Composition of PM2.5 and PM1 on High And Low Pollution Event Days and its relation to Indoor Air Quality In A Home For The Elderly

Anna Buczynska[a], Agnieszka Krata[a], Rene Van Grieken[a], Andrew Brown[b], Gabriela Polezer[b], Karolien De Wael[a], Sanja Potgieter-Vermaak[b,c*].

[a]Department of Chemistry, University of Antwerp, Antwerp, Belgium.
Anna.buczynska@ua.ac.be; rene.vangrieken@ua.ac.be
[b]Division of Chemistry & Environmental Science, Faculty of Science & Environment, Manchester Metropolitan University, Manchester, United Kingdom,
s.potgieter@mmu.ac.uk; andrew.brown8@stu.mmu.ac.uk, gabopolexer@gmail.com
[c]Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.

ABSTRACT

Many studies probing the link between air quality and health have pointed towards associations between particulate matter (PM) exposure and decreased lung function, aggravation of respiratory diseases, premature death and increased hospitalisation admissions. It is believed that the chemical composition and physical properties of PM may contribute significantly to these adverse health effects. As part of a Belgian Science Policy project ("Health effects of particulate matter in relation to physical-chemical characteristics and meteorology"), the chemical composition (elemental and ionic) and physical properties (PM mass concentrations) of PM were investigated, indoors and outdoors of old age homes in Antwerp. The case reported here specifically relates to high versus normal pollution event periods. PM mass concentrations for PM1 and PM2.5 fractions were determined gravimetrically after collection via impaction. These samples were analysed by EDXRF spectrometry and IC for their elemental and ionic compositions, respectively. During high pollution event days, indoor PM mass concentrations reached 53 $\mu g \ m^{-3}$ and 32 $\mu g \ m^{-3}$ while outside concentrations were 101 $\mu g \ m^{-3}$ and 46 $\mu g \ m^{-3}$ for PM2.5 and PM1, respectively. The sum of nss-sulphate, nitrate and ammonium, dominated the PM composition, and contributed the most towards an increase in the PM during the episode days constituting 64% of ambient PM2.5 compared to 39% on non-episode days. Other PM components, such as mineral dust, sea salt or heavy metals were found to be considerably higher during PM episodes. Zn and Pb were found at the highest concentrations in both PM2.5 and PM1. Acid-base ionic balance equations were calculated and point to acidic aerosols during event days and acidic to alkaline aerosols during non-event days. No significant sources of indoor pollutants could be identified inside the old-age home as high correlations were found between outdoor and indoor PM, confirming mainly the outdoor origin of indoor air.

Keywords: indoor air quality, high pollution event, PM characterisation, acidic aerosol, elderly

1

1. Introduction

Numerous epidemiological and clinical studies have been conducted over the last decade and a half and they indicate associations between particulate matter (PM) exposure and various health effects (Strak et al., 2012; Stranger et al., 2009 and references therein; Fuentes-Leonarte et al., 2009; Jacobs et al., 2012 and references therein). It is shown that increases in PM exposure often lead to increased hospital admissions, especially in susceptible cohorts such as the elderly and individuals with cardiopulmonary diseases (Di Ciaula., 2012). Although earlier studies focused on PM mass concentrations, it is nowadays commonly believed that the chemical and biological composition of the particulate matter may also contribute significantly to detrimental health effects (Gemenetzis et al., 2006; Bell et al., 2009).

A Belgian Science Policy project ("Health effects of particulate matter in relation to physical-chemical characteristics and meteorology"), which this study was a part of, intended to investigate acute, short-term health effects of PM and its composition in the elderly part of the population (Jacobs et al. 2012). The sampling of air pollution was designed, so that there was a contrast in ambient PM concentrations between the first and second visit of a patient during which a set of clinical measurements was performed. More information may be found in Jacobs et al. (2012). This was possible thanks to the predictions of PM concentrations (4 days in advance) made by Ircel (Belgian Interregional Environment Agency). The air particulate matter was sampled both indoors and outdoors of the building. Since this part of the population spends most of their time indoors, monitoring the indoor air and close outdoor environment in place of the personal

66   exposure seems justified. Brunekreef et al. (2005) found highly correlated time-series of

67   pairs of personal, indoor and outdoor fixed site PM2.5 and black smoke concentrations in

68   a small population of elderly cardiovascular patients. - The concentration of the PM

69   inside of a building is mainly governed by indoor generation of particles, the

70   concentration of the particles outside, the rate of air exchange and the depositional

71   characteristics of the particles (Gemenetzis et al., 2006). For those reasons this study

72   monitored both environments.

73   This paper is thus one of a handful reporting on the chemical (elemental composition

74   and water-soluble ion concentrations, including secondary aerosols) and physical (mass

75   concentrations) differences between ambient and indoor concentrations of PM2.5 and

76   PM1 during periods of high and low pollution events in old-age home (Czagani

77   Broechem, Belgium). We chose this location as it was characterised by the highest

78   pollution event observed in Antwerp during the course of the project (2007-2010). The

79   sampling campaign covers days before, during and after the event. Thus, in addition to

80   investigation of the relationship between the outdoor and indoor pollutants, a comparison

81   between days with "normal" PM concentrations or so-called non-episode days (NED's)

82   and episode days (ED's) could be made.

83   A target value of 25 μg m^{-3} for PM2.5 entered into force in 2010 under the Ambient

84   Air Quality and Cleaner Air Act for Europe (Council Directive 2008/50/EC) and will

85   enter into force as a limit value in 2015. Although a yearly average indoor PM2.5

86   guideline value of 15 μg m^{-3} in Flanders, Belgium exists, we decided to use the 24-h

87   PM10 indoor air quality guideline value (Stranger et al., 2007) of 40 μg m^{-3}. In this study,

88   the PM10 concentration was not measured; however, based on our unpublished results

89   from simultaneous PM10 and PM2.5 mass measurements in various indoor locations in

90   Belgium, PM2.5 accounts on average for 73% of PM10 mass concentration. Therefore,

91   the 24h PM2.5 indoor value higher than 29.2 µg m^{-3} stands for an ED in this study and

92   lower than 29.2 µg m^{-3} stands for a NED. This value is not unreasonable taking into

93   account that the WHO guideline values for short term PM2.5 exposure is 25 µg m^{-3} 24-h

94   mean, and as recently as 2011, this value has also been adopted as an indoor air guideline

95   value (WHO, 2011).

96

97   **2. EXPERIMENTAL**

98

99   **2.1 Sampling location**

100

101   Broechem is a village (12 km^2) located in the province of Antwerp, around 10 km to the

102   east of the Antwerp city (N50º10', E4º36') with about 4000 inhabitants. The sampling

103   was performed in the Czagani old-age home, with around 120 inhabitants and 100

104   workers at the time of the sampling. The old-age home has a surface area of about 6500

105   m^2 and three floors. The building, built in 1994, is both mechanically and naturally

106   vented. The ground floor (where sampling was performed), was a carpeted open space, it

107   served as a dining room, cafeteria and the reception; the cleaning thereof was performed

108   6 days per week. The building is situated about 1 km from the highway and 300 m from a

109   major village road.

110   Local pollution sources include mainly traffic and domestic heating. Other potential

111   sources include the harbour of Antwerp (located to the north of the city), a large

112 petrochemical plant, a municipal waste incinerator, and a nonferrous plant to the south of

113 Antwerp (Stranger, 2005).

114

115 **2.2 Sampling methodology**

116

117 PM was collected indoors and outdoors simultaneously by means of impaction (Harvard

118 impactors from Air Diagnostics and Engineering Inc., Naples, ME, USA) and operated at

119 a flow rate of 23 L min $^{-1}$ for PM1 collection and 10 L min^{-1} for PM2.5 collection.

120 Membrane Teflon filters were used (2 µm pore size and 37 mm in diameter) to collect the

121 particles over periods of 24 hours. Filter changing took place in the mornings, during

122 which time the flow rate was checked. Indoor sampling took place in the ground floor

123 dining room and the impactors were positioned so that the inlets were as close as possible

124 to the breathing zone of people (about 1 m above the ground). Outdoor sampling was

125 done at the back of the building in order to avoid direct influence from the automobile

126 exhaust emissions originating from a small parking lot in front of the building. Since the

127 building was only 3 storeys high, the ground floor concentrations are assumed

128 representative for all floors. As shown by Gemenetzis et al. (2006) in the study conducted

129 in university rooms in Greece, although a slight decrease in PM10 and PM2.5 mass

130 concentrations was observed with an increase in the elevation level, it could be

131 considered as negligibly small up to the 5th floor. The effect of elevation (up to the 40th

132 floor) on indoor particulate concentrations was also studied by Chao et al. (2002), who

133 reports no significant difference in the PM10 and PM2.5 mass concentrations at different

134 levels.

135

136   Co-located duplicate samples of PM2.5 were collected both in indoor and outdoor sites,

137   they were however used only for the determination of the mass concentration and were

138   not subjected to further examinations for elemental and ionic measurements. Thus, the

139   PM mass concentration values are the arithmetic mean of two measurements. The results

140   of the duplicate sampling of PM2.5 agreed with each other to within 5%, exceeding this

141   difference only four times, with the highest being 16%.

142

143   **2.3. Analysis**

144

145   The masses of the collected particulates were determined gravimetrically using a

146   microbalance with a resolution of 1 μg (Mettler Toledo MX5, Mettler Toledo, Columbus,

147   USA) in an environmentally controlled laboratory. Filters were conditioned at 20 °C and

148   50% relative humidity, for at least 24h before weighing, and stored in Petri dishes until

149   sampling. After sample collection, they were conditioned again, weighed and stored at

150   4 °C until the analysis.

151   The filters were analysed firstly by means of X-ray fluorescence (Epsilon-5 XRF,

152   PANAnalytical, The Netherlands) in order to determine the bulk elemental

153   concentrations of selected elements (Al, As, Ca, Cd, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Sb,

154   Se, Si, Sr, Ti, V, Zn) and afterwards subjected to Ion Chromatographic (IC) analysis

155   (Dionex DX-120, Dionex, USA) for anion (Cl^-, NO_3^-, SO_4^{2-}) and cation (Ca^{2+}, K^+, Mg^{2+},

156   Na^+, NH_4^+) concentrations. Procedures followed have been described elsewhere (Avigo

157   et al., 2008; Stranger et al., 2009). The IC detection limits (LODs) were estimated from

158   blank filters (three standard deviations of the concentration found in blank) using the

159   average air volume of PM2.5 and PM1 samples taken during the sampling campaign.

160   LODs were ranging from 3 ng m^{-3} for magnesium to 72 ng m^{-3} for sodium cation in

161   PM2.5, and from 1 ng m^{-3} to 30 ng m^{-3} in PM1 for the same cations, respectively.

162   Magnesium and calcium ions were generally found in very low amounts. Magnesium was

163   detected above its LOD in 63% of all samples, calcium, in 46%. All other ions were

164   detected in significant amounts in all samples. The precision was better than 3.6% for all

165   analytes (Bencs et al., 2008). For XRF analysis, the detection limits ranged from 0.7 for

166   vanadium and 32 ng m^{-3} for aluminium in PM2.5 and from 0.3 ng m^{-3} for vanadium to 13

167   ng m^{-3} for aluminium in PM1. Cd, Se and Sb were below the detection limits in all

168   samples, for other elements there were 11% of non-detects. The precision, expressed as

169   relative standard deviation of three repetitions was generally below 5%. Quality check of

170   these analyses was performed by calculating the correlation coefficients between

171   elemental-sulphur with sulphate-sulphur. R^2 values of 1 and 0.99 were found for indoor

172   and outdoor PM2.5, respectively. The PM1 correlation coefficients were 0.99 for both

173   indoor and outdoor PM. For chloride the values were somewhat lower, in indoor PM1

174   two outliers had to be excluded, the correlations had the R^2 equal to 0.98 and 0.95 in

175   PM2.5 indoors and outdoors, and 0.84 in indoor and 0.97 in outdoor PM1.

176   Identification of the origin of air masses was done for each day of the sampling

177   using 5-day backward trajectories performed with Hysplit model

178   (http://www.arl.noaa.gov/HYSPLIT.php). Initial heights of 2 m and 20 m above ground

179   level were investigated.

180   All statistical calculations were performed using an IBM SPSS Statistics, version

181   22.0 software package (IBM Corp., Armonk, NY, USA).

182

183   **3. RESULTS AND DISCUSSION**

184

185   **3.1 Mass concentrations**

186

187   Descriptive statistics of daily PM2.5 and PM1 concentrations for the whole campaign,

188   episode days and non-episode days are summarized in Table 1. Mean outdoor

189   concentrations of 77.0μg m^{-3} and 36.7 μg m^{-3} for PM2.5 and PM1, respectively, are

190   reported for episode days. Mean indoor concentrations were 43 % and 29 % lower for

191   PM2.5 and PM1, respectively (Table 1). PM1 therefore constitutes 53% of PM2.5 on

192   average (48±12 % for EDs and 55±11 % on NEDs) in outdoor air and 64 ±8 % (62±12 %

193   for EDs and 65±9 % on NEDs) indoors.. Maximum PM2.5 concentrations reached

194   101 μg m^{-3} (46.1 μg m^{-3} for PM1) outdoors and 53.5 μg m^{-3} (31.9 μm m^{-3} for PM1)

195   indoors. In context to the overall research project investigations, these values are

196   considerably higher than any of those measured during five other campaigns, in different

197   old-age homes in Belgium between years 2007-2010. These values are also much higher

198   than some of the values published across the literature, for example: in Birmingham

199   7.9 μg m^{-3} was reported for residential indoor PM2.5 (Jones et al. 2000), and 9.1 μg m^{-3}

200   in Oxford, England (Lai et al. (2004)). A maximum of 56 μg m^{-3} was observed for

201   outdoor PM2.5 in Canada (Cheng et al., 1998), and 66 μg m^{-3} (PM2.5 12 h day sample)

202   in a study of air quality in offices near a busy street in the centre of Antwerp (Horemans

203 and Van Grieken, 2010). The outdoor values are also higher than those found in the study

204 of Stranger et al. (2009) reporting on residential indoor air quality in Belgium, although

205 the average indoor concentration and maximum values reported were similar to the ones

206 reported here. Moreover, EDs' PM2.5 outdoor values exceeded those reported for PM10

207 during a yearly study at six different sites in Belgium (urban background to rural; 24-h

208 samples taken once a week) (Vercauteren et al. 2011). However, literature also indicates

209 much higher concentrations elsewhere, especially in Asia, for example, Ye et al. (2003),

210 in a yearly study in Shanghai, reported weekly averages of PM2.5 equal to 156 μg m^{-3}.

211 Chen et al. (2003) in their study of pollution episodes set the threshold value for ED's

212 and NED's at 150 μg m^{-3}.

213

214 Figure 1 gives the average ambient daily temperature, wind speed and relative humidity

215 during the study. Days with elevated PM concentrations (13, 18, 19 February) are

216 characterized by the lowest temperatures (0.8-1.4°C) and wind speeds (1.6-2.5 m s^{-1}).

217 The only exception is the 20th February where high concentrations of PM were measured

218 despite a maximum temperature of 6.4 °C and a wind speed of 2.8 m s^{-1}. Vecchi et al.(

219 2004), noticed typically an increase by 20-35% in both PM1 and PM2.5 on days when

220 wind velocity was lower than 2 m s^{-1}. In this study the increase of PM concentration

221 registered on episode days was much higher, on average 2.5 to almost 3 times higher,

222 compared to non-episode days. Wintertime increases in ambient pollutant concentrations

223 are frequently attributable to a combination of low level, persistent temperature

224 inversions and increases in emissions related to heating (Ye et al., (2003)). Additionally,

225 lower temperatures occurring during the winter season favour the persistence of particle

226 phase with respect to the gas phase, e.g. NH_4NO_3 (Vecchi et al., (2004)). Inversion was

227 evident on most days of high pollution events in our study (See Figure 1S in

228 supplementary material). Additionally, backward trajectory analyses revealed that

229 anticyclonic circulation of the air masses coincided with the episode days. On the 13th of

230 February, the impact of 120h trajectories was almost entirely regional (Germany, The

231 Netherlands and Belgium) and between 18th and 20th February the air masses originated

232 in the arctic region, passing Norway, Sweden, Germany and finally creating an

233 anticyclone over Belgium. As pointed out by Viana et al. (2007a), anticyclonic scenarios

234 lead to the development of thermal inversions, air mass stagnation and accumulation of

235 locally emitted pollutants. During NED's, air masses seemed to be impacted to a larger

236 extent by cleaner air from the Atlantic Ocean and the North Sea before reaching the

237 sampling location .This is especially visible during the third week of the study, in which

238 air masses travelled very long distances over the Atlantic Ocean before reaching

239 Belgium.

240 **Table 1.** Summary of the PM mass concentrations ($\mu g\ m^{-3}$) registered during the study.

	INDOOR		**OUTDOOR**	
	PM2.5	PM1	PM2.5	PM1
Minimum	10.6	5.8	11.4	5.3
Mean	**24.8**	**15.7**	**43.4**	**22.1**
Median	17.6	11.3	32.8	18.4
Standard deviation	14.6	8.7	27.7	13.1
Maximum	53.5	31.9	100.6	46.1

Event	**43.7**	**27.0**	**77.0**	**36.7**
Standard deviation	7.2	3.3	20.1	12.0
Non event	**15.4**	**10.0**	**26.7**	**14.8**
Standard deviation	2.9	2.0	8.1	5.2

241
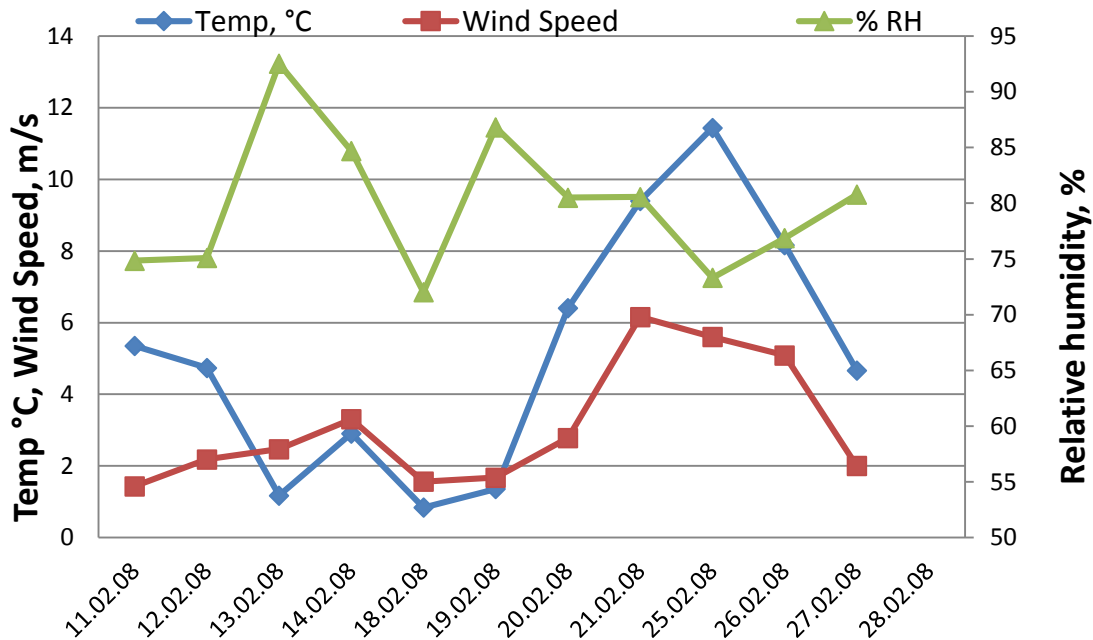
242

243 **Figure 1**. Ambient meteorological conditions during the sampling campaign
244

245 **3.2 Indoor - outdoor correlations in PM**

246

247 The degree of outside PM infiltration was gauged by determining straight-line indoor-

248 outdoor correlations for two fractions PM2.5-1 and PM1, thus using the value of the

249 correlation coefficient, R^2, as the indicator (Figure 2). PM2.5-1 fraction was obtained by

250 subtracting the concentrations found in PM2.5 and PM1. Mass concentration profiles for

251 PM2.5-1 match each other and this correlation is illustrated by an R^2 of 0.93. A lower R^2

252   of 0.74 was observed for PM1, but after removal of an outlier (13.02.08) the value was

253   close to that of the PM2.5-1 as is seen in the insert of Figure 2. The coefficients for both

254   fractions were considerably higher than those reported for PM2.5 in residences in

255   California (Geller et al., 2002), where the correlation coefficient was equal to 0.37. This

256   indicates that mass concentration increases on the outside are reflected on the inside and

257   one could deduce that a substantial fraction of indoor particles in our study penetrated -

258   from the outdoor environment.

259
260   The correlation between PM1 and PM2.5 (R^2) was equal to 0.86 when PM outdoors was

261   compared, and 0.97 for the indoor concentrations. The I/O ratios for PM2.5 was always

262   below 1, and for PM1, exceeded 1 only twice (thus 17% of cases, amounting to 1.08 and

263   1.36). This, together with high correlations of indoor to outdoor air reported above,

264   suggest no major indoor sources of particulate matter in the studied old-age home. PM1

265   decreased indoors by 29 % on average compared to outdoors and the PM2.5-1 fraction by

266   57 %. These decreases were similar on EDs and NEDs. It thus suggests a more effective

267   indoor penetration of fine particles than of supermicron PM2.5-1 particles. The building,

268   hence, offers a relatively good protection against exposure to supermicron particles and

269   to its components, although larger deposition velocities of these particles on window,

270   door and furniture surfaces could also have played a role.

271
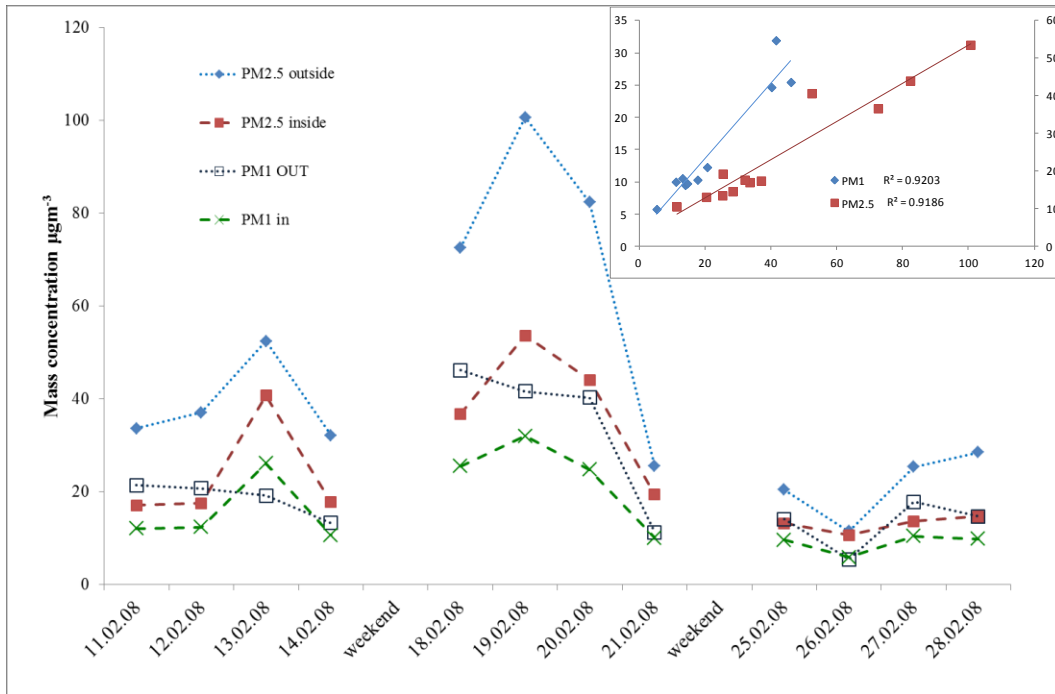
272
273
274   **Figure 2.** Indoor : Outdoor relationships for PM2.5 and PM1.
275

276
277   **3.3. Chemical mass closure of PM**

278

279   Chemical mass closure of the PM2.5, PM1 and PM2.5-1 was calculated using the results

280   obtained from both the IC and XRF analyses (Table 2). PM2.5-1 composition was

281   obtained by subtracting the concentrations found in PM2.5 and PM1; therefore larger

282   uncertainties may be associated with this fraction. Subsequently, the relative

283   contributions of PM components were calculated to illustrate the differences between

284   ED's and NED's and outdoor and indoor environments (Figure 3). As pointed out already

285   by Putaud et al. (2004), relative contributions reflect the differences in the sources and

286   processes controlling the aerosol composition as they are independent of dilution.

287   Additionally, outdoor-to-indoor transport of particles may modify the composition of

288   PM. Meng et al. (2007) found distinct infiltration factors (fraction of ambient PM found

13

289   indoors) for several components of PM2.5. For those reasons, the contributions of

290   secondary inorganic aerosols, crustal matter, sea salt, smoke and other elements

291   (including heavy metals) to collected PM size fractions was studied in detail.Crustal

292   matter, sea salt, non-crustal K (smoke origin) non-sea salt (nss) SO_4^{2-} were assessed

293   using the approaches published previously (Chan et al. (1997), Maenhaut et al. (2002),

294   Sillanpää et al. (2006)). Sea salt content was calculated from Na^+ and Cl^- concentrations,

295   nss-SO_4^{2-} from measured SO_4^{2-} and Na^+ and for both calculations, the composition of

296   standard sea water was taken into account. The concentrations of inorganic secondary

297   species (NH_4^+, NO_3^-) and "other" elements (As, Cr, Cu, Mn, Ni, Pb, Sr, V, Zn) were

298   determined directly from measurements.

299   Substantial amounts of PM, named "unidentified", resulted from subtracting the

300   reconstituted mass of each sample from total PM mass determined gravimetrically. Most

301   likely it consists largely of organic (OC) and elemental carbon (EC), which were not

302   measured in this study. Both, percentages of unidentified fraction and absolute values

303   obtained for PM2.5 (30% on outdoor ED's corresponding to 24.6 $\mu g\ m^{-3}$, and up to 60%

304   indoors on NED's, corresponding to 9.2 $\mu g\ m^{-3}$) are in agreement with the values

305   obtained for OC and EC component in other studies conducted in Belgium and Europe, in

306   which the major component of urban or regional background PM2.5 and PM10 appeared

307   to be organic matter (Maenhaut et al. (2002), Putaud et al., (2004), Querol et al. (2004a),

308   Sillanpää et al.(2006)). The OC+EC component is thought to originate mainly from

309   traffic emissions, heating and other combustion related processes. The "unidentified"

310   fraction prevailed in PM1 with concentrations twice that of the supermicron PM2.5-1

311   fraction.A fraction of an unaccounted PM mass may be as well water associated with

312   hygroscopic aerosol components (Maenhaut et al. (2002), Querol et al. (2004b)).

313   The relative contribution of unidentified species of particulate matter on ED's is

314   significantly lower than on NED's for both indoor and outdoor PM. This component thus

315   contributed less to the total PM on episode days than on non-episode days, although in

316   absolute values, it was about two times higher on ED's. The increase occurred both in

317   PM1 and PM2.5-1 to a similar extent.

318

319   **Table 2.** Contribution of PM components to outdoor and indoor PM2.5, PM1 and PM2.5-
320   1 on ED's and NED's. Concentration value ($\mu g\ m^{-3}$) is accompanied by 1σ.
321

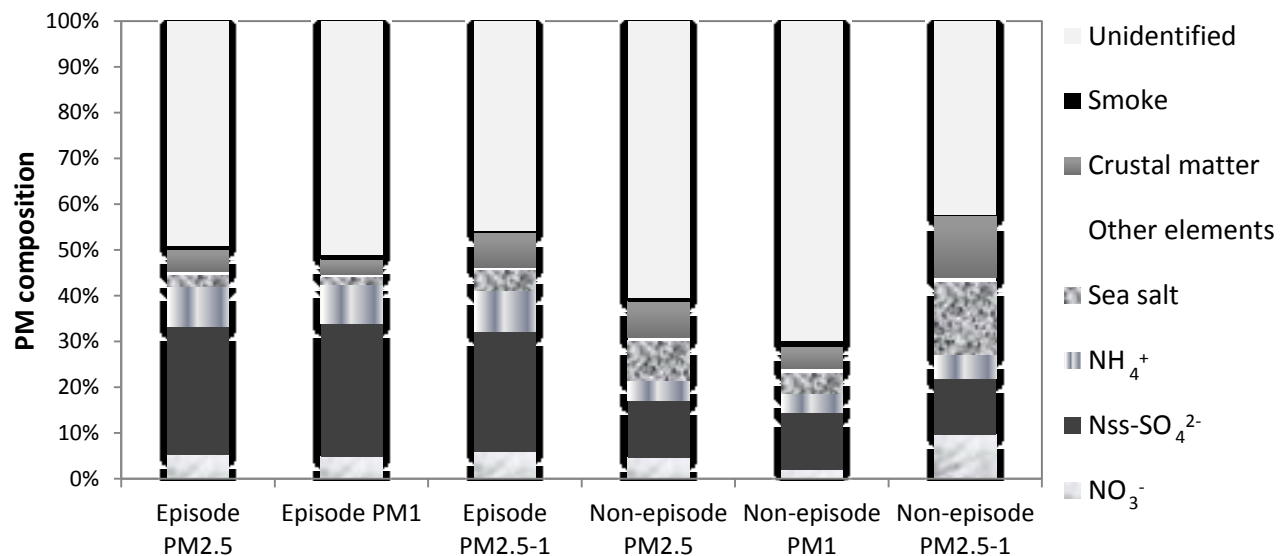| Outdoors								
	NO_3^-	Nss-SO_4^{2-}	NH_4^+	Sea salt	Other elements	Crustal matter	Smoke	Unidentified
ED PM2.5	22.9 ±5.3	18.2± 9.5	11.0±3.0	2.3± 0.9	0.26± 0.11	2.3± 0.7	0.30± 0.11	24.6 ± 9.4
ED PM1	11.3 ±4.7	5.8± 2.5	4.2± 1.3	1.1± 0.4	0.13± 0.06	0.4± 0.2	0.27± 0.10	16.0 ± 4.8
ED PM2.5-1	11.5± 3.6	12.4± 7.7	6.9± 2.9	1.3± 0.6	0.13± 0.05	1.9± 0.5	0.04± 0.03	8.6 ± 4.3
NED PM2.5	5.4 ±3.0	3.0± 1.5	2.0± 0.9	1.6± 0.6	0.14± 0.08	1.6± 1.2	0.14± 0.05	12.7 ± 5.9
NED PM1	3.1 ±1.5	1.7± 0.4	1.2± 0.4	0.6± 0.2	0.07± 0.04	0.3± 0.1	0.14± 0.07	7.8 ± 4.2
NED PM2.5-1	2.3 ±2.1	1.4± 1.2	0.8± 0.6	1.0± 0.5	0.07± 0.05	1.4± 1.1	0.01± 0.02	4.8 ± 3.0
Indoors								
ED PM2.5	2.2 ±1.2	12.1± 6.9	3.8± 1.7	1.2± 0.3	0.21± 0.08	2.1± 0.2	0.30± 0.08	21.2 ± 3.7
ED PM1	1.3 ± 0.8	7.9± 4.0	2.3± 1.1	0.4± 0.1	0.12± 0.03	0.9± 0.3	0.25± 0.06	13.8 ± 1.6
ED PM2.5-1	1.0 ± 0.6	4.2± 3.0	1.4± 0.7	0.7± 0.3	0.09± 0.05	1.2± 0.3	0.04± 0.03	7.4 ± 2.9
NED PM2.5	0.7 ± 0.3	1.9± 1.0	0.7± 0.3	1.3± 0.6	0.11± 0.05	1.2± 0.4	0.14± 0.03	9.2 ± 2.3
NED PM1	0.2 ± 0.1	1.2± 0.9	0.4± 0.3	0.5± 0.1	0.07± 0.03	0.5± 0.1	0.12± 0.05	7.0 ± 2.4
NED PM2.5-1	0.5 ± 0.2	0.7± 0.6	0.3± 0.2	0.9± 0.5	0.04± 0.02	0.7± 0.3	0.02± 0.02	2.3 ± 1.6

322

323

324

325 (a)

326
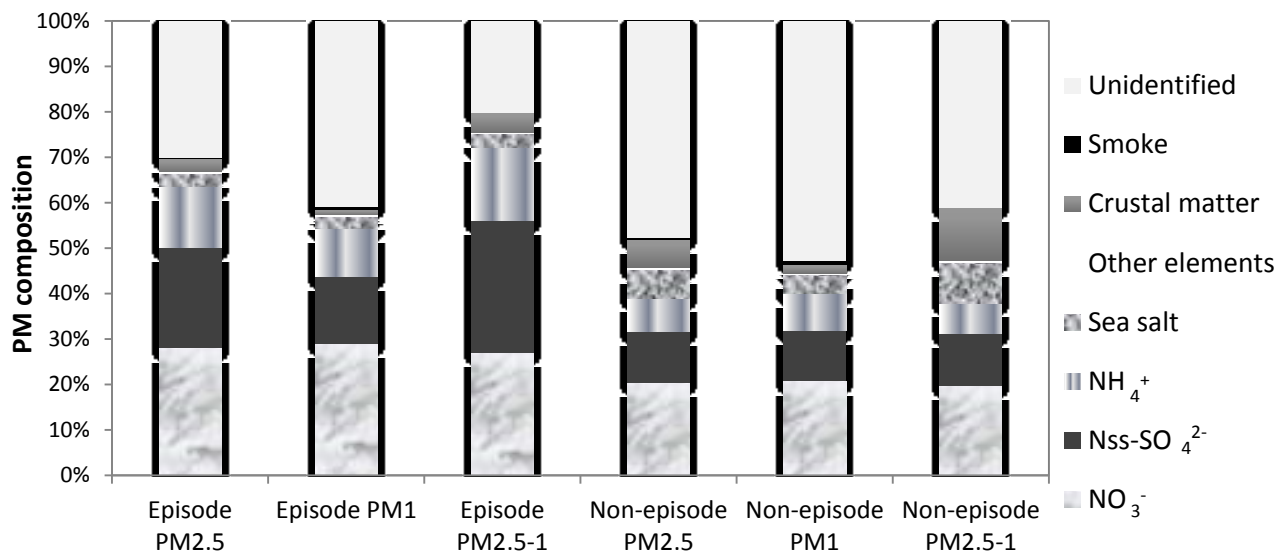
327
328
329 (b)

330
331
332 **Figure 3.** Relative contribution of PM components to outdoor (a) and indoor (b) PM2.5,
333 PM1 and PM2.5-1 on ED's and NED's.
334

335

336 *Secondary inorganic aerosol species (SIA)*

337   Nss-sulphate constituted 99% of ambient PM 2.5 sulphate on ED's in all studied fractions

338   and about 92% (96% of PM1 sulphate and 80% of PM2.5-1 sulphate) on NED's. In

339   addition, on ED's the percentage range of nss-sulphate was very narrow - from 98% to

340   100%, on NED's, it was more variable. In PM1 it varied between 91% and 97% and in

341   PM2.5-1, between 43% and 97%. The highest relative contribution of sea-sulphate was

342   seen in the third week of the study, when the air masses passed a long distance over the

343   Atlantic Ocean and it was preferably associated with fraction PM2.5-1.

344   Nss-sulphate, nitrate and ammonium, dominate the composition of PM, constituting 64%

345   of PM2.5 during ED's (52 μg m^{-3}) and 39% on NED's (10 μg m^{-3}). Hence, not only an

346   absolute increase in the concentration was seen but also the relative contribution

347   increased by a factor of 1.6 on ED's compared to NED's. SIA absolute concentrations

348   were 5-6 times higher during ED's compared to NED's both indoors and outdoors. Ram

349   et al. (2012) reported an increase in concentration by a factor of 2 -3 in their study of SIA

350   during fog and haze days . Although the percentage values reported by Ram et al. (2012)

351   were much lower, the same tendency was seen, namely about a 2 fold increase in

352   contribution from clear to foggy days. The episode days in our study were apparently not

353   only influenced by a limited pollutant dilution connected to occurrence of temperature

354   inversions, but also most probably by an increased formation of secondary species due to

355   the preferable meteorological conditions. As stated by Ram et al. (2012) at lower ambient

356   temperature and wind speed, high RH and SO_2 and in the presence of higher particle

357   concentration the conversion of gaseous SO_2 to particle SO_4^{2-} is expected to be higher.

358   Amongst secondary species, nitrate prevailed mostly in ambient air, whilst nss-sulphate,

359   was the dominant ion in the indoor air. The nitrate indoor/outdoor (I/O) ratio was only

360   0.14 on the average while the nss-sulphate ratio was equal to 0.66 for PM2.5. For PM1,

361   these values were 0.10 and 0.96 for nitrate and nss-sulphate, respectively. The trend of

362   fine particles showing higher I/O ratios for sulphate was also observed by Jones et al.

363   (2000).

364   The low I/O nitrate ratio indicates a significant decrease of nitrate concentration indoors

365   due to the higher temperature compared to the outdoor air and thus transformation of

366   particle ammonium nitrate to ammonia and nitric acid gasses (Parker et al. (2008)) (NO_3^-

367   conversion between particle and the gas phase is strongly temperature dependant). Nitrate

368   appears to be evenly distributed between PM1 and PM2.5-1 on ED's, both in absolute

369   values and relative contributions in ambient (29% and 27%, respectively) and indoor (5%

370   and 6%) concentrations. On NED's the nitrate prevails in PM1 but its relative

371   contribution is the same in ambient PM1 and PM2.5-1 (20%); in indoor air it constitutes

372   only 2% of PM1 and 10% of PM2.5-1.

373   Nss-sulphate on the other hand, during episode days is preferentially associated with the

374   supermicron fraction (PM2.5-1), and so is ammonia; the concentration of nss-sulphate in

375   this fraction is 2 times higher than in PM1 and in case of ammonia 1.6 times higher. The

376   relative contribution follows a similar trend. Indoors, both nss-sulphate and ammonia

377   have a higher concentration in PM1 than PM2.5-1 which could be attributed to lower

378   infiltration capacity of supermicron particles. As demonstrated earlier, the I/O for

379   sulphate in PM1 was close to 1 on average for all days and much lower in PM2.5. The

380   relative contributions indoors are similar in both size fractions (29% and 26% for EDs

381   and 12% during NEDs). On NED's slightly higher concentrations of nss-sulphate and

382   ammonia are found in PM1 than PM2.5-1 in indoor as well as ambient air.

383   The NH_4^+ / SO_4^{2-} molar concentration ratios were calculated and were found to be 1.8 and

384   1.9 for PM2.5 and PM1, respectively, for outdoor concentrations and 0.9 and 0.8 for

385   indoor PM2.5 and PM1 concentrations..The maximum ratio was 3 in PM2.5 and 2.8 in

386   PM1 during one of the episode days. Scatter plots (not shown) of μequivalent

387   concentrations of NH_4^+ versus SO_4^{2-} showed a significant correlation for both outdoor

388   and indoor fractions (R^2 = 0.80 and 0.72 for outdoor PM2.5 and PM1, and 0.98 for

389   indoor PM2.5 and 0.99 for indoor PM1). Generally, at low ammonia concentrations,

390   neutralization of sulphate is favoured over nitrate; nitrate is stabilized by ammonium at

391    $NH_4^+ / SO_4^{2-} >1.5$; this threshold was set at 2 in the study of Squizzato et al., (2013)

392   (Squizzato et al., (2013) and references therein). In our study, nitrate dominates over

393   sulphate in ambient air. When the sum of the μequivalent concentrations of NO_3^- and

394   SO_4^{2-} concentrations were plotted against that of NH_4^+ (Figure 4) the R^2 for outdoor

395   values were in the range of 0.97 - 0.99. The ED's are indicated in red to illustrate their

396   significantly higher concentrations. The slopes of the linear regression lines in all cases

397   suggest an ammonia deficit; therefore invoke the possible role of mineral neutralisation.

398   However, the calcium and magnesium concentrations were very low and one may

399   conclude that an acidic aerosol prevailed. Although Querol et al. (2001) has found the

400   slope value close to 1 for PM2.5 in Barcelona, Spain (1.5 for PM10), others reported

401   ammonium deficits similar to our study, for e.g. Yao et al. (2002) found the slope equal to

402   1.2-1.4. Taking into account that the average molar concentration ratios, also referred to

403   as a neutralization ratio (NR) (Bencs et al. (2008), Squizzato et al., (2013)), for $NH_4^+ /$

404    $NO_3^- + nss\text{-}SO_4^{2-}$ are 0.8 and 0.7 outdoors and indoors for PM2.5, and 0.8 for PM1

405 indoors and outdoors, one can conclude that the ammonium deficit is similar for both

406 environment.
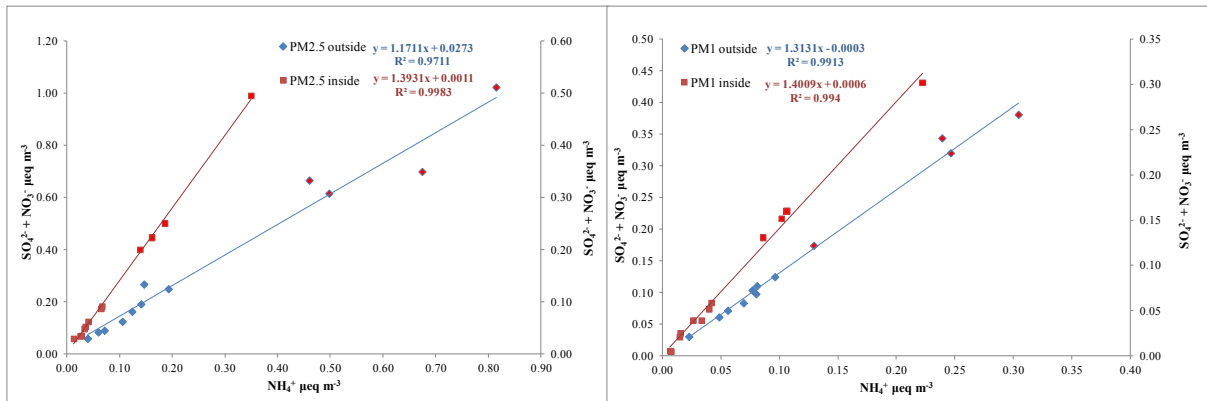
407

408 **Figure 4. Correlations between ammonium and the sum of nitrate and sulphate ions**

409 **in PM1 and PM2.5 (expressed as micro equivalents per m^3)**

410

411 *Crustal matter*

412

413 Crustal matter was calculated using the equation 1.16 (1.90Al+2.15Si+1.41Ca+1.67Ti

414 +2.09Fe) (Chan et al. (1997), Maenhaut et al. (2002), Sillanpää et al. (2006)).

415 Additionally, enrichment factors were calculated for all elements. Enrichment factor

416 analysis is based on comparison of the specific element's concentration (Fe in this case)

417 to the concentration of a so-called reference element in air relative to their concentration

418 ratio in Earth's crust (Mason, 1966). The enrichment factor close to one indicates that the

419 crust is the likely source of the element whilst very high EF, points to origin other than

420 crustal. All the above mentioned elements, have enrichment factors close to 1 (0.1-2.4),

421 confirming their natural origin. Crustal matter contributes to about 3% (2.3 µg m^{-3}) of the

422 total PM2.5 mass outdoors during episode days and up to 6% (1.6 µg m^{-3}) on non-episode

423 days. These values are similar to those found for mineral fraction in Ghent, Belgium,

424 namely 3% for winter PM2.5 and 4% for summer (Viana et al. (2007a)).

425   The mineral fraction is enriched in the supermicron PM2.5-1 particles by a factor of

426   about 4-5, compared to PM1. Indoors, this prevalence decreases to a factor of 1.5. Hence,

427   it constitutes 5% of the indoor PM2.5 on episode days and 8% on NED's. It is mostly

428   derived from wind-blown soil dust in the outdoor environment or from re-suspension of

429   the floor dust from human activities indoors. It is worth mentioning that the concentration

430   of this fraction in PM2.5-1 is lower indoors than outdoors (I/O=0.7), whilst in PM1 it is

431   higher (I/O=2, with the exclusion of one detected ($p<0.05$) outlier of 8). All days were

432   taken into account. Amongst the crust elements analysed, Al outdoors in the PM1

433   fraction was often found below the detection limit (9 days out of 12), in indoor PM1,

434   only 1 day was below this limit. It may thus lead to some inaccuracies in estimating the

435   contribution of crustal matter outdoors. Other four elements (Ca, Fe, Si, Ti) taken into

436   account for "crustal matter" calculation had concentrations between 2 and 165 times

437   above their respective detection limits in both environments. The inaccuracies are thus

438   not expected to be large. The elevated ratios for indoor PM1 could be attributed to re-

439   suspension by movement of people. This was not seen for PM2.5-1, perhaps due to much

440   lower outdoor contribution to indoor levels in this fraction than in PM1. The indoor PM

441   is a sum of particles generated indoors and those which infiltrated from the outdoor

442   environment. Similarly, Horemans and Van Grieken (2010), found the contribution of

443   soil dust (calculated in the same manner) in PM1, collected in offices in Antwerp

444   (Belgium), higher indoors than outdoors during the day and slightly lower during the

445   night, and was explained as being a result of daily office activities, which prevent

446   gravitational settling.

447

448 ***Sea salt***

449

450 Sea salt content was calculated using the concentrations of Cl^-, Na^+ and a standard

451 composition of sea water. As this approach may have a disadvantage of attributing a part

452 of Cl^- which may originate from urban/industrial activities to sea salt., an alternative

453 approach was also tested, which assumes that sea salt contains 30.8% of Na (Maenhaut et

454 al. (2002)). The latter approach may on the other hand overestimate the salt content, since

455 Cl^- may be lost from sea salt particles in the atmosphere, especially from the fine PM

456 fraction (Maenhaut et al. 2002, Bencs et al. 2008). Interestingly, during NED's (and one

457 of the episode days, 13th February, which was influenced by solely regional anticyclonic

458 air masses), the approach using both ions estimated the content of sea salt to be 40% less

459 than the other approach, confirming thus the loss of Cl^- ions and overestimation of sea

460 salt content using Na^+ content only. This did not seem the case during the other episode

461 days, where the approach using both the content of Cl^- and Na^+ ions estimated the salt

462 content to be about 40% higher than when using Na^+ only. An increase in Cl

463 concentration (both as soluble Cl^- and total Cl) was visible during the episode days

464 (except for the 13th of February), in all PM fractions outdoors, whilst Na^+ concentration

465 remained constant through the whole campaign, with minimal changes confirming that

466 the increased chloride concentration could not be attributed to sea salt. This can possibly

467 mean that a part of Cl^- originated from other sources than sea salt on most days with high

468 pollution and that the sea salt content might be overestimated during those days. Another

469 possibility is as stated by Ye et al. (2003); that the chloride might have originated from

470 the sea salt in large particles but has been displaced by the reaction with nitric acid,

471 followed by the reaction with ammonia to form smaller particles. Higher concentration of

472   pollutants on ED's might have enhances this process. The fact that the molar ratio of Cl^-

473    $/Na^+$ is not close to unity (if close to one, according to Ye et al. (2003), it may indicate

474   sea salt origin of chloride) further suggests the possible presence of ammonium chloride,

475   which would result in an even more acidic aerosol. Indoors, the chloride concentration

476   was largely reduced compared to respective outdoor values, especially on episode days..

477   I/O ratios of such calculated sea salt were thus 0.5 on EDs and 0.8 on NEDs in both

478   PM2.5 and PM1. Sodium is the only ion that shows the I/O ratio of 1 in both PM

479   fractions. The sea salt contributes to about 3% (2.3 $\mu g\ m^{-3}$) of the total ambient PM2.5 on

480   ED's and 6% on NED's (1.6 $\mu g\ m^{-3}$). It is enriched in the supermicron fraction PM2.5-1,

481   having about 2 times higher concentration than in fraction PM1 during NED's. During

482   ED's these differences are less prounced (Table 2). Generally, the contribution of this

483   fraction is similar in our study to the results obtained for ambient Ghent PM, where it

484   constituted about 5% (1.2 $\mu g\ m^{-3}$) of winter PM2.5 (Viana et al. (2007a)).

485

486   *Other elements*

487   The fraction "other elements", was calculated, similarly to Sillanpää et al. 2006, by

488   summation of the Sr, Cr, Ni, Mn, Cu, Zn, As, Pb and V concentrations. For samples

489   below the detection limit, random numbers below the detection limits were generated for

490   the calculation of the averages. This fraction contributes negligibly to the sampled PM,

491   namely 0.3-0.8% of various size ranges (Table 2). Amongst these elements, Sr had the

492   lowest EFs (1.7-2.6), comparable with other soil derived elements. Mn and Cr show

493   medium enrichment, therefore displaying both natural and anthropogenic origin and are

494   followed by slightly higher values for V and Ni. Cu, Zn, As, Pb, are highly enriched (EFs

495 >100), implying mainly anthropogenic origin of those species. The results of

496 concentration measurements and EFs calculations are presented in Table 3.

497

498 **Table 3.** The elemental concentrations (ng m^{-3}) of PM2.5 and PM1.
499

	PM2.5 Outdoor			PM1 Outdoor		
Element	ED	ND	EF $_{crust}$	ED	ND	EF $_{crust}$
As	6	3	433	4	2	1380
Cr	5	3	8	1	<LOD	12
Cu	19	22	101	8	7	135
K	508	259	3	320	165	8
Mn	17	12	4	6	4	5
Ni	9	4	17	5	3	48
Pb	51	31	695	31	17	1660
Sr	2	2	2	1	<LOD	3
V	10	5	12	7	3	39
Zn	137	60	232	63	30	520

	PM2.5 Indoor			PM1 Indoor		
Element	ED	ND	EF $_{crust}$	ED	ND	EF $_{crust}$
As	5	2	688	3	2	942
Cr	3	2	11	2	1	14
Cu	17	24	156	9	11	163
K	452	212	4	313	152	6
Mn	14	9	4	7	4	4
Ni	6	3	18	4	2	31
Pb	40	22	715	26	15	1124
Sr	3	2	3	1	<LOD	2
V	8.1	3	12	6	3	23
Zn	108	40	250	60	28	398

500 *the average value without the one elevated point of 812 ng m^{-3}
501

502 The "other elements" are mostly heavy metals that were present in relatively low

503 concentrations in the outdoor environment and only as trace quantities in the indoor air.

504 A few remarks concerning these elements are however of importance. In general, Pb had

505 one of the highest concentrations in this class, ranging from 15 ng m^{-3} (NED's indoor

506 PM1) to 51 ng m^{-3} (ED's ambient PM2.5). The National Ambient Air Quality Standard

507 (NAAQS) for Pb (3 month rolling 0.15 µg m^{-3}) is therefore not exceeded, neither was it

508 exceeded under the New European Directive (Directive 2008/50/EC-

24

509   http://ec.europa.eu/environment/air/quality/legislation/directive.htm) where the standard

510   is 0.5 µg m^{-3} based on a yearly average. The new directive that came into play on

511   31.12.2012 (http://ec.europa.eu/environment/air/quality/standards.htm) for As (6 ng m^{-3})

512   was exceeded during ED's for PM2.5, but it should be noted that our concentrations are

513   reported as 24-h averages and the standard is an annual average. Other elemental

514   concentrations regulated by the new directive are Ni and Cd, both of which were well

515   below the standard. Except for Cu and Cr, all other minors and traces in general exhibited

516   increases in concentration on ED's, ranging from 1.1 to 2.5 times higher than on NED's.

517   It is also noticeable that V, Fe and Ni showed on average a 1.9 increase in concentration

518   during ED's. These three metals are of interest as Jacobs et al. (2012) reported a

519   significant association between their concentrations and the systolic blood pressure and

520   pulse pressure of the elderly in this (and 5 other) old age homes. During non-episode days

521   the concentration levels of elements in this group are comparable with the levels reported

522   in other studies of outdoor PM2.5 in Antwerp, Belgium (Götschi et al.(2005), Stranger et

523   al. (2009)). On ED's only Cu and Zn exceeded levels reported as winter average for

524   Antwerp (Götschi et al.(2005)) by 1.4 times. In another work by Horemans and Van

525   Grieken, (2010), 12h (both day and night) PM1 and PM2.5 averages calculated for those

526   elements inside offices in Antwerp, were much higher than our NED's indoor levels. On

527   ED's, Zn, Ni and V were elevated in our study by 1.5-3.5 times.

528   Elements such as: As, Ni, Pb, V and Zn accumulate to a large extent in the fine fraction

529   as opposed to for example Ti; Figure 5 shows the fractional distributions (PM1 and

530   PM2.5-1) of these elements with Ti given for comparison. They are characterized by high

531   PM1/PM2.5 ratios of 0.5-0.7 in ambient air and 0.6-0.7 in indoor air. These ratios

532 generally increase for indoor air compared to outdoor air as expected due to the ease of

533 infiltration of fine particles. Additionally, in Figure 5, sulphur was shown as it exhibits

534 the largest difference in the fractional distribution between ED's and NED's (about 20%).

535 For other elements variation below 10% can be seen.

536 Pearson correlation coefficients (not shown) were calculated for these elements to

537 investigate which elements may originate from a common source. Cr was excluded from

538 correlation analyses as it was detected in about 50% cases only. Among *other elements*,

539 V correlated very well with Ni (r =0.92, p<0.001 for PM2.5 outdoors) both are

540 considered as originating in Europe from oil combustion (Swietlicki and Krejci, (1996)).

541 Their concentration was two times higher on ED's compared to NED's. Cu did not

542 correlate with other elements from this group, it is fairly correlated with Ca, Si and Ti in

543 ambient PM1 (r=0.66-0.72, p=0.008-0.020) what may suggest some contribution of re-

544 suspended road dust source as Cu is a known tracer for break wear (Viana et al., (2007b),

545 Cyrys et al. (2003)). In PM2.5 these correlations are weaker (r=0.43-0.63) and are only

546 significant for Ca (r=0.62, p=0.028). Other anthropogenic origin elements (Zn, As, Pb)

547 correlated very well with each other (r>0.71-0.95, p<0.01) both in PM1 and PM2.5. Of

548 interest is a very high correlation between Zn, K and Cl (r=0.97 - 0.99, p<0.001) in

549 ambient PM1. In PM2.5, the correlation between Zn and K is still high (r=0.99, p<0.001)

550 but with Cl it is slightly weaker (r=0.74 - 0.77, p<0.01), probably because of higher

551 contribution of sea salt Cl in this fraction. K is generally associated with biomass

552 combustion (Götschi et al. (2005)) and waste incinerators (Maenhaut et al. (2002)) whilst

553 Zn, is considered to originate from traffic and/or industrial activities such as non-ferrous

554 smelters. Cl, apart from its natural sea salt origin, is thought to originate from industrial

555   emissions of hydrochloric acid and from waste incineration (Götschi et al. (2005)). As

556   already mentioned, the air masses influencing the high pollution days created an

557   anticyclone over the territories of Belgium, The Netherlands and Germany, favouring the

558   accumulation of pollutants not only from local traffic emissions and local industrialized

559   areas (Antwerp) but also from more distant locations such as for example highly

560   industrialized Ruhr region (Stranger, 2005) in Germany.

561
562   (a)

563
564   (b)
565
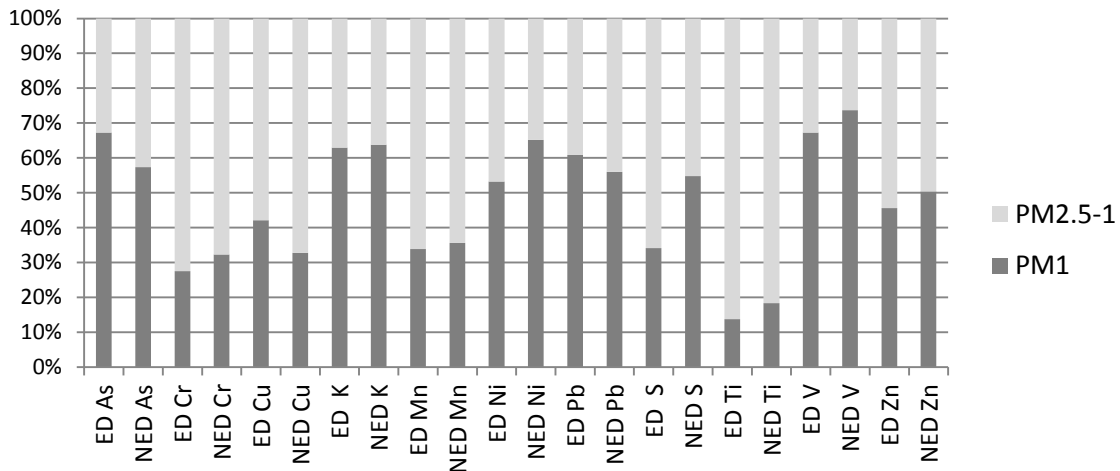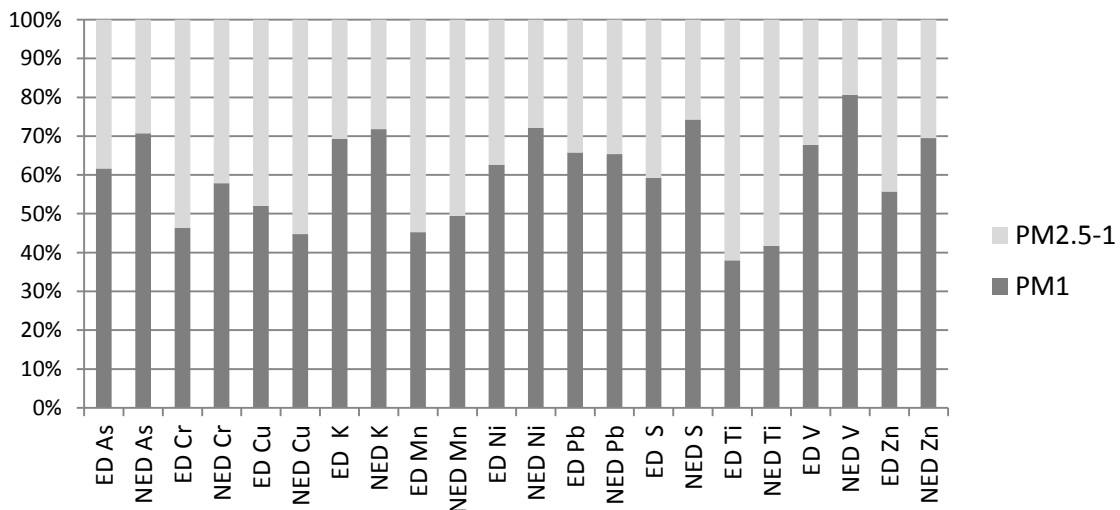
566
567   **Figure 5.** Partitioning of various elements between PM1 and PM2.5-1 fractions outdoors
568   (a) and indoors (b) during EDs and NEDs.

569 *Smoke*

570 The contribution of smoke (or non-crustal K) was calculated as concentration of K - 0.6

571 of that of Fe (Maenhaut et al., (2002)). This fraction contributes to about 0.5 % of PM2.5

572 (0.3 μg m^{-3}), it is preferentially associated with PM1, ranging from 0.7 % in ambient

573 PM1 on ED's to 1.2% of indoor PM1 during NED's.The indoor concentration equals

574 outdoor, as already mentioned elsewhere, due to the high efficiency of fine particles to

575 penetrate the building envelope. The average concentration of this fraction during episode

576 days is twice as high as that on normal days.

577

578 **3.4. Ion balance**

579

580 In order to evaluate the acid-base balance of aerosols the ion balance equations (Shen et

581 al., 2009; Zhang et al., 2002) were calculated in both PM fractions according to equations

582 (1) and (2) for cations (C) and anions (A), respectively, whereby the concentration for

583 each ion is in μg m^{-3}. The contribution of Mg^{2+} and Ca^{2+} were very low, in agreement

584 with Stranger, 2005, thus random numbers were generated for samples which exhibited

585 levels lower than LODs.

586

587   (1) $C\ (\mu Eq\ m^{-3}) = [NH_4^+]/18 + [Na^+]/23 + [K^+]/39 + [Mg^{2+}]/12 + [Ca^{2+}]/20$

588

589   (2) $A\ (\mu Eq\ m^{-3}) = [NO_3^{2-}]/62 + [SO_4^{2-}]/48 + [Cl^-]/35.5$

590

591   The C/A ratios were subsequently calculated. On average, during the episode days all

592   fractions, except for PM2.5 indoors, were slightly acidic (C/A = 0.9), whilst on normal

593   days the aerosol particles were on average slightly basic with the C/A values between 1

594   and 1.3 for different fractions. Statistically significant differences between ED's and

595   NED's were, however, only found indoors in PM2.5 (p=0.009) and PM1 (p=0.022).

596   During ED's the C/A values in outdoor PM2.5 ranged between 0.82 and 1.08, whilst in

597   PM1, between 0.80 and 0.91. During NED's in outdoor PM2.5 variation between 0.74

598   and 1.30 was found and in PM1 between 0.93 and 1.33. Indoors, during ED's PM2.5 C/A

599   values were between 0.90 and 1.02 and in PM1 between 0.89 and 0.91, on NED's these

600   values ranged from 0.96 to 1.58 in PM2.5 and 0.98 to 1.47 in PM1 (in this fraction two

601   values above 3 were seen). Neutral to alkaline aerosols coincided with the minima's of

602   the registered PM mass (third week of the study, Figure 2), thus both anions and cations

603   showed lower concentrations than during other days of the study. The highest sea salt

604   content was registered (2 days out of 4) on those days, and a direct influence of North Sea

605   and Atlantic Ocean air masses was noticed.

606

607 **4. Conclusions**

608

609   A comprehensive insight into the composition of PM 2.5 and PM1 on high and low

610   pollution days and outdoor to indoor comparisons of PM sampled in old-age home was

611   provided. This paper is complementary to a study by Jacobs et al. 2012, which

612   investigated acute, short-term health effects of PM and its composition in the elderly part

613   of the population. Extremely high ambient PM2.5 and PM1 values were registered during

614   some days of this study. The investigation of PM composition revealed that although all

615   components were found to be considerably higher during episode days than during non-

616   episode days, it was the secondary inorganic aerosols that contributed the most towards

617   an increase in the PM pollution as their relative contribution was higher by a factor of

618   1.6. Therefore, the episode days were not only influenced by a limited pollutant dilution

619   connected to occurrence of temperature inversions, but also most probably by an

620   increased formation of secondary inorganic pollutants due to preferable meteorological

621   conditions. The 120h air mass backward trajectories influencing the high pollution days

622   showed an anticyclonic scenarios with no or less direct influences of the North Sea or

623   Atlantic Ocean air masses than during the low pollution days. The anticyclone was

624   formed over the territories of Belgium, The Netherlands and Germany thus facilitating

625   the accumulation of both local and regional pollutants. Natural contribution (mineral dust

626   and sea salt) was relatively less important on ED's than NED's, the same was true for the

627   "other elements" which included mostly heavy metals and for unaccounted mass which is

628   in our study most probably composed of OC, EC and water. An ammonium deficit for

629   PM was deducted in this study, especially on ED's. On average, the PM fractions on

630   ED's were then slightly acidic (C/A = 0.9), whilst on normal days more variation was

631   seen, and C/A ranged from acidic to alkaline (C/A>1-1.3) in ambient air. Neutral to

632   alkaline aerosols coincided with the minima's of the registered PM mass. Amongst heavy

633   metals Zn and Pb were found at the highest concentrations in both PM2.5 and PM1.

634   No significant sources of indoor pollutants could be identified inside the old-age home.

635   Generally, the PM1 mass concentration decreased indoors by 29 % compared to

636   outdoors, whilst PM2.5-1 fraction by 57 %; this decrease was similar on ED's and

637   NED's. This is in agreement with the fact that fine mode particles penetrate the building

638   envelope easier than supermicron mode. High correlations were found between outdoor

639   and indoor PM, confirming the mainly outdoor origin of air pollution inside the Czagani

640   old-age home.

641

642   **Acknowledgements**

654

655   **References**

656

657 Avigo, J.D., Godoi, F.L., Janissek, P.R., Makarovska, Y., Krata, A., Potgieter-Vermaak,
658 S., Alfoldy, B., Van Grieken, R., Godoi, R.H.M., 2008. Particulate matter analysis at
659 elementary schools in Curitiba, Brazil. Analytical and Bioanalytical Chemistry 391, 1459
660 - 1468.

661

662 Bell, M.L., Ebisu, K., Peng, R.D., Samet, J.M., Dominici, F., 2009. Hospital Admissions
663 and Chemical Composition of Fine Particle Air Pollution. American Journal of
664 Respiratory Critical Care Medicine 179, 1115–1120.

665

Bencs, L.,Ravindra,K., de Hoog, J., Rasoazanany, E. O., Deutsch, F., Bleux, N., Berghmans, P., Roekens, E., Krata, A., Van Grieken, R., 2008. Mass and ionic composition of atmospheric fine particles over Belgium and their relation with gaseous air pollutants. Journal of Environmental Monitoring 10, 1148-1157.

Chan, Y.C., Simpson, R.W., Mctainsh, G.H., Volwles, P.D., Cohen, D.D., Bailey, G.M., 1997. Characterisation of chemical species in $PM_{2.5}$ and PM_{10} aerosols in Brisbane, Australia. Atmospheric Environment 37, 3773-3785.

Chao, C.Y., Wong, K.K., 2002. Residental indoor PM10 and PM2.5 in Hong Kong and the elemental composition. Atmospheric Environment 36, 265-277.

Chen, S.J., Hsieh, L.T., Tsai, C.C., Fang, G.C., 2003. Characterization of atmospheric PM10 and related chemical species in southern Taiwan during the episode days. Chemosphere 53, 29-41.

Cheng, L., Sandhu, H.S., Angle, R.P., Myrick, R.H., 1998. Characteristics of inhalable particulate matter in Alberta cities. Atmospheric Environment 32, 3835-3844.

Cyrys, J., Stölzel, M., Heinrich, J., Kreyling, W.G., Menzel, N., Wittmaack, K., Tuch, T., Wichmann, H-E., 2003. Elemental composition and sources of fine and ultrafine ambient particles in Erfurt, Germany. The Science of the Total Environment 305, 143-156.

Di Ciaula, A., 2012. Emergency visits and hospital admissions in aged people living close to a gas-fired power plant. European Journal of Internal Medicine 23, 53-58

Draxler, R.R. and Rolph, G.D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD.

Fuentes-Leonarte, V., Tenías, J.M., Ballester, F., 2009. Levels of Pollutants in Indoor Air and Respiratory Health in Preschool Children: A Systematic Review. Pediatric Pulmonology 44, 231–243.

Geller, M.D., Chang, M., Sioutas, C., Ostro, B.D., Lipsett, M., 2002. Indoor/Outdoor relationship and chemical composition of fine and coarse particles in the southern California deserts. Atmospheric Environment 36, 1099-1110.

Gemenetzis, P., Moussas, P., Arditsoglou, A., 2006. Mass concentration and elemental composition of indoor PM2,5 and PM10 in University rooms in Thessaloniki, northern Greece. Atmospheric Environment 40, 3195-3206.

709 Hu, M., He., L.Y., Zhang, Y.H., Wang, M., Kim, Y.P., Moon, K.C., 2002. Seasonal
710 variation of ionic species in fine particles at Qingdao, China. Atmospheric Environment
711 36, 5853-5859.
712
713 Jacobs, L., Buczynska, A., Walgraeve, C., Delcloo, A., Potgieter-Vermaak, S., Van
714 Grieken, R., Demeestere, K., Dewulf, J., Van Langenhove, H., De Backer, H., Nemery,
715 B., Nawrot, T.S., 2012. Acute changes in pulse pressure in relation to constituents of
716 particulate air pollution in elderly persons. Environmental Research 117, 60 – 67.
717
718 Jones , N.C., Thornton, C.A., Mark, D., Harrison, R.M., 2000. Indoor/outdoor
719 relationship of particulate matter in domestic homes with roadside, urban and rural
720 locations. AtmosphericEnvironment 34, 2603-2612.
721
722 Krupinska, B., Worobiec, A., Rotondo, G, G., Novakovic, V., Kontozova, V., Ro, C.,
723 Van Grieken, R., De Wael, K., 2009. Assessment of the air quality (NO2, SO2, O3 and
724 particulate matter) in the Plantin-Moretus Museum/Print Room in Antwerp, Belgium, in
725 different seasons of the year. Microchemical Journal 102, 49 – 53.
726
727 Lai, H.K., Kendall, M., Ferrier, H., Lindup, I., Alm, S., Hänninen, O.,2004. Personal
728 exposures and microenvironment concentrations of PM2.5, VOC, NO2, CO in Oxford,
729 UK. Atmospheric Environment 38, 6399–410.
730
731 Mason, S., 1966. Principles of Geochemistry. Wiley, New York, p.45-46.
732
733 Maenhaut, W., Cafmeyer, J., Dubtsov, S., Chi, X., 2002. Detailed mass size distributions
734 of elements and species, and aerosol chemical mass closure during fall 1999 at Gent,
735 Belgium. Nuclear Instruments and Methods in Physics Research B 189, 238-242.
736
737 Meng, Q.Y., Turpin, B. J., Lee, J.H., Polidori, A.,, Weisel, C.P., Morandi, M., Colome,
738 S., Zhang, J., Stock, T., Winer, A.,2007. How Does Infiltration Behavior Modify the
739 Composition of Ambient PM 2.5 in Indoor Spaces? An Analysis of RIOPA Data.
740 Environmental Science and Technology 41, 7315-7321.
741
742 Parker, J.L., Larson, R.R., Eskelson, E., Wood, E.M., Veranth, J.M., 2008. Particle size
743 distribution and composition in a mechanically ventilated school building during air
744 pollution episodes. Indoor Air 18, 386-393.
745
746 Putaud,J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S.,
747 Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N.,
748 Müller, C., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H.T., Tørseth,
749 K., Wiedensholer, A., 2004. A European aerosol phenomenology—2: chemical
750 characteristics of particulate matter at kerbside, urban, rural and background sites in
751 Europe. Atmospheric Environment 38, 2579-2595.
752

753 Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C.R., Cots, N., Massague, G.,
754 Puig, O., 2001. PM10 and PM2.5 source apportionment in the Barcelona Metropolitan
755 area, Catalonia, Spain. Atmospheric Environment 35, 6407-6419.
756
757 Querol, X., Alastuey, A., Ruiz, C.R., Artiñano, B., Hansson, H.C., Harrison, R.M.,
758 Buringh, E., ten Brink, H.M., M. Lutz, Bruckmann, P., Straehl, P., Schneider, J., 2004a.
759 Speciation and origin of PM10 and PM2.5 in selected European cities. Atmospheric
760 Environment 38, 6547-6555.
761
762 Querol, X., Alastuey, A., Viana, M.M., Rodriguez, S., Artiñano, B., Salvador, P.,
763 Garcia do Santos, S., Fernandez Patier, R., Ruiz, C.R., de la Rosa, J., Sanchez de la
764 Campa, A. , Menendez, M., Gil, J.I., 2004b. Speciation and origin of PM10 and PM2.5 in
765 Spain. Aerosol Science 35, 1151-1172.
766
767 Ram, K., Sarin, M. M., Sudheer, A. K., Rengarajan, R., 2012. Carbonaceous and
768 secondary inorganic aerosols during wintertime fog and haze over urban sites in the Indo-
769 Gangetic plain. Aerosols and Air Quality Research 12, 359-370.
770
771 Rattigan, O.V., Reilly, J., Judd, C.D., Moore, K.F., Das, M., Sherman, D.E., Dutkiewicz,
772 V.A., Collett, J.L., Jr. and Husain, L., 2001. Sulfur dioxide oxidation in clouds at
773 Whiteface Mountain as a function of drop size. Journal of Geophysical Research 106,
774 17347–17358.
775
776 Shen, Z., Cao, J., Arimoto, R., Han, Z., Zhang, R., Han, Y., Liu, S., Okuda, T., Nakao, S.,
777 Tanaka, S., 2009. Ionic composition of TSP and PM2.5 during dust storms and air
778 pollution episodes at Xi'an, China. Atmospheric Environment 43, 2911-2918.
779
780 Sillanpää, M., Hillamo, R., Saarikoski, S., Frey, A., Pennanen, A., Makkonen, U.,
781 Spolnik, Z., Van Grieken, R., Braniš, M., Brunekreef, B., Chalbot, M.-C., Kuhlbusch, T.,
782 Sunyer, J., Kerminen, V.-M., Kulmala, M., Salonen, R.O., 2006. Chemical composition
783 and mass closure of particulate matter at six urban sites in Europe. Atmospheric
784 Environment 40, S212-S223.
785
786 Squizzato, S., Masiol, M., Brunelli, A., Pistollato, S., Tarabotti, E., Rampazzo, G.,
787 Pavoni, B., 2013. Factors determining the formation of secondary inorganic aerosol: a
788 case study in the Po Valley (Italy). Atmospheric Chemistry and Physics 13, 1927-1939
789
790 Strak, M., Janssen, N.A.H., Godri, K.J., Gosens, I., Mudway, I.S., Cassee, F.R., Lebret,
791 E., Kelly, F.J., Harrison, R.M., Brunekreef, B., Steenhof, M., Hoek, G., 2012.
792 Respiratory health effects of airborne particulate matter: The role of partical size,
793 composition, and oxidative potential. Environmental Health Perspectives 123, 1183-
794 1189.
795
796 Stranger, M., 2005. Characterisation of health related particulate and gas-phase
797 compounds in multiple indoor and outdoor sites in Flanders. PhD dissertation, University
798 of Antwerp.

799
800 Stranger, M., Potgieter-Vermaak, S.S., Van Grieken, R., 2007. Comparative overview of
801 indoor air quality in Antwerp, Belgium. Environment International 33, 789-797.
802
803 Stranger, M., Potgieter-Vermaak, S.S., Van Grieken, R., 2009. Particulate matter and
804 gaseous pollutants in residences in Antwerp, Belgium. Science of the Total Environment
805 407, 1182 – 1192.
806
807 Swietlicki, E. and Krejci, R., 1996. Source characterisation of the Central European
808 atmospheric aerosol using multivariate statistical methods. Nuclear Instruments and
809 Methods in Physics Research B 109/110, 519-525.
810
811 Vecchi, R., Marcazzan, G., Valli, G., Ceriani, M., Antoniazzi, C., 2004. The role of
812 atmospheric dispersion in the seasonal variation of PM1 and PM2.5 concentration and
813 composition in the urban area of Milan (Italy). Atmospheric Environment 38, 443-4446.
814
815 Vercauteren, J., Matheeussen, C., Wauters, E., Roekens, E, Van Grieken R,
816 Krata, A, Makarovska, Y, Maenhaut, W, Chi, X, Geypens, B., 2011.Chemkar PM10: An
817 extensive look at the local differences in chemical composition of PM10 in Flanders,
818 Belgium. Atmospheric Environment 45, 108-116.
819
820 Viana, M., Maenhaut, W., Chi, X., Querol, X., Alastuey, A., 2007a. Comparative
821 chemical mass closure of fine and coarse aerosols at two sites in south and west Europe:
822 Implications for EU air pollution policies, Atmospheric Environment 41, 315-326.
823
824 Viana, M., Querol, X., Götschi, T., Alastuey, A., Sunyer, J., Forsberg, B., Heinrich, J.,
825 Norbäck, D., Payo, F., Maldonado, J., Künzli, N., 2007b. Atmospheric Environment 41,
826 1395-1406.
827
828 Wang, Y., Zhuang, G., Sun, Y.,An, Z., 2006. The variation of characteristics and
829 formation mechanisms of aerosols in dust, haze, and clear days in Beijing. Atmospheric
830 Environment 40, 6579–6591.
831
832 Yao, X., Chan, C.K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., Ye, B. 2002. The
833 water-soluble ionic composition of PM2.5 in Shanghai and Beijing, China. Atmospheric
834 Environment 36, 4223-4234.
835
836 Ye, B., Ji, X., Yang, H., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P.A., 2003.
837 Concentration and chemical composition of PM2.5 in Shanghai for a 1-year period.
838 Atmospheric Environment 37, 499-510.
839
840 Zhang, X.Y., Cao, J.J., Li, L.M., Arimoto, R., Cheng, Y., Huebert, B., Wang, D., 2002.
841 Characterization of Atmospheric Aerosol over XiAn in the South Margin of the Loess
842 Plateau, China. Atmospheric Environment 36, 4189-4199.
843