ 0.01	0.01	0.15	0.10 $\pm$ 0.03	0.01	0.26
Cl$^-$	0.37 $\pm$ 0.11	0.11	1.26	0.89 $\pm$ 0.30	0.03	3.52
NO$_3^-$	4.10 $\pm$ 1.14	0.66	11.10	5.28 $\pm$ 1.32	0.48	13.3
SO$_4^{2-}$	3.70 $\pm$ 1.13	0.96	15.6	4.99 $\pm$ 2.07	0.23	16.9
NH$_4^+$	1.74 $\pm$ 0.45	0.48	4.33	1.88 $\pm$ 0.66	0.12	6.05
K$^+$	0.21 $\pm$ 0.08	0.05	1.14	0.25 $\pm$ 0.08	0.04	0.84
Mg^{2+}	0.03 $\pm$ 0.01	0.01	0.10	0.03 $\pm$ 0.01	0.01	0.08
Ca^{2+}	0.05 $\pm$ 0.01	0.01	0.14	0.07 $\pm$ 0.02	0.02	0.18

812 (CL: Confidence limit)
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815 **Table 3: Mean elements (ng m^{-3}) composition of PM$_{2.5}$ over Menen during different seasons**
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Elements	Spring			Summer		
	Average ± CL$_{0.95}$	Min	Max	Average ± CL$_{0.95}$	Min	Max
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	1576	599 ±109	141	1160
Cl	125 ±17	48.3	244	116 ±20	51	261

Elements	Autumn			Winter		
	Average ± CL$_{0.95}$	Min	Max	Average ± CL$_{0.95}$	Min	Max
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	1011	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	1258	830 ±250	212	2538
Cl	227 ±55	93.4	822	432 ±147	80	1817

817 (CL: Confidence limit)
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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	<u>0.65</u>	<u>0.63</u>
NO_3^-	<u>0.58</u>	**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**

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**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	<u>0.60</u>	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	<u>0.49</u>	<u>0.63</u>	0.21
K	<u>0.57</u>	0.26	<u>0.49</u>	0.22
Ca	**0.68**	<u>0.60</u>	0.05	0.18
Ti	<u>0.54</u>	**0.76**	0.05	0.12
Fe	<u>0.50</u>	**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	<u>-0.52</u>	0.00	0.23	<u>0.49</u>
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**

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832   **Figure 1: Location of Menen (Source: Google Earth).**
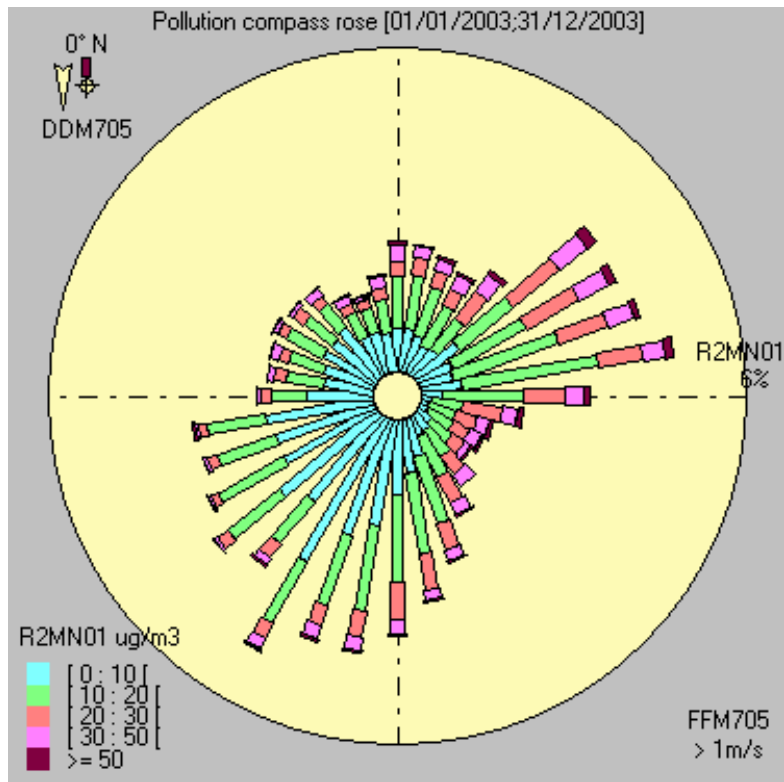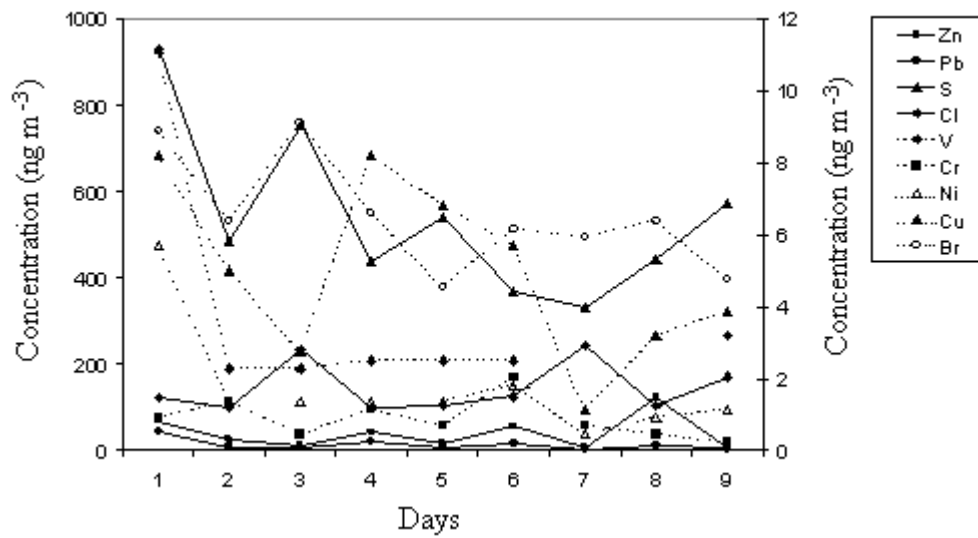
Figure 2: Pollution roses for PM$_{2.5}$ at Menen during 2003

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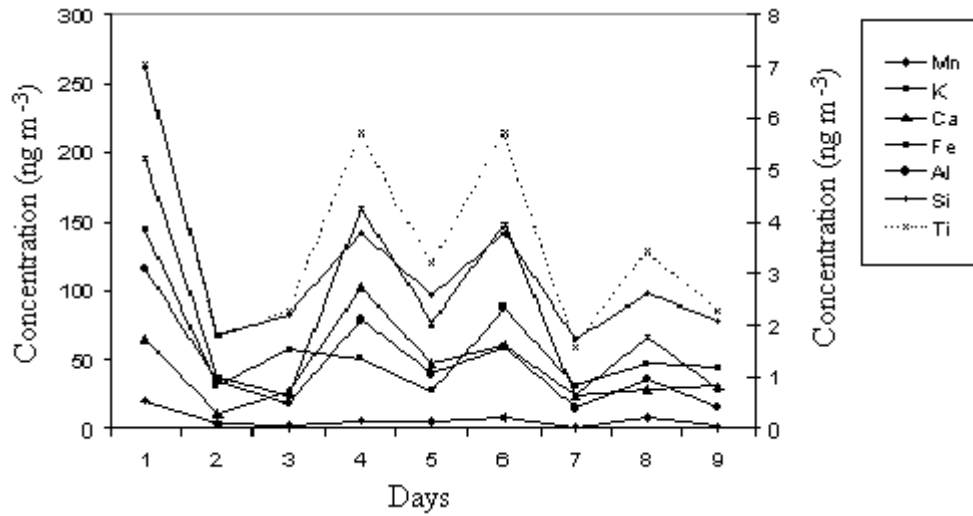
Figure 3a: Occurrence of the crustal elements in PM$_{2.5}$ over Menen (Doted lines depicts the concentration on secondary y-axis)
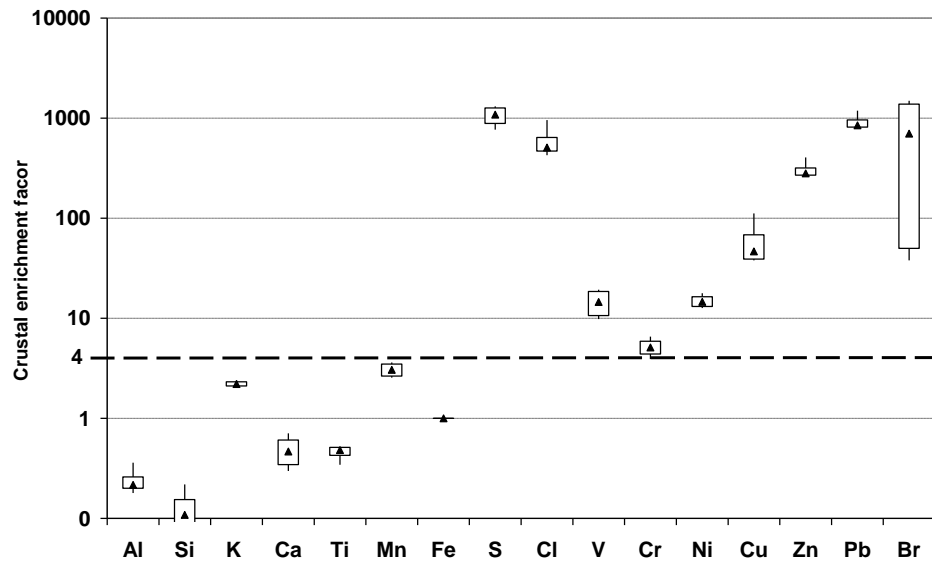

Figure 3b: Occurrence of the anthropogenic elements in PM$_{2.5}$ over Menen (Doted lines depicts the concentration on secondary y-axis)
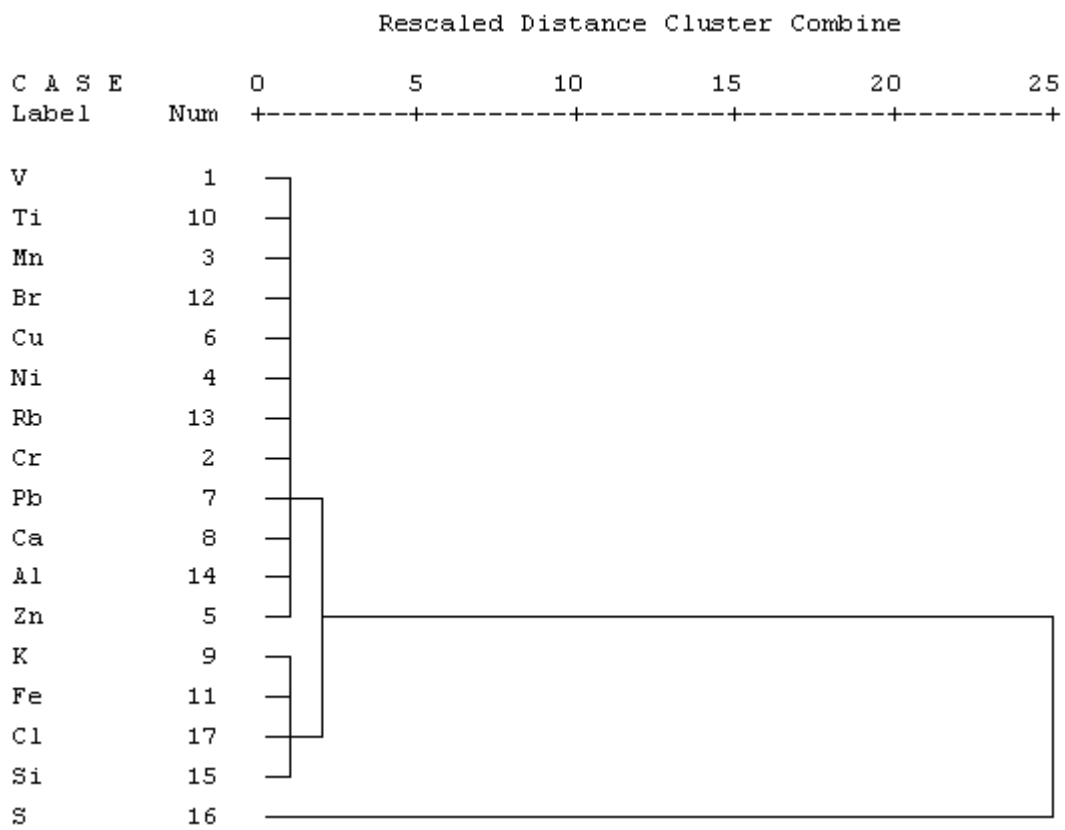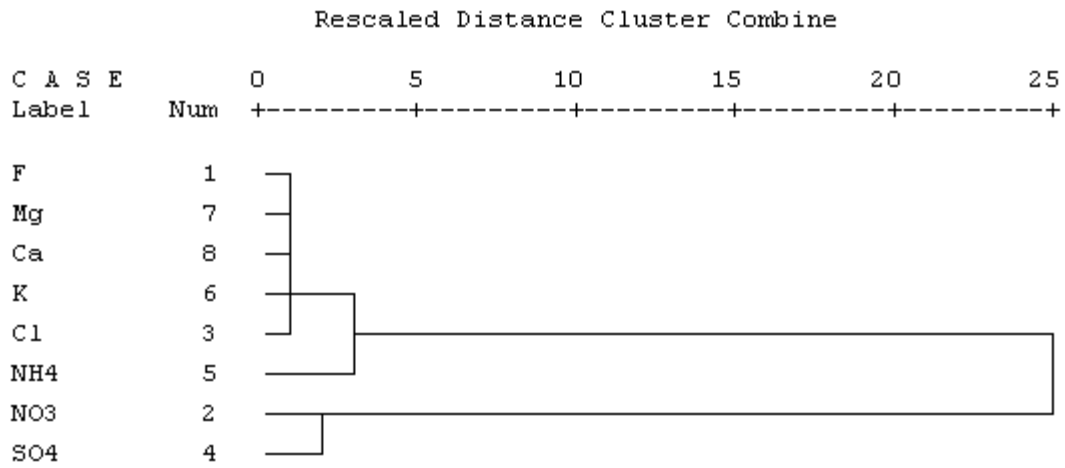
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850 **Figure 4: Crustal EF for PM$_{2.5}$ samples collected in Menen: median (black triangle), minimum /**
851 **maximum value and interquartile range (white rectangle)**

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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    ─┘
```

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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    ─────────────────────────────────────────────┘
```

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858   **Figure 5: Hierarchical cluster analysis of ions (above) and elements (below) using seasonal average**
859   **levels at Menen.**

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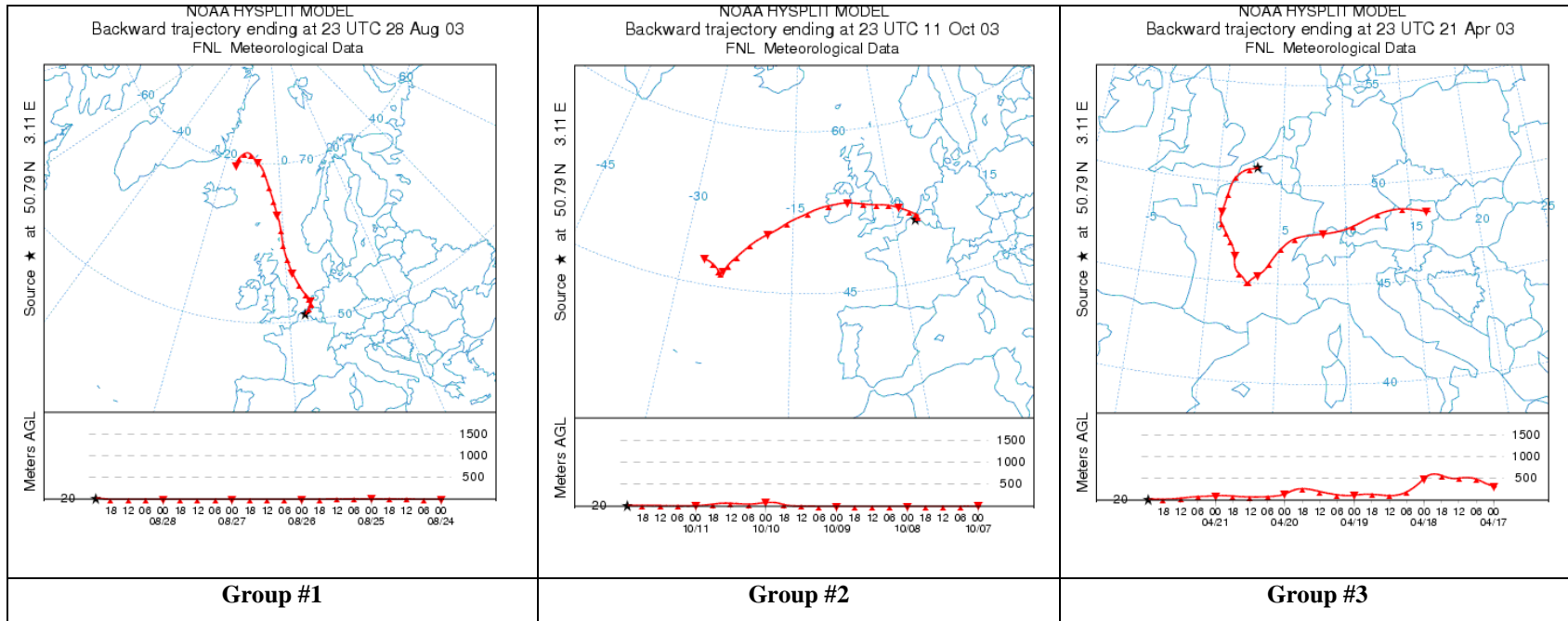
Figure 6: Typical backward trajectories corresponding to the 3 groups.

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