Mass and ionic composition of atmospheric fine particles over Belgium and their relation with gaseous air pollutants

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Mass, major ionic components (MICs) of $PM_{2.5}$, and related gaseous pollutants (SO_2, NO_x, NH_3, HNO_2, and HNO_3) were monitored over six locations of different anthropogenic influence (industrial, urban, suburban, and rural) in Belgium. SO_4^{2-}, NO_3^- NH_4^+, and Na^+ were the primary ions of $PM_{2.5}$ with averages diurnal concentrations ranging from 0.4-4.5, 0.3-7.6, 0.9-4.9, and 0.4-1.2 $\mu g/m^3$, respectively. MICs formed 39 % of $PM_{2.5}$ on an average, but it could reach up to 80-98 %. The SO_2, NO, NO_2, HNO_2, and HNO_3 levels showed high seasonal and site-specific fluctuations. The NH_3 levels were similar over all the sites (2-6 $\mu g/m^3$), indicating its relation to the evenly distributed animal husbandry activities. The sulfur and nitrogen oxidation ratios for $PM_{2.5}$ point towards a low-to-moderate formation of secondary sulfate and nitrate aerosols over five cities/towns, but their fairly intensive formation at the rural Wingene. Cluster analysis revealed the association of three groups of compounds in $PM_{2.5}$; (i) NH_4NO_3, KNO_3; (ii) Na_2SO_4; and (iii) $MgCl_2$, $CaCl_2$, MgF_2, CaF_2, corresponding to anthropogenic, sea-salt, and mixed (sea-salt + anthropogenic) aerosols, respectively. The neutralization and cation-to-anion ratios indicate that MICs of $PM_{2.5}$ appeared mostly as $(NH_4)_2SO_4$ and NH_4NO_3 salts. Sea-salt input was maximal during winter reaching up to 12 % of $PM_{2.5}$. The overall average Cl-loss for sea-salt particles of $PM_{2.5}$ at the six sites varied between 69 and 96 % with an average of 87 %. Principal component analysis revealed vehicular emission, coal/wood burning and animal farming as the dominating sources for the ionic components of $PM_{2.5}$.

Keywords: $PM_{2.5}$ aerosols, water-soluble ionic compounds, seasonal variations, criteria gaseous pollutant, emission source, secondary aerosol formation

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1. **Introduction**

Sources, characterization and health effects of fine atmospheric aerosols significantly differ from coarse particulates.[1-5] Fine particulate matter, referred to as PM$_{2.5}$, can penetrate deeper into the human respiratory-tract, thus increasing the risk of pulmonary and mutagenic diseases.[6] The major ionic constituents (MICs), also referred as water-soluble, ionic species in the literature, can comprise up to 60-70 % of the total particulate mass[7] and show significant seasonal and site-specific variations.[2,5] Epidemiological data also indicate seasonal differences to the same particulate exposure; for instance, more hospitalizations in summer than winter.[11] Acid-forming constituents of MIC (e.g., sulfates, nitrates), related also to acidic rain, can cause severe effects on human health.[8,9] Moreover, they may increase the solubility of toxic organic compounds by acting as surface active agents, thus increasing their toxicity.[10]

Fine aerosols also play an important role in global climate changes, directly, by altering the total radiation budget of the earth-atmosphere via absorbing and scattering solar radiation, and indirectly, by changing the depth and albedo of clouds. [12,13] Ionic components of atmospheric aerosols can change the size, composition, particle density, and lifetime of aerosols owing to their hygroscopic nature, making their effects rather difficult to predict. Many recent studies[6,14] highlight the impact of fine particles on both human health and global climate and suggests priority to identify and chemically characterize this fraction. However, till date, only few studies have reported the mass and MICs composition of PM$_{2.5}$ aerosol in Europe[15-25], but not even one in relation to the simultaneous monitoring of associated gaseous pollutants.

Considering this need, in this work, the mass and MICs of PM$_{2.5}$, their diurnal and seasonal patterns together with gaseous air pollutants were studied at six locations of diverse anthropogenic influence. The study also focuses on the relationship between

65 ionic species and gaseous pollutants; particularly, on the formation of secondary

66 aerosols of sulfates and nitrates and sea-salt particle contribution. Several approaches

67 were also applied to enhance the accuracy of the emission source identification of

68 $PM_{2.5}$.

2. Experimental

2.1 Site characteristics

71   Six sampling locations were selected in Northern Belgium (Flanders) based on

72 their different anthropogenic activities (Fig. 1), i.e., (i) Petroleumkaai in Antwerp

73 (industrial site, petroleum harbor with oil-refineries and plants), (ii) Borgerhout district

74 in Antwerp, (urban site with high traffic density (40-50 thousand cars/day), (iii) Zelzate

75 (suburban site at a major road intersection, nearby motorway, and influence of steel-

76 industry), (iv) Hasselt (suburban site, at the bank of the Albert Channel with shipping at

77 nearby sluice gates, close to a highway with medium/low traffic density, and a fairly

78 nearby newspaper (press) industry), (v) Wingene (rural, agricultural area of very low

79 traffic density, but the most intensive pig farming over Flanders), and (vi) Mechelen

80 (suburban site with low traffic density, some industrial impact from detergent (laundry)

81 manufacturing).

2.2 Sampling of gases and aerosols

83   All sampling sites were visited twice, and minimum six-week-long sampling

84 campaigns were scheduled for various seasons (Table 1) and details also shown in a

85 Gantt chart (Supplementary Table S1). Wind-speed (WS), wind direction (WD), relative

86 humidity (RH), air temperature (T_{air}), air pressure (p_{air}), and precipitation (PR) were

87 recorded at meteorological stations of VMM nearby the sampling sites and at the

88 Luchtbal M802 station near Antwerp.

89   Automated Rupprecht & Patashnik (R&P) Model Partisol Plus samplers with a

90   calibrated air-flow rate of 1 m³/h were used for 24-hour, midnight-to-midnight sampling

91   of $PM_{2.5}$ and PM_{10} onto Zefluor Teflon filters of 47 mm diameter and 2 μm pore size

92   (Pall Gelman Laboratory, Ann Arbor, MI, USA). The filters were weighed on a

93   Sartorius M5P-000V001 micro-balance before and after sampling, according to the EN

94   12341 protocol. Simultaneous sampling of gaseous NH_3, SO_2, HNO_2, and HNO_3 was

95   performed on a 24-hour base with an air-flow of 0.6 m^3/h over a coated set of absorber-

96   tubes attached to either a honeycomb denuder of VITO equipped with a $PM_{2.5}$ sampler-

97   head, or an R&P Partisol Speciation Sampler "chemcomb". The coatings of the tubes

98   were prepared with solutions of 2 % (m/v) citric acid in methanol, and 2 % (m/v)

99   Na_2CO_3 in ultra-pure water (Milli-Q RG, Millipore) for sampling alkaline and acidic

100   gases, respectively. All the chemicals used were of analytical grade, or better quality.

101   Wingene, Mechelen, and Petroleumkaai were sampled with denuders. Except

102   Wingene, levels of SO_2 and NO_x were monitored on a half-hourly base with TEI 43C

103   and TEI 42C (Thermo Fisher Scientific, Waltham, MA, USA) automatic analyzers

104   based on UV-fluorescence and chemi-luminescence methods, respectively. The half-

105   hourly values were averaged to get diurnal data.

106   **2.3 Ion-chromatography conditions**

107   Ion-chromatography (IC) analysis was performed on a Dionex Model DX-120

108   (Dionex, Sunnyvale, CA, USA) ion chromatograph equipped with Dionex IonPack

109   CS12A cation and AS14 anion exchanger columns and a CDM-3 conductivity detector.

110   For sample introduction, the solutions were injected through a 20 μl loop with a Dionex

111   AS-50 autosampler. The eluents for the anion and cation exchangers were solutions of

112   3.5 mM Na_2CO_3 plus 1.0 mM $NaHCO_3$, and 11 mM H_2SO_4, respectively, with flow

113   rates of 1.2 and 1.0 ml/min, respectively. For conductivity suppression of eluents, the

114   Dionex ASRS-ULTRA and CSRS-ULTRA columns were applied for the anion and

115   cation exchangers, respectively. Calibration was made against two sets of standards,

116   each containing five solutions of either anions, or cations to be determined. Limit of

117   detection (LOD) data were calculated from eleven independent determinations of field

118   blank filters, which were subjected to the same chemical procedure as the sample filters.

119   The LODs were found to be 0.1, 0.03, 0.02, 0.003, 0.004, 0.002, 0.01, 0.06, 0.1, 0.2,

120   0.6, and 0.1 $\mu g/m^3$ for Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_3^{2-}, and

121   SO_4^{2-}, respectively. The precision of the determinations for each analyte was better than

122   3.6 %. Certified Multianion and Multication Standard Solutions of PRIMUS (Sigma-

123   Aldrich, 210 Steinheim, Switzerland) as reference materials were applied for checking

124   the accuracy of the IC method.

125   **2.4 Sample preparation**

126   Each sample filter was leached in 15 ml Milli-Q water in a Branson 2210

127   (Bransonic, Danbury, CT, USA) ultrasonic bath using 15 min trembling time as

128   described by Eyckmans et al.[26] The absorber-tubes of the denuders were leached in 10

129   ml Milli-Q water. The leachates and sample filters were stored in sealed plastic vessels

130   at 4 ^{o}C till processing. Each leachate was filtered through a Millex-GV membrane filter

131   with 0.22 μm pore size to prevent any particle entering the IC columns.

132   **2.5 Statistical evaluation**

133   The methods of bivariate correlation analysis with the Pearson's correlation

134   coefficient (r) at two-tailed significance level (p), hierarchical cluster analysis (HCA),

135   and principal component analysis (PCA) was applied using the SPSS software package

136   (version 13.0). For PCA, the methods of Varimax-rotation and Kaiser-normalization

137   were applied. Only principal components having >10 % of total variance of the data sets

138   were used as factors. For HCA, the molar concentration data of ions were standardized

139   with the Z-score method, and then the Ward's method of clustering was applied with

140   squared Euclidean distance as a measure.

141   3. Results and discussion

142   3.1 Synoptic meteorological conditions

143   The weather in Flanders is qualified as moderate with fairly mild seasons

144   (Supplementary Table S2). For the sampling period, the daily average T_{air} and p_{air}

145   ranged between 3.2-17 ^{o}C and 1010-1024 hPa, respectively. The average daily level of

146   the usually high RH was fluctuating between 60-84 %. The prevailing WD was

147   observed to be south-western, i.e., air-masses coming from the Atlantic Ocean/British

148   Channel. In the first campaign, the winds blew predominantly from marine regions,

149   whereas a mixed continental/marine influence was experienced during the second

150   campaign (Table 1). The daily average WS, measured at 30 m height, ranged from 3.3

151   to 5.5 m/s, reflecting low atmospheric stability. Due to the primary contribution of

152   marine air-masses in the first campaign, a considerable extent of rain (643 mm/284 day)

153   was observed, whereas less precipitation was found during the second campaign (583

154   mm/285 day).

155   3.2 Distribution of $PM_{2.5}$ mass and ionic components

156   *3.2.1 Variation in $PM_{2.5}$ levels* – According to a recent legislation by the European

157   Commission (EC) to be attained till 2010, the daily mean concentration of $PM_{2.5}$ may

158   not exceed a yearly average of 25 $\mu g/m^3$. The average diurnal concentrations (ADCs) of

159     $PM_{2.5}$ ranged from 11 and 45 $\mu g/m^3$ over the six locations in Belgium. At these sites, the

160   average $PM_{2.5}$ data exceeded the EC-limit, i.e., for urban Borgerhout and Zelzate during

161   winter, and even for the rural/agricultural Wingene during spring (Table 2). Moreover,

162   the levels of $PM_{2.5}$ observed at Petroleumkaai and Mechelen were also found close to

163   the EC-limit value. These values are also comparable to those observed for the city of

164   Ghent in Belgium during winter in 2004-2005 (28.6 µg/m^3).[2] However, the average

165   summer PM$_{2.5}$ levels were around half of the winter values, e.g., Wingene and

166   Mechelen. This is in line with the average PM$_{2.5}$ for Ghent (12.4 µg/m^3) in summer. [2]

167   *3.2.2 Ratio of MIC to PM$_{2.5}$* – The MICs generally represented a significant fraction of

168   PM$_{2.5}$ with an average ratio of 34-50 % (Table 2). Similar ratios for Ghent have been

169   found in summer and winter, i.e., 38 and 43 %, respectively.[2] Mechelen site was the

170   only exception with a lower value of 18 % in the late spring/early summer campaign,

171   due to the more contribution of organic carbon. The diurnal concentration ratio of MICs

172   to PM$_{2.5}$ was found to be highly fluctuating in the range of 6-98 %.

173   **3.2 Seasonal and site-specific variation in the ionic composition of PM$_{2.5}$**

174   *3.2.1 Cations* – Na$^+$ and NH$_4^+$ were the most abundant cations in PM$_{2.5}$, and their ADCs

175   varied from 0.4-1.2 µg/m^3 and 0.9-4.9 µg/m^3, respectively (Table 1). Both species

176   showed a rather even distribution over sites and seasons. Peak values of Na$^+$ and NH$_4^+$

177   were found in winter for the industrial Petroleumkaai and the urban Borgerhout sites,

178   respectively. Minimum values for both elements were registered during spring/summer

179   campaigns at other sites (e.g., Mechelen, Zelzate, and Wingene). The higher levels of

180   Na$^+$ could be related to the maximum sea salt input, while the high NH$_4^+$ content was

181   due to the thermal stability of NH$_4$NO$_3$ in winter as opposed to summer. Similar results

182   have also been reported by Viana et al.[2] for Ghent, suggesting that the long-range

183   transport of air masses from the Atlantic Ocean determines the levels of these species.

184   Thus the present results show that the sea-salt input is maximal in winter over Belgium,

185   which is an opposite finding of what has been observed in Southern Europe.[2]

186   K$^+$ was found at a lower amount than the former cations. Its ADC ranged up to

187   0.24 μg/m^3 with peak values at the industrial and/or heavy/medium trafficked sites,

188   indicating the primary origin of K$^+$ from coal/wood and/or fuel/industrial combustion.

189   The Ca^{2+} and Mg^{2+} contents in PM$_{2.5}$ were relatively low for each site, varying between

190   0.01-0.05 μg/m^3. Exceptions were Zelzate and Hasselt in the late winter/early-spring

191   campaigns. These species are most likely related to exposed soil, unpaved roads and

192   construction works, and hence, such activities do not contribute much to the MICs of

193   PM$_{2.5}$.

194   ***3.2.2 Anions –*** High ADCs of SO$_4^{2-}$ (>2.3 μg/m^3) have generally been observed

195   compared to that of other anions, except for Wingene and Mechelen during spring with

196   values of 0.79 and 0.43 μg/m^3, respectively. Increased SO$_4^{2-}$ concentrations have

197   generally been reported for summer and spring.[16-29] This trend, however, was not

198   followed at Zelzate and Mechelen, which showed higher SO$_4^{2-}$ levels during winter.

199   However, elevated concentrations of this species have been used as an indicative of

200   emission from industrial coal combustion in Western Europe,[30] but coal combustion

201   does not dominate in the Flanders region, and hence, the sources can be attributed to the

202   long range transport of air masses from other regions.

203   The ADC of NO$_3^-$ was similarly high or even higher than those of SO$_4^{2-}$ during

204   the cold season. The important sources of NO$_3^-$ and SO$_4^{2-}$ in the atmosphere are the

205   secondary aerosols produced by oxidation of their gaseous precursors, NO$_2$ and SO$_2$,

206   respectively, emitted from various anthropogenic activities.[31,32] In big cities, NO$_2$

207   mainly originates from vehicular emission. Since this emission is generally distributed

208   evenly over the year, the variation in the NO$_3^-$ level might be strongly related to the

209   oxidation of NO/NO$_2$ (e.g., by O$_3$), and also meteorological factors, such as T$_{air}$, RH,

210   intensity of sunlight, and atmospheric stability.

211   During spring, Wingene showed very high ADCs of NO_3^- and NH_4^+, mainly due

212   to the intensive pig farming and fertilization. In summer, their concentrations decreased

213   most likely due to the thermal instability of NH_4NO_3 at higher ambient temperature

214   (above 25 ^{o}C), and also to reduced fertilization activities during this season. On the

215   contrary, the ADC of SO_4^{2-} increased in this period, due to the enhanced traffic,

216   connected with harvest (e.g., a more intensive use of diesel-fuelled vehicles over the

217   crops), and to a more rapid oxidation of SO_2.

218   The level of Cl^- showed considerable fluctuation with an ADC varying between

219   0.01-0.66 $\mu g/m^3$. Earlier studies have reported Cl^- depletion of sea-salt particles for

220   coastal areas in reaction with sulfuric and/or nitric acids.[33,34] Chloride mostly originates

221   from aerosols produced over the sea, thus its concentration highly depends on the

222   weather conditions. During the winter campaign, a fairly high ADC of Cl^- (0.35 $\mu g/m^3$)

223   was found in Zelzate, likely due to its relative closeness to the sea (~50 km), and the

224   prevalence of marine winds in this period. Furthermore, minimum levels of Cl^- in

225   summer can also result from its volatilization in the form of NH_4Cl by reaction of sea-

226   salt with NH_4NO_3.[35] Fluoride was detected at a quite low level (ADC: 0.01-0.02 $\mu g/m^3$).

227   Its peak value (0.03 $\mu g/m^3$) was observed at Zelzate in the first campaign, due to the

228   emission from the nearby steel-smelters, similarly to those of Cl^-, Ca^{2+}, Mg^{2+}, and K^+.

229   Apart from some very unique days of the sampling, PO_4^{3-} and SO_3^{2-} were not

230   detected. NO_2^- has only been found in Wingene (0.38 $\mu g/m^3$), Hasselt (0.04 $\mu g/m^3$), and

231   Mechelen (0.17 $\mu g/m^3$) during the late winter/spring period, and also in Wingene (0.12

232    $\mu g/m^3$), Hasselt (0.01-0.04 $\mu g/m^3$), and Petroleumkaai (0.1 $\mu g/m^3$) in summer and

233   winter. These increased concentrations were possible due to the heterogeneous

234   formation of NO_2^- at a higher level of its gaseous precursor (HNO_2), supported also by

235 atmospheric conditions (high RH, precipitation, and/or low intensity of sunlight), as

236 explained below.

3.4 Variation in the level of aerosol-forming gases

238 *3.4.1 Denuder data* – The ADCs of HNO_2 and HNO_3 were found to be similarly low

239 (0.3 μg/m^3) in Wingene (Table 3). In Mechelen, a similar pattern was observed in late

240 spring/summer with slightly increased values (0.8-1.0 μg/m^3), whereas in the cold

241 season the level of HNO_2 was almost an order of magnitude higher (2.0 μg/m^3) than that

242 of HNO_3. Outstandingly high levels of HNO_2 were also detected at Petroleumkaai in

243 both (autumn and winter) campaigns. This was probably due to an increased

244 concentration, and thus, a higher extent of deposition of NO_2, partly, by the high

245 amount of precipitation (Table 3), which increasing its conversion rate to HNO_2. NO_2 is

246 known to heterogeneously converted to HNO_2, when deposits onto various surfaces

247 such as grass, aerosols partly, with the assistance of humidity.[36] The Petroleum-harbor

248 is often with high concentrations of NO_x and suspended particulate (e.g., smoke), which

249 provides an appropriate medium to promote such reactions. The lower rate of

250 photochemical decomposition of HNO_2 by less favored atmospheric conditions (e.g.,

251 low intensity of sunlight) may also contribute to the accumulation of this pollutant at the

252 sites concerned.

253 The ADC of SO_2 was fairly low in the rural Wingene and the suburban site of

254 Mechelen (1.4-6 μg/m^3). Peak values were observed at Petroleumkaai, both in the early

255 fall and winter campaigns, 29 and 51 μg/m^3, respectively, reflecting the influence of oil-

256 refineries and related activities (e.g., ship-traffic).

257 The ADC of NH_3 (2-6 μg/m^3) did not fluctuate considerably over sampling sites

258 and/or seasons. Nor even during the fertilization period (spring) in Wingene, when

259 PM$_{2.5}$ was characterized by a high level of NH$_4^+$. Wingene is referred to as the centre of

260 pig farming, thus the emission of NH$_3$ should be maximum over this site. However, the

261 presence of NH$_3$ at a fairly constant atmospheric level at the sampling sites shows its

262 homogeneous spread over Flanders. Moreover, NH$_3$ does not primarily originate from

263 fertilization activities, but from animal keeping. Pig farming emits some 20 000 tons of

264 NH$_3$ per year over Flanders (it used to be 50 000 ton per year in 1990). Some 45 % of

265 this emission is in the Province of West Flanders, where Wingene is situated. The NH$_3$

266 emission originates from cattle stables, manure storage locations, manure spreading,

267 meadows and fertilizers in a decreasing order. Less important sources of NH$_3$ are the

268 agricultural crops and biomass burning/bio-fuel usage.[37]

269 *3.4.2 Direct monitoring* – The ADCs of NO and NO$_2$ were the highest at the heavy-

270 trafficked site of Borgerhout, ranging up to ~60 μg/m^3. Lower concentrations were

271 observed at the other sites of lower traffic density, ranging between 8-35 and 31-45

272 μg/m^3 for NO and NO$_2$, respectively. Higher ADCs of NO and NO$_2$ have been found in

273 the cold season. This trend was also observed for SO$_2$, apart from Wingene. The ADCs

274 of SO$_2$ acquired with direct and indirect monitoring were in fairly good agreement

275 (Table 3).

276   The temporal variation in SO$_2$, NO, and NO$_2$ levels obtained with direct

277 monitoring followed well the trend of SO$_2$, HNO$_2$, and HNO$_3$ levels achieved with the

278 indirect method, as well as trends of the related ionic components in PM$_{2.5}$ (Fig. 2).

279 Therefore, this relationship was evaluated with the aid of conversion factors as follows.

280 **3.5 Gaseous species and their relation with secondary PM$_{2.5}$ aerosol**

281 *3.5.1 Sulfur and nitrogen oxidation ratios* – To determine the degrees of atmospheric

282 conversion of SO$_2$ to SO$_4^{2-}$ and of NO$_2$ to NO$_3^-$, the sulfur and nitrogen oxidation ratios,

283   SOR and NOR, respectively, have been evaluated.[29,31,32,42] The SOR (or NOR)

284   expresses the extent of oxidation of S (or N) in terms of the ratio of sulfate S (or nitrate

285   N) to total S (or N) in sulfate (or nitrate) plus sulfur (or nitrogen) dioxide. Non-sea-salt

286   (NSS) SO_4^{2-} can be derived from total SO_4^{2-} and Na^+ levels as follows[42] (all

287   concentrations are in $\mu g/m^3$):

288                   $NSS\text{-}SO_4^{2-} = \text{total } SO_4^{2-} - 0.231 Na^+$ (1)

289   The SOR and NOR can be calculated as follows:

290                           $$SOR = \frac{S_{NSS-SO_4^{2-}}}{S_{NSS-SO_4^{2-}} + S_{SO_2}}$$ (2)

291                           $$NOR = \frac{N_{NO_3^-}}{N_{NO_3^-} + N_{NO_x}}$$ (3)

292   where the units of $S_{NSS-SO_{42-}}$ and S_{SO_2} are $\mu g\ S/m^3$, and the units of $N_{NO_{3-}}$ and N_{NO_2} are

293    $\mu g\ N/m^3$.

294   The SOR for $PM_{8.0}$ exceeding 0.1 shows that SO_2 is photochemically oxidized in

295   the atmosphere.[42] The present SOR data confirm a rather intensive formation of sulfate

296   aerosols over Wingene and a low-to-moderate conversion for other sites in Flanders

297   (Table 4). Apparently, they did not reveal any site-specific and/or seasonal trend for

298   Hasselt, Borgerhout, and Petroleumkaai, but for Zelzate a higher SOR in

299   summer/autumn than winter. The outstandingly high SORs observed for Wingene may

300   be explained with the increased traffic of agricultural vehicles during the sampling

301   periods, which utilize the 'agricultural' diesel with high sulfur content. Long range

302   transport of ship-emission related sulfur from the ship-routes of the North Sea is also a

303   plausible explanation. Furthermore, the high SOR could also be explained with the rural

304   characteristics of this site, where most of the SO_4^{2-} is secondary (i.e., no primary

305 sources nearby). It appears that SOR values are only lower, when SO_4^{2-} comes from

306 primary sources (e.g., marine or anthropogenic SO_4^{2-}). Interestingly, the SOR value is

307 higher in spring than summer (Table 4). This indicates a faster transformation of SO_2 to

308 SO_4^{2-}, due to the higher number of sunny days with enhanced levels of O_3, and a

309 contribution of other sources to SO_4^{2-} levels (e.g., traffic of diesel-fuelled vehicles)

310 during spring. Then again, surprisingly higher SOR has also been found for the

311 suburban site of Mechelen in the late autumn/winter than the late spring/summer

312 campaign.

313   The NOR data varied between 0.004-0.08 with an average value of 0.03,

314 supporting an effective formation of nitrate aerosols, but to a lower extent than that of

315 sulfates (Table 4). The NOR is generally found to be lower than SOR.[44] The present

316 NOR data have shown a higher site-specific and seasonal variation than SORs. The

317 partition of inorganic NO_3^- between gaseous HNO_3 and particulate NH_4NO_3 is driven

318 towards the latter in the cold season.[45] Most of the NOR data for Flanders support this

319 observation. The exception was Wingene again with a higher NOR value for spring than

320 summer, which is expected, since the ambient temperature is higher in summer than

321 spring. Interestingly, the NOR data of Wingene followed the same seasonal trend as

322 observed for SORs; whereas the seasonal variation for SOR and NOR was the opposite

323 for other sites, a similar trend to that reported for SO_4^{2-} and NO_3^-.[3,35] The trend for

324 Wingene might be explained with the high amount of precipitation during the summer

325 period, which can regulate the concentration of gases and aerosols.

326   On the base of SOR data one can classify a site as a source and/or a receptor

327 area.[46] The SOR in the ranges of 0.05-0.35 and 0.15-0.49 in winter, and 0.09-0.48 and

328 0.30-0.63 in summer, correspond to source and receptor areas, respectively. For PM_{10}

329 aerosol, however, the SOR values are generally higher by around 1.2-fold.[32]

330   Consequently, one can define ranges of SOR for $PM_{2.5}$ i.e., 0.04-0.30 and 0.13-0.42 in

331   winter, and 0.08-0.41 and 0.26-0.54 in summer, correspond to source and receptor

332   areas, respectively Using this sorting almost all the sites studied can be classified as

333   source areas, irrespective of the season. The only exception is Wingene, which behaves

334   as a receptor area in spring and a combined source/receptor area during summer.

335   *3.5.2 Neutralization ratio (NR)* – The NR, by definition, expresses the degree of

336   neutralization of aerosol acidity: [43]

337
$$NR = \frac{NH_4^+}{NSS - SO_4^{2-} + NO_3^-} \qquad (4)$$

338   The molar concentration of NH_4^+ is taken as the amount needed to neutralize the

339   acidity (all the concentrations are in mol/m^3). The NR is indicative of the ratio of NH_4^+

340   or H^+, presents in the ammonium sulfate, and does not reflects real ion-balance; hence,

341   its value may be observed over unity (for excess of atmospheric NH_3 reacting with

342   NH_4HSO_4). When the NR is unity, or higher, it indicates the presence of sulfate and

343   nitrate predominantly as their ammonium salts, while lower values of NR imply the

344   presence of acidic sulfate and nitrate, which are then neutralized by Na^+, Ca^{2+}, Mg^{2+},

345   etc. The NRs were well above unity for various sites and/or seasons (Table 4),

346   indicating the excess of NH_4^+, likely as NH_4Cl aerosols, existing by evaporation and/or

347   decomposition in the gas-phase. These NR values are significantly higher than those

348   found over other continents. [43, 47]

349   The molar cation-to-anion ratios for NH_4^+ and the major anions exceeded unity

350   and highly varied for all sites, indicating that a part of NH_4^+ probably exists in the gas

351   phase by vaporization. In the gas phase, first, NH_3 neutralizes H_2SO_4 to form sulfate

352   aerosols. After then, the excess NH_3 reacts with HNO_3 to form NH_4NO_3.[45] Hence, it

353   seems that aerosol particles appeared mostly in the forms of $(NH_4)_2SO_4$ and NH_4NO_3

354 salts over Flanders. Small, but still significant amounts of anions missing for the charge

355 compensation of the excess of cations observed at few sites (Table 4) is likely due to the

356 presence of carbonaceous and/or organic anions in $PM_{2.5}$, which could not be detected

357 with the IC methodology applied.

3.6 Sea-salt particle contribution

359 The average molar Na^+ to Cl^- ratios for $PM_{2.5}$ ranged from 2.0 to 11 over the

360 sites/campaigns. The ratio of sea-salt in $PM_{2.5}$, calculated according to Maenhaut et al.[14]

361 was found to be 7.0 and 8.1 % for the first and second campaigns, respectively. These

362 values are a bit higher than the literature values for Ghent, i.e., 4 and 5 % for summer

363 2004 and winter 2004-2005, respectively.[2] However, they are close to the values (4.2

364 and 5.0 %) found for the urban site of Borgerhout (Table 2). The enhanced sea-salt

365 input to Flanders observed during this study can be explained with the prevailing marine

366 winds over the sampling period (Table 1).

367 As a first approach to estimate the sea-salt Cl-loss, suspended Na^+ was assumed

368 to be derived only from sea-salt particles.[42] Considering that Cl_{sea} is the amount of Cl^-

369 originally present in sea-salt,

$$Cl_{sea} = 1.8Na^+ \qquad (5)$$

371 then one can calculate the chloride residual rate (Cl_{res}) and chloride loss (Cl_{loss}) as

372 follows:

$$Cl_{res}=Cl^-/Cl_{sea} \qquad (6)$$

$$Cl_{loss}=Cl_{sea}-Cl^- \qquad (7)$$

375 For the first and second campaigns, Cl_{sea} ranged from 0.7-1.5 and from 0.8-2.2

376 $\mu g/m^3$, respectively, while Cl_{loss} varied between 0.5-1.4, and 0.8-2.1 $\mu g/m^3$, respectively

377 (Table 4), corresponding to 69-95 % and 92-96 % sea-salt Cl-loss with average values

378   of 79 and 93 %, respectively. Most of these values are comparatively higher than those

379   observed at coastal cities,[32] suggesting a more limited transport of fine sea-salt particles

380   from the marine environment to terrestrial areas, due to more intensive atmospheric

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

382   Other possibility for Cl-loss is the conversion of fine sea-salt to coarse, "aged"

383   particles with a short atmospheric life-time, due to rapid deposition. The Cl-loss from

384   sea-salt particles has been found to be higher for fine particles.[48] In this study, sites

385   situated further from the sea (e.g., Hasselt) and/or possessing strong anthropogenic

386   influence (e.g., Petroleumkaai) showed higher Cl-loss in $PM_{2.5}$. It followed, therefore,

387   that the rural Wingene, as the closest (~30 km) site to the coast, experienced the lowest

388   Cl-loss.

389   **3.7 Source apportionment of $PM_{2.5}$ in Belgium**

390   ***3.7.1 Correlation analysis –*** SO_4^{2-} and NH_4^+ was reported as the most abundant species

391   in $PM_{2.5}$, while NO_3^- and Na^+ were found in both fine and coarse particles of 2.5-100

392   μm size.[38] NO_3^- mainly exists in coarse mode together with alkaline ions, such as Ca^{2+}

393   and K^+.[39,40] In this study, a strong correlation of NO_3^- was found with NH_4^+ (r=0.95,

394   p=0.01), and also with Ca^{2+} (r=0.73, p=0.01) and K^+ (r=0.78, p=0.01) in $PM_{2.5}$.

395   Moreover, correlation of NO_3^- was observed with Na^+ (r=0.4). Particulate NO_3^- is

396   mainly formed by oxidation of NO_x to HNO_3, which then forms particles through the

397   reaction either with NaCl, or NH_3.[41] SO_4^{2-} was weakly correlated with other ions of

398     $PM_{2.5}$, indicating its widespread presence and formation from SO_2 over Flanders.

399   However fluoride could be of natural (crustal) origin but it seems primarily from

400   anthropogenic sources (e.g., steel/aluminum smelters, coal fueled power plants, and

401   super-phosphate fertilizer manufacture). Oravisjarvi et al.[50] have also suggested that

402   particles between 2.5 and 10 μm in size are more related to a soil source instead of

403    $PM_{2.5}$. The level of F^- was significantly anti-correlated with that of Na^+ (r=-0.66,

404   p=0.05), and weakly with that of SO_4^{2-} (r=-0.55). The level of Cl^- was strongly

405   correlated with those of Mg^{2+} (r=0.85, p=0.01) and Ca^{2+} (r=0.62, p=0.05), but weakly

406   correlated with that of F^- (r=0.53, p=0.05). These findings suggest the local,

407   anthropogenic origin of F^-, given that the high levels of Na^+ imply transport of aerosols

408   from the sea, and therefore, a lower influence of local anthropogenic sources of

409   particulate. The strong correlation of Cl^- with both Mg^{2+} and Ca^{2+} suggests their origin

410   in $PM_{2.5}$ mostly from aerosols produced over the sea.

411   *3.7.2 Cluster analysis* – HCA revealed three dominating groups of compounds in MICs

412   of $PM_{2.5}$ i.e. (i) NH_4NO_3, KNO_3; (ii) Na_2SO_4; and (iii) $MgCl_2$, $CaCl_2$, MgF_2, CaF_2.

413   Mixtures of these groups were also present, certainly, with a lower abundance. The first

414   group represents aerosols that originate mostly from combustions of coal/wood and

415   secondary aerosol formation. The second is Na_2SO_4, which is formed in reaction of sea-

416   salt with H_2SO_4. The third group is assumed to be the reaction-products of sea-salt with

417   anthropogenic (mainly combustion) aerosols and/or soil-dust.

418   *3.7.3 Source apportionment by PCA*

419   To enhance the accuracy of emission sources identification and their relative

420   contribution, the method of PCA was also applied. Normalized levels of gaseous, ionic,

421   and fine particles were used for PCA and subsequent results are shown in Table 5. The

422   factor loading correlates these variables and they represent the most important

423   information on which interpretation of the factors is based. However, it has to be

424   noticed that Table 5 shows only factors having an eigen value above 1 with a variance

425   of more than 10% and this results in two main factors for each site. First factor is

426   generally more correlated with the variables than the second factors because these

427 factors are extracted successively, each one accounting for as much of remaining

428 variables as possible.

429   For all the sites, factor 1 shows high factor loadings for N- and S-species, which

430 indicates the formation of secondary aerosols, and supports the conclusions for SOR

431 and NOR. Both NO_3^- and SO_4^{2-} are largely produced as secondary aerosols during coal

432 combustion, biomass burning and vehicular emission.[45] They seem to be also dominant

433 sources of MIC of $PM_{2.5}$ in Belgium, which is a similar result to that found for

434 Beijing.[46] Factor 1 also has high factor loadings of Cl^- and F^- at Petroleumkaai and for

435 factor 2 at Hasselt, respectively. Both sites have significant ship-traffic and also

436 influenced by industrial emissions. Hence, Cl^- at these sites may also originate from

437 anthropogenic activities. At Hasselt a nearby paper industry may also explain the factor

438 loading for Cl^-. These sites also show high factor loadings of F^-, the source of which

439 could be associated with steel/aluminum smelters [50], coal fueled power plants and

440 super-phosphate fertilizer manufacture. K^+ has high loading for factor 1 at Hasselt and

441 Mechelen and for factor 2 at Borgerhout and Wingene. SO_4^{2-} has also high factor

442 loadings for Hasselt and Mechelen. Several studies have used high loading of these

443 species as an indication of coal/wood burning.[34,49] Moreover, at Borgerhout the

444 domestic heating (likely coal/wood burning) during the cold season and at Hasselt the

445 emission from the movement of ships have also an influence on the factor loading.

446   The factor 1 also shows high factor loadings for NH_3 and NH_4^+. The former is

447 the most abundant gaseous alkaline component of the atmosphere. The major sources of

448 NH_3 include in animal farming, fertilizers and decomposition of organic matter.

449 Generally, NH_3 is not transported over long distances,[37] as it is rapidly converted into

450 NH_4^+ aerosols at a rate of 30 % h^{-1}. Consequently, the results of factor analysis also

451 confirm the uniform distribution of these activities in Belgium.

4. Conclusions

452

453   The water-soluble, ionic compounds have been found to be representing a

454   significant part of $PM_{2.5}$ aerosols with a varying composition over six locations in

455   Belgium. Their contribution sometimes reached 80-90 % of the total mass of $PM_{2.5}$

456   aerosols, and showed rather alkaline chemical characteristics. This observation also

457   raises more questions about the health related effects and human risks for this aerosol

458   fraction. Fine particles are formed primarily by combustion and/or secondary chemical

459   reactions in the atmosphere. The fairly high SO_4^{2-} and NO_3^- concentrations in Belgium

460   suggest that photochemical oxidation occurs, and more secondary aerosols can be

461   produced in the atmosphere. This is also confirmed by the present calculations for SOR,

462   NOR, and NR ratios. A part of the secondary aerosols of ammonium salts likely

463   decompose by releasing NH_3, according to the shift in the compensation point of NH_3,

464   for example, by fast changing weather conditions. The resultant acidic decomposition

465   products are readily neutralized with other common salts of the atmosphere.

466   This study indicates the contribution of sea-salt particles from the sea to the

467   urban areas. Particles of sea-salt origin showed a considerable decrease in $PM_{2.5}$ with an

468   increasing distance from the coast. Moreover, their level in $PM_{2.5}$ was very dependent

469   on the meteorological conditions and atmospheric removal processes. PCA shows the

470   existence of mixed sources of vehicular emissions, coal/wood burning, industrial

471   activities and animal farming in Belgium. The present study also provides an aid in the

472   implementation of the new European $PM_{2.5}$ air quality standard, and also, the accessed

473   data can be useful to evaluate the human health risk of $PM_{2.5}$ aerosols.

479

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Table 1. Average values of the diurnal concentrations of major ionic species in $PM_{2.5}$ (µg/m³) over six locations in Flanders during various seasons

Location – campaign	Sampling period (day/month/year)	Season	Main wind directions	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	n
Petroleumkaai-1	18/09/2001-29/10/2001	A	SW	0.77	1.74	n.d.	n.d.	n.d.	0.01	0.07	0.76	4.12	36
Petroleumkaai-2	19/12/2002-23/02/2003	Wi	S-SW/NE	1.22	2.48	0.14	n.d.	n.d.	n.d.	0.12	3.15	2.69	52
Borgerhout-1	06/11/2001-10/12/2001	A-Wi	SW	0.54	2.40	0.14	0.02	0.03	0.02	0.19	3.22	4.23	32
Borgerhout-2	10/02/2003-07/04/2003	Wi-Sp	E/E-NE/SE	1.12	4.94	0.24	0.01	0.05	n.d.	0.10	7.63	4.30	45
Zelzate-1	11/12/2001-30/01/2002	Wi	SW/W-SW	0.74	2.62	0.20	0.04	0.05	0.01	0.35	3.60	4.48	51
Zelzate-2	13/08/2002-26/09/2002	Su-A	N/N-NE	0.52	1.25	0.09	n.d.	0.01	0.02	0.09	0.58	3.30	40
Hasselt-1	01/02/2002-26/03/2002	Wi-Sp	SW/W-SW	0.50	1.46	0.10	0.04	0.03	0.01	0.22	2.76	2.31	46
Hasselt-2	27/09/2002-04/11/2002	A	SW/W	0.72	1.31	0.08	n.d.	n.d.	0.02	0.13	1.72	2.53	38
Mechelen-1	16/05/2002-26/06/2002	Sp-Su	SW	0.38	0.89	0.06	0.01	n.d.	0.02	0.16	0.40	0.43	30
Mechelen-2	05/11/2002-03/01/2003	A-Wi	S/SE/E	0.78	2.06	0.20	n.d.	n.d.	n.d.	0.07	2.51	3.48	38
Wingene-1	27/03/2002-15/05/2002	Sp	SW/N/N-NE	0.40	3.54	0.17	0.01	0.03	0.02	0.20	6.53	0.79	41
Wingene-2	27/06/2002-12/08/2002	Su	SW/W/NW	0.42	1.31	0.11	n.d.	n.d.	n.d.	0.09	0.34	3.26	45

Abbreviations: A –autumn, Wi – winter, Sp – spring, Su – summer,
n – number of daily data used for calculating average concentrations

n.d. – not detected with the methodology applied in this work

Table 2 Average values and fluctuations (expressed as the standard deviation – ±SD) of the diurnal (24 h) concentrations for $PM_{2.5}$, and ratios of major ionic species to $PM_{2.5}$

Location – campaign	Season	Average precipitation (mm)	Level of $PM_{2.5}$ ($\mu g/m^3$)		MIC in $PM_{2.5}$ (%)	
			Range	Average ± SD	Range	Average ± SD
Petroleumkaai-1	A	3.0 ± 6.0	7.9 - 60	20 ±11	20 - 54	34 ±8
Petroleumkaai-2	Wi	3.5 ± 5.9	6.3 - 62	21 ±12	20 - 98	48 ±16
Borgerhout-1	A-Wi	2.7 ± 4.7	0.2 - 63	29 ± 15	19 - 53	35 ±9
Borgerhout-2	Wi-Sp	0.9 ± 1.8	14 - 100	45 ±22	9 - 64	38 ±13
Zelzate-1	Wi	1.8 ± 3.5	1.6 - 68	26 ±16	26 - 91	50 ±13
Zelzate-2	Su-A	1.0 ± 2.4	5.9 - 44	16 ±8	11 - 83	37 ±10
Hasselt-1	Wi-Sp	3.2 ± 4.3	5.5 - 59	19 ±13	13 - 72	41 ±11
Hasselt-2	A	2.1 ± 3.0	4.4 - 39	16 ±8	7 - 58	40 ±12
Mechelen-1	Sp-Su	2.1 ± 5.1	7.1 - 21	12 ±7	7 - 54	18 ±10
Mechelen-2	A-Wi	2.6 ± 4.0	9.2 - 60	24 ±13	17 - 57	36 ±10
Wingene-1	Sp	1.3 ± 2.3	7.0 - 64	28 ±16	19 - 59	36 ±11
Wingene-2	Su	2.2 ± 5.0	5.2 - 23	11 ±4	6 - 81	49 ±13

Table 3 Average values and fluctuations (±SD) of the diurnal concentrations of gaseous species (in $\mu g/m^3$) from direct monitoring and indirect method (denuder sampling and IC analysis), together with the averages of the diurnal precipitation

Location – campaign	Season	Average precipitation (mm)	Direct monitoring			Denuder sampling and IC analysis			
			NO	NO_2	SO_2	HNO_2	HNO_3	SO_2	NH_3
Petroleumkaai-1	A	3.0 ± 6.0	24 ± 16	42 ± 11	26 ± 14	3 ± 1	0.4 ± 0.2	29 ± 15	5 ± 2
Petroleumkaai-2	Wi	3.5 ± 5.9	35 ± 34	46 ± 15	34 ± 24	4 ± 2	0.2 ± 0.2	51 ± 32	6 ± 3
Borgerhout-1	A-Wi	2.7 ± 4.7	58 ± 49	53 ± 10	17 ± 8	-	-	-	-
Borgerhout-2	Wi-Sp	0.9 ± 1.8	38 ± 32	61 ± 20	18 ± 12	-	-	-	-
Zelzate-1	Wi	1.8 ± 3.5	30 ± 41	37 ± 15	19 ± 9	-	-	-	-
Zelzate-2	Su-A	1.0 ± 2.4	12 ± 12	31 ± 9	6 ± 4	-	-	-	-
Hasselt-1	W-Sp	3.2 ± 4.3	-	-	5 ± 4	-	-	-	-
Hasselt-2	A	2.1 ± 3.0	-	-	5 ± 2	-	-	-	-
Mechelen-1	Sp-Su	2.1 ± 5.1	8 ± 4	32 ± 8	6 ± 3	0.8 ± 0.3	1.0 ± 0.7	3 ± 2	4 ± 1
Mechelen-2	A-Wi	2.6 ± 4.0	30 ± 28	45 ± 13	8 ± 6	2 ± 2	0.3 ± 0.2	6 ± 6	2 ± 3
Wingene-1	Sp	1.3 ± 2.3	-	-	-	0.5 ± 0.3	0.3 ± 0.2	3 ± 3	6 ± 4
Wingene-2	Su	2.2 ± 5.0	-	-	-	0.3 ± 0.1	0.3 ± 0.1	1.4 ± 0.6	5 ± 2

Abbreviations: A –autumn, Wi – winter, Sp – spring, Su – summer,

Table 4 Average values and variations (±SD) for non-sea-salt sulfate, SOR, NOR, NR, sea-salt, and Cl-contribution/loss of $PM_{2.5}$ for various locations and seasons

Location	Season[a]	Non-sea-salt sulfate (µg/m³)	SOR[b]	NOR[b]	NR	Cl_{sea} (µg/m³)	Cl_{res}	Cl_{loss} (µg/m³)	Sea-salt (%)	Cation extra charge (mol)	n[c]
Campaign 1.											
Petroleumkaai	A	3.9 ± 2.6	0.11 ± 0.09	0.005 ± 0.007	1.8 ± 0.3	1.5 ± 0.4	0.05 ± 0.03	1.4 ± 0.4	8.2 ± 5.2	0.01	36
Borgerhout	A-Wi	4.1 ± 2.9	0.13 ± 0.08	0.009 ± 0.007	1.3 ± 0.5	1.0 ± 0.4	0.22 ± 0.23	0.8 ± 0.5	4.2 ± 3.1	0.02	32
Zelzate	Wi	4.3 ± 2.8	0.15 ± 0.10	0.02 ± 0.01	1.3 ± 0.3	1.4 ± 0.6	0.26 ± 0.36	1.0 ± 0.5	9.5 ± 10	0.03	51
Hasselt	Wi-Sp	2.1 ± 1.5	0.23 ± 0.09	-	1.2 ± 0.3	0.9 ± 0.4	0.20 ± 0.24	0.7 ± 0.3	7.5 ± 7.3	0.01	46
Wingene	Sp	0.7 ± 2.2	0.71 ± 0.27	0.03 ± 0.01	2.4 ± 1.9	0.7 ± 0.6	0.48 ± 0.85	0.5 ± 0.6	5.0 ± 6.1	0.10	41
Mechelen	Sp-Su	0.4 ± 1.3	0.10 ± 0.20	0.07 ± 0.11	2.2 ± 0.8	0.7 ± 0.4	0.27 ± 0.32	0.5 ± 0.4	6.1 ± 3.7	0.05	30
Campaign 2.											
Petroleumkaai	Wi	2.4 ± 1.4	0.10 ± 0.08	0.05 ± 0.04	1.9 ± 0.3	2.2 ± 0.5	0.06 ± 0.08	2.1 ± 0.6	11.8 ± 7.4	0.09	52
Borgerhout	Wi-Sp	4.1 ± 3.1	0.14 ± 0.10	0.08 ± 0.05	1.8 ± 0.3	2.1 ± 1.1	0.06 ± 0.07	2.0 ± 1.1	5.0 ± 3.9	0.12	44
Zelzate	Su-A	3.2 ± 1.9	0.26 ± 0.12	0.01 ± 0.01	1.8 ± 1.1	1.0 ± 0.7	0.11 ± 0.30	0.9 ± 0.7	6.5 ± 5.1	0.01	40
Hasselt	A	2.4 ± 1.5	0.23 ± 0.11	-	1.4 ± 0.3	1.3 ± 0.8	0.08 ± 0.09	1.2 ± 0.7	11.0 ± 12	0.02	38
Wingene	Su	3.2 ± 1.8	0.45 ± 0.17	0.004 ± 0.002	2.0 ± 0.6	0.8 ± 0.5	0.50 ± 2.60	0.8 ± 0.5	7.4 ± 6.1	0.02	45
Mechelen	A-Wi	3.3 ± 1.9	0.21 ± 0.08	0.04 ± 0.03	1.4 ± 0.4	1.4 ± 0.7	0.05 ± 0.05	1.4 ± 0.6	6.4 ± 5.0	0.04	38

[a] Abbreviations: A – autumn, Wi – winter, Sp – spring, Su – summer
[b] SOR and NOR were calculated with the data of direct gas-monitoring, except Wingene, for the denuder data was applied
[c] Number of diurnal data used for the calculation

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17 Table 5 Factor analyses of the major ionic components, PM$_{2.5}$, PM$_{10}$ and gaseous pollutants for various locations.
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| Species	Petroleumkaai		Borgerhout		Zelzate		Hasselt		Wingene		Mechelen	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Gaseous[*]												
NO (a)	0.999	0.027	0.962	0.142	0.995	-0.076	-	-			0.603	0.685
NO$_2$ (a)	0.872	0.428	0.977	0.115	0.774	0.516	-	-			0.777	0.377
SO$_2$ (a)	-0.979	0.150	0.974	0.033	0.310	-0.265	0.917	-0.229			0.808	0.465
HNO$_2$ (b)	0.931	0.346	0.865	0.202	0.330	0.708	-	-	0.829	-0.065	0.815	0.540
HNO$_3$ (b)	-0.185	0.080	-	-	0.933	0.116	-	-	0.259	0.616	-0.737	0.200
SO$_2$ (b)	-0.426	0.899	0.368	0.100	0.922	0.259	-	-	0.927	-0.054	0.828	0.402
NH$_3$ (b)	0.771	-0.402	-0.243	0.676	-	-	-	-	0.803	0.288	-0.049	0.974
Ionic												
Na$^+$	-0.629	-0.548	-0.805	-0.583	0.179	-0.020	-0.493	-0.087	-0.291	0.361	0.889	0.070
NH$_4^+$	0.946	0.029	-0.237	0.964	0.973	0.983	0.876	0.370	0.929	0.149	0.915	0.235
K$^+$	-	-	0.347	0.773	-	-	0.694	0.484	0.197	0.578	0.829	0.487
Mg^{2+}	-	-	-	-	-	-	-0.093	0.027			-	
Ca^{2+}	-	-	-	-	-	-	0.487	0.195			-	
F$^-$	-0.435	-0.867	-	-	-	-	0.036	-0.915			-	
Cl$^-$	0.967	-0.161	-	-	-	-	-0.142	-0.895			-	
NO$_3^-$	0.977	-0.041	0.121	0.985	-0.212	0.939	0.872	0.318	0.934	-0.183	0.945	0.274
SO$_4^{2-}$	0.905	0.063	-0.822	0.428	0.945	0.121	0.723	0.656	0.084	0.888	0.932	0.113
PM$_{2.5}$	0.954	0.144	0.550	0.822	0.012	0.998	0.990	0.061	0.904	-0.234	0.917	0.325
Eigenvalue	11.09	2.46	7.62	3.96	6.69	4.30	6.54	2.49	5.43	1.87	10.67	1.48
Varience (%)	73.90	16.43	58.59	30.49	55.75	35.86	54.46	20.78	49.37	17.04	76.20	10.55
Cumulative	73.90	90.33	58.59	89.08	55.75	91.61	54.46	75.23	49.37	66.41	76.20	86.75

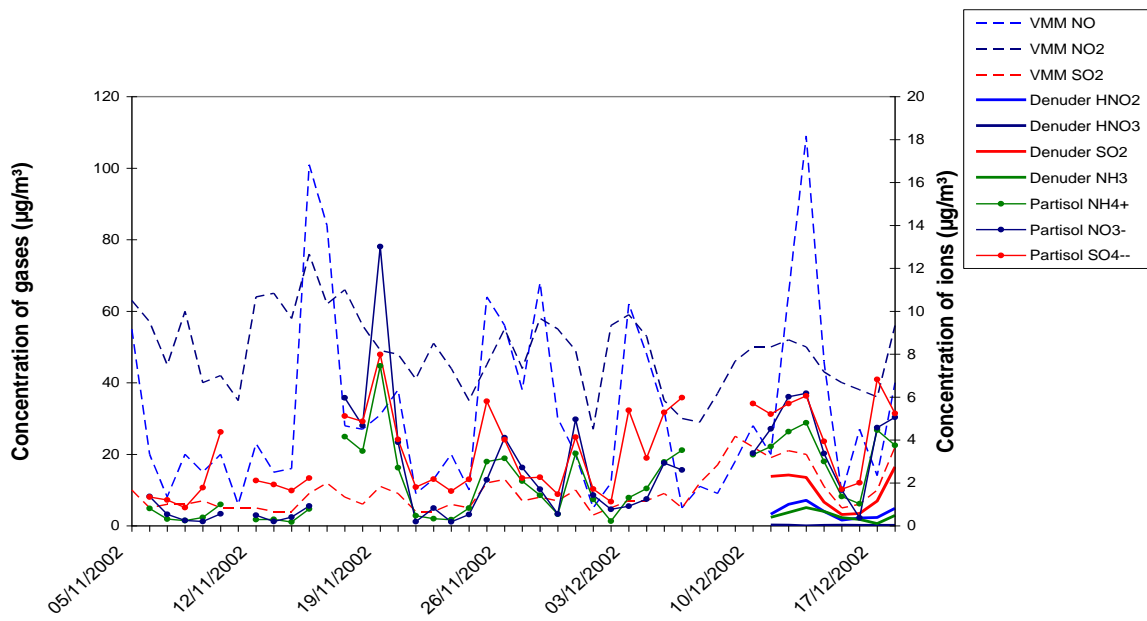19 [*] Direct gas monitoring (a) or denuder sampling and IC analysis (b)
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Figure 1. Map showing sampling location in the northern part of Belgium (Source: Google Earth).

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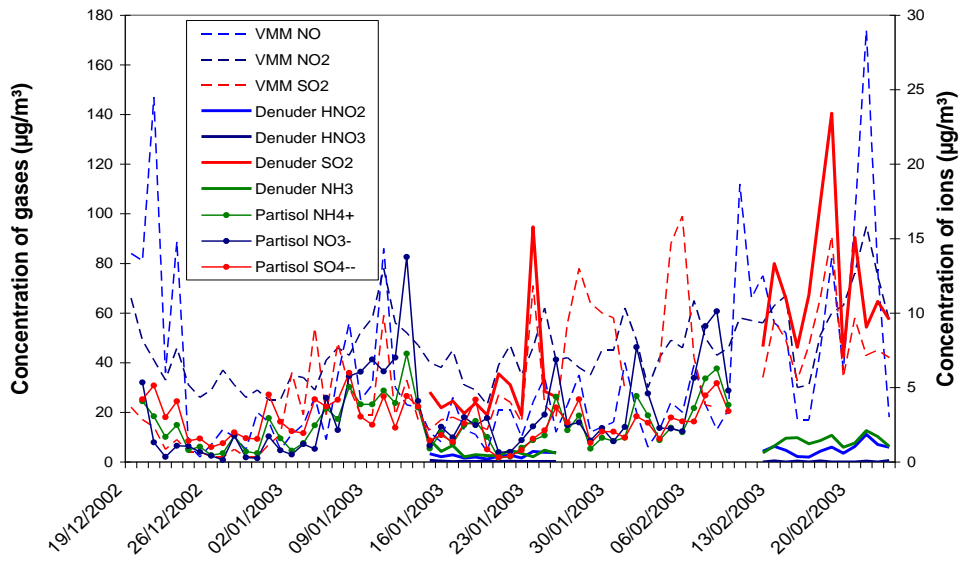
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34 Figure 2. Temporal variation in the levels of gases and related ionic species in $PM_{2.5}$ at the industrial site of
35 Petroleumkaai (above) and at the suburban Mechelen (below)

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