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 µg/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 µg/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 ionic species and gaseous pollutants; particularly, on the formation of secondary aerosols of sulfates and nitrates and sea-salt particle contribution. Several approaches were also applied to enhance the accuracy of the emission source identification of $PM_{2.5}$.

2. Experimental

2.1 Site characteristics

Six sampling locations were selected in Northern Belgium (Flanders) based on their different anthropogenic activities (Fig. 1), i.e., (i) Petroleumkaai in Antwerp (industrial site, petroleum harbor with oil-refineries and plants), (ii) Borgerhout district in Antwerp, (urban site with high traffic density (40-50 thousand cars/day), (iii) Zelzate (suburban site at a major road intersection, nearby motorway, and influence of steel-industry), (iv) Hasselt (suburban site, at the bank of the Albert Channel with shipping at nearby sluice gates, close to a highway with medium/low traffic density, and a fairly nearby newspaper (press) industry), (v) Wingene (rural, agricultural area of very low traffic density, but the most intensive pig farming over Flanders), and (vi) Mechelen (suburban site with low traffic density, some industrial impact from detergent (laundry) manufacturing).

2.2 Sampling of gases and aerosols

All sampling sites were visited twice, and minimum six-week-long sampling campaigns were scheduled for various seasons (Table 1) and details also shown in a Gantt chart (Supplementary Table S1). Wind-speed (WS), wind direction (WD), relative humidity (RH), air temperature (T_{air}), air pressure (p_{air}), and precipitation (PR) were recorded at meteorological stations of VMM nearby the sampling sites and at the Luchtbal M802 station near Antwerp.

Automated Rupprecht & Patashnik (R&P) Model Partisol Plus samplers with a calibrated air-flow rate of 1 m^3/h were used for 24-hour, midnight-to-midnight sampling of $PM_{2.5}$ and PM_{10} onto Zefluor Teflon filters of 47 mm diameter and 2 μm pore size (Pall Gelman Laboratory, Ann Arbor, MI, USA). The filters were weighed on a Sartorius M5P-000V001 micro-balance before and after sampling, according to the EN 12341 protocol. Simultaneous sampling of gaseous NH_3, SO_2, HNO_2, and HNO_3 was performed on a 24-hour base with an air-flow of 0.6 m^3/h over a coated set of absorber-tubes attached to either a honeycomb denuder of VITO equipped with a $PM_{2.5}$ sampler-head, or an R&P Partisol Speciation Sampler "chemcomb". The coatings of the tubes were prepared with solutions of 2 % (m/v) citric acid in methanol, and 2 % (m/v) Na_2CO_3 in ultra-pure water (Milli-Q RG, Millipore) for sampling alkaline and acidic gases, respectively. All the chemicals used were of analytical grade, or better quality.

Wingene, Mechelen, and Petroleumkaai were sampled with denuders. Except Wingene, levels of SO_2 and NO_x were monitored on a half-hourly base with TEI 43C and TEI 42C (Thermo Fisher Scientific, Waltham, MA, USA) automatic analyzers based on UV-fluorescence and chemi-luminescence methods, respectively. The half-hourly values were averaged to get diurnal data.

2.3 Ion-chromatography conditions

Ion-chromatography (IC) analysis was performed on a Dionex Model DX-120 (Dionex, Sunnyvale, CA, USA) ion chromatograph equipped with Dionex IonPack CS12A cation and AS14 anion exchanger columns and a CDM-3 conductivity detector. For sample introduction, the solutions were injected through a 20 μl loop with a Dionex AS-50 autosampler. The eluents for the anion and cation exchangers were solutions of 3.5 mM Na_2CO_3 plus 1.0 mM $NaHCO_3$, and 11 mM H_2SO_4, respectively, with flow rates of 1.2 and 1.0 ml/min, respectively. For conductivity suppression of eluents, the

Dionex ASRS-ULTRA and CSRS-ULTRA columns were applied for the anion and cation exchangers, respectively. Calibration was made against two sets of standards, each containing five solutions of either anions, or cations to be determined. Limit of detection (LOD) data were calculated from eleven independent determinations of field blank filters, which were subjected to the same chemical procedure as the sample filters. 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, 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 SO_4^{2-}, respectively. The precision of the determinations for each analyte was better than 3.6 %. Certified Multianion and Multication Standard Solutions of PRIMUS (Sigma-Aldrich, 210 Steinheim, Switzerland) as reference materials were applied for checking the accuracy of the IC method.

2.4 Sample preparation

Each sample filter was leached in 15 ml Milli-Q water in a Branson 2210 (Bransonic, Danbury, CT, USA) ultrasonic bath using 15 min trembling time as described by Eyckmans et al.[26] The absorber-tubes of the denuders were leached in 10 ml Milli-Q water. The leachates and sample filters were stored in sealed plastic vessels at 4 ^oC till processing. Each leachate was filtered through a Millex-GV membrane filter with 0.22 μm pore size to prevent any particle entering the IC columns.

2.5 Statistical evaluation

The methods of bivariate correlation analysis with the Pearson’s correlation coefficient (r) at two-tailed significance level (p), hierarchical cluster analysis (HCA), and principal component analysis (PCA) was applied using the SPSS software package (version 13.0). For PCA, the methods of Varimax-rotation and Kaiser-normalization were applied. Only principal components having >10 % of total variance of the data sets were used as factors. For HCA, the molar concentration data of ions were standardized with the Z-score method, and then the Ward's method of clustering was applied with squared Euclidean distance as a measure.

3. Results and discussion

3.1 Synoptic meteorological conditions

The weather in Flanders is qualified as moderate with fairly mild seasons (Supplementary Table S2). For the sampling period, the daily average T_{air} and p_{air} ranged between 3.2-17 ^{o}C and 1010-1024 hPa, respectively. The average daily level of the usually high RH was fluctuating between 60-84 %. The prevailing WD was observed to be south-western, i.e., air-masses coming from the Atlantic Ocean/British Channel. In the first campaign, the winds blew predominantly from marine regions, whereas a mixed continental/marine influence was experienced during the second campaign (Table 1). The daily average WS, measured at 30 m height, ranged from 3.3 to 5.5 m/s, reflecting low atmospheric stability. Due to the primary contribution of marine air-masses in the first campaign, a considerable extent of rain (643 mm/284 day) was observed, whereas less precipitation was found during the second campaign (583 mm/285 day).

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

3.2.1 Variation in $PM_{2.5}$ levels – According to a recent legislation by the European Commission (EC) to be attained till 2010, the daily mean concentration of $PM_{2.5}$ may not exceed a yearly average of 25 µg/m^3. The average diurnal concentrations (ADCs) of $PM_{2.5}$ ranged from 11 and 45 µg/m^3 over the six locations in Belgium. At these sites, the average $PM_{2.5}$ data exceeded the EC-limit, i.e., for urban Borgerhout and Zelzate during winter, and even for the rural/agricultural Wingene during spring (Table 2). Moreover, the levels of $PM_{2.5}$ observed at Petroleumkaai and Mechelen were also found close to the EC-limit value. These values are also comparable to those observed for the city of Ghent in Belgium during winter in 2004-2005 (28.6 µg/m^3).[2] However, the average summer $PM_{2.5}$ levels were around half of the winter values, e.g., Wingene and Mechelen. This is in line with the average $PM_{2.5}$ for Ghent (12.4 µg/m^3) in summer. [2]

3.2.2 Ratio of MIC to $PM_{2.5}$ – The MICs generally represented a significant fraction of $PM_{2.5}$ with an average ratio of 34-50 % (Table 2). Similar ratios for Ghent have been found in summer and winter, i.e., 38 and 43 %, respectively.[2] Mechelen site was the only exception with a lower value of 18 % in the late spring/early summer campaign, due to the more contribution of organic carbon. The diurnal concentration ratio of MICs to $PM_{2.5}$ was found to be highly fluctuating in the range of 6-98 %.

3.2 Seasonal and site-specific variation in the ionic composition of $PM_{2.5}$

3.2.1 Cations – Na^+ and NH_4^+ were the most abundant cations in $PM_{2.5}$, and their ADCs varied from 0.4-1.2 µg/m^3 and 0.9-4.9 µg/m^3, respectively (Table 1). Both species showed a rather even distribution over sites and seasons. Peak values of Na^+ and NH_4^+ were found in winter for the industrial Petroleumkaai and the urban Borgerhout sites, respectively. Minimum values for both elements were registered during spring/summer campaigns at other sites (e.g., Mechelen, Zelzate, and Wingene). The higher levels of Na^+ could be related to the maximum sea salt input, while the high NH_4^+ content was due to the thermal stability of NH_4NO_3 in winter as opposed to summer. Similar results have also been reported by Viana et al.[2] for Ghent, suggesting that the long-range transport of air masses from the Atlantic Ocean determines the levels of these species. Thus the present results show that the sea-salt input is maximal in winter over Belgium, which is an opposite finding of what has been observed in Southern Europe.[2]

K^+ was found at a lower amount than the former cations. Its ADC ranged up to 0.24 μg/m^3 with peak values at the industrial and/or heavy/medium trafficked sites, indicating the primary origin of K^+ from coal/wood and/or fuel/industrial combustion. The Ca^{2+} and Mg^{2+} contents in $PM_{2.5}$ were relatively low for each site, varying between 0.01-0.05 μg/m^3. Exceptions were Zelzate and Hasselt in the late winter/early-spring campaigns. These species are most likely related to exposed soil, unpaved roads and construction works, and hence, such activities do not contribute much to the MICs of $PM_{2.5}$.

***3.2.2 Anions* –** High ADCs of SO_4^{2-} (>2.3 μg/m^3) have generally been observed compared to that of other anions, except for Wingene and Mechelen during spring with values of 0.79 and 0.43 μg/m^3, respectively. Increased SO_4^{2-} concentrations have generally been reported for summer and spring.[16-29] This trend, however, was not followed at Zelzate and Mechelen, which showed higher SO_4^{2-} levels during winter. However, elevated concentrations of this species have been used as an indicative of emission from industrial coal combustion in Western Europe,[30] but coal combustion does not dominate in the Flanders region, and hence, the sources can be attributed to the long range transport of air masses from other regions.

The ADC of NO_3^- was similarly high or even higher than those of SO_4^{2-} during the cold season. The important sources of NO_3^- and SO_4^{2-} in the atmosphere are the secondary aerosols produced by oxidation of their gaseous precursors, NO_2 and SO_2, respectively, emitted from various anthropogenic activities.[31,32] In big cities, NO_2 mainly originates from vehicular emission. Since this emission is generally distributed evenly over the year, the variation in the NO_3^- level might be strongly related to the oxidation of NO/NO_2 (e.g., by O_3), and also meteorological factors, such as T_{air}, RH, intensity of sunlight, and atmospheric stability.

During spring, Wingene showed very high ADCs of NO_3^- and NH_4^+, mainly due to the intensive pig farming and fertilization. In summer, their concentrations decreased most likely due to the thermal instability of NH_4NO_3 at higher ambient temperature (above 25 ^oC), and also to reduced fertilization activities during this season. On the contrary, the ADC of SO_4^{2-} increased in this period, due to the enhanced traffic, connected with harvest (e.g., a more intensive use of diesel-fuelled vehicles over the crops), and to a more rapid oxidation of SO_2.

The level of Cl^- showed considerable fluctuation with an ADC varying between 0.01-0.66 μg/m^3. Earlier studies have reported Cl^- depletion of sea-salt particles for coastal areas in reaction with sulfuric and/or nitric acids.[33,34] Chloride mostly originates from aerosols produced over the sea, thus its concentration highly depends on the weather conditions. During the winter campaign, a fairly high ADC of Cl^- (0.35 μg/m^3) was found in Zelzate, likely due to its relative closeness to the sea (~50 km), and the prevalence of marine winds in this period. Furthermore, minimum levels of Cl^- in summer can also result from its volatilization in the form of NH_4Cl by reaction of sea-salt with NH_4NO_3.[35] Fluoride was detected at a quite low level (ADC: 0.01-0.02 μg/m^3). Its peak value (0.03 μg/m^3) was observed at Zelzate in the first campaign, due to the emission from the nearby steel-smelters, similarly to those of Cl^-, Ca^{2+}, Mg^{2+}, and K^+.

Apart from some very unique days of the sampling, PO_4^{3-} and SO_3^{2-} were not detected. NO_2^- has only been found in Wingene (0.38 μg/m^3), Hasselt (0.04 μg/m^3), and Mechelen (0.17 μg/m^3) during the late winter/spring period, and also in Wingene (0.12 μg/m^3), Hasselt (0.01-0.04 μg/m^3), and Petroleumkaai (0.1 μg/m^3) in summer and winter. These increased concentrations were possible due to the heterogeneous formation of NO_2^- at a higher level of its gaseous precursor (HNO_2), supported also by atmospheric conditions (high RH, precipitation, and/or low intensity of sunlight), as explained below.

3.4 Variation in the level of aerosol-forming gases

3.4.1 Denuder data – The ADCs of HNO_2 and HNO_3 were found to be similarly low (0.3 $\mu g/m^3$) in Wingene (Table 3). In Mechelen, a similar pattern was observed in late spring/summer with slightly increased values (0.8-1.0 $\mu g/m^3$), whereas in the cold season the level of HNO_2 was almost an order of magnitude higher (2.0 $\mu g/m^3$) than that of HNO_3. Outstandingly high levels of HNO_2 were also detected at Petroleumkaai in both (autumn and winter) campaigns. This was probably due to an increased concentration, and thus, a higher extent of deposition of NO_2, partly, by the high amount of precipitation (Table 3), which increasing its conversion rate to HNO_2. NO_2 is known to heterogeneously converted to HNO_2, when deposits onto various surfaces such as grass, aerosols partly, with the assistance of humidity.[36] The Petroleum-harbor is often with high concentrations of NO_x and suspended particulate (e.g., smoke), which provides an appropriate medium to promote such reactions. The lower rate of photochemical decomposition of HNO_2 by less favored atmospheric conditions (e.g., low intensity of sunlight) may also contribute to the accumulation of this pollutant at the sites concerned.

The ADC of SO_2 was fairly low in the rural Wingene and the suburban site of Mechelen (1.4-6 $\mu g/m^3$). Peak values were observed at Petroleumkaai, both in the early fall and winter campaigns, 29 and 51 $\mu g/m^3$, respectively, reflecting the influence of oil-refineries and related activities (e.g., ship-traffic).

The ADC of NH_3 (2-6 $\mu g/m^3$) did not fluctuate considerably over sampling sites and/or seasons. Nor even during the fertilization period (spring) in Wingene, when

$PM_{2.5}$ was characterized by a high level of NH_4^+. Wingene is referred to as the centre of pig farming, thus the emission of NH_3 should be maximum over this site. However, the presence of NH_3 at a fairly constant atmospheric level at the sampling sites shows its homogeneous spread over Flanders. Moreover, NH_3 does not primarily originate from fertilization activities, but from animal keeping. Pig farming emits some 20 000 tons of NH_3 per year over Flanders (it used to be 50 000 ton per year in 1990). Some 45 % of this emission is in the Province of West Flanders, where Wingene is situated. The NH_3 emission originates from cattle stables, manure storage locations, manure spreading, meadows and fertilizers in a decreasing order. Less important sources of NH_3 are the agricultural crops and biomass burning/bio-fuel usage.[37]

3.4.2 Direct monitoring – The ADCs of NO and NO_2 were the highest at the heavy-trafficked site of Borgerhout, ranging up to ~60 $\mu g/m^3$. Lower concentrations were observed at the other sites of lower traffic density, ranging between 8-35 and 31-45 $\mu g/m^3$ for NO and NO_2, respectively. Higher ADCs of NO and NO_2 have been found in the cold season. This trend was also observed for SO_2, apart from Wingene. The ADCs of SO_2 acquired with direct and indirect monitoring were in fairly good agreement (Table 3).

The temporal variation in SO_2, NO, and NO_2 levels obtained with direct monitoring followed well the trend of SO_2, HNO_2, and HNO_3 levels achieved with the indirect method, as well as trends of the related ionic components in $PM_{2.5}$ (Fig. 2). Therefore, this relationship was evaluated with the aid of conversion factors as follows.

3.5 Gaseous species and their relation with secondary $PM_{2.5}$ aerosol

3.5.1 Sulfur and nitrogen oxidation ratios **–** To determine the degrees of atmospheric conversion of SO_2 to SO_4^{2-} and of NO_2 to NO_3^-, the sulfur and nitrogen oxidation ratios, SOR and NOR, respectively, have been evaluated.[29,31,32,42] The SOR (or NOR) expresses the extent of oxidation of S (or N) in terms of the ratio of sulfate S (or nitrate N) to total S (or N) in sulfate (or nitrate) plus sulfur (or nitrogen) dioxide. Non-sea-salt (NSS) SO_4^{2-} can be derived from total SO_4^{2-} and Na^+ levels as follows[42] (all concentrations are in μg/m^3):

$$\text{NSS-SO}_4^{2-} = \text{total SO}_4^{2-} - 0.231\text{Na}^+ \qquad (1)$$

The SOR and NOR can be calculated as follows:

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

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

where the units of $S_{NSS\text{-}SO42\text{-}}$ and S_{SO2} are μg S/m^3, and the units of $N_{NO3\text{-}}$ and N_{NO2} are μg N/m^3.

The SOR for $PM_{8.0}$ exceeding 0.1 shows that SO_2 is photochemically oxidized in the atmosphere.[42] The present SOR data confirm a rather intensive formation of sulfate aerosols over Wingene and a low-to-moderate conversion for other sites in Flanders (Table 4). Apparently, they did not reveal any site-specific and/or seasonal trend for Hasselt, Borgerhout, and Petroleumkaai, but for Zelzate a higher SOR in summer/autumn than winter. The outstandingly high SORs observed for Wingene may be explained with the increased traffic of agricultural vehicles during the sampling periods, which utilize the ‘agricultural’ diesel with high sulfur content. Long range transport of ship-emission related sulfur from the ship-routes of the North Sea is also a plausible explanation. Furthermore, the high SOR could also be explained with the rural characteristics of this site, where most of the SO_4^{2-} is secondary (i.e., no primary sources nearby). It appears that SOR values are only lower, when SO_4^{2-} comes from primary sources (e.g., marine or anthropogenic SO_4^{2-}). Interestingly, the SOR value is higher in spring than summer (Table 4). This indicates a faster transformation of SO_2 to SO_4^{2-}, due to the higher number of sunny days with enhanced levels of O_3, and a contribution of other sources to SO_4^{2-} levels (e.g., traffic of diesel-fuelled vehicles) during spring. Then again, surprisingly higher SOR has also been found for the suburban site of Mechelen in the late autumn/winter than the late spring/summer campaign.

The NOR data varied between 0.004-0.08 with an average value of 0.03, supporting an effective formation of nitrate aerosols, but to a lower extent than that of sulfates (Table 4). The NOR is generally found to be lower than SOR.[44] The present NOR data have shown a higher site-specific and seasonal variation than SORs. The partition of inorganic NO_3^- between gaseous HNO_3 and particulate NH_4NO_3 is driven towards the latter in the cold season.[45] Most of the NOR data for Flanders support this observation. The exception was Wingene again with a higher NOR value for spring than summer, which is expected, since the ambient temperature is higher in summer than spring. Interestingly, the NOR data of Wingene followed the same seasonal trend as observed for SORs; whereas the seasonal variation for SOR and NOR was the opposite for other sites, a similar trend to that reported for SO_4^{2-} and NO_3^-. [3,35] The trend for Wingene might be explained with the high amount of precipitation during the summer period, which can regulate the concentration of gases and aerosols.

On the base of SOR data one can classify a site as a source and/or a receptor 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 0.30-0.63 in summer, correspond to source and receptor areas, respectively. For PM_{10} aerosol, however, the SOR values are generally higher by around 1.2-fold.[32]

Consequently, one can define ranges of SOR for $PM_{2.5}$ i.e., 0.04-0.30 and 0.13-0.42 in winter, and 0.08-0.41 and 0.26-0.54 in summer, correspond to source and receptor areas, respectively Using this sorting almost all the sites studied can be classified as source areas, irrespective of the season. The only exception is Wingene, which behaves as a receptor area in spring and a combined source/receptor area during summer.

3.5.2 Neutralization ratio (NR) – The NR, by definition, expresses the degree of neutralization of aerosol acidity: [43]

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

The molar concentration of NH_4^+ is taken as the amount needed to neutralize the acidity (all the concentrations are in mol/m^3). The NR is indicative of the ratio of NH_4^+ or H^+, presents in the ammonium sulfate, and does not reflects real ion-balance; hence, its value may be observed over unity (for excess of atmospheric NH_3 reacting with NH_4HSO_4). When the NR is unity, or higher, it indicates the presence of sulfate and nitrate predominantly as their ammonium salts, while lower values of NR imply the presence of acidic sulfate and nitrate, which are then neutralized by Na^+, Ca^{2+}, Mg^{2+}, etc. The NRs were well above unity for various sites and/or seasons (Table 4), indicating the excess of NH_4^+, likely as NH_4Cl aerosols, existing by evaporation and/or decomposition in the gas-phase. These NR values are significantly higher than those found over other continents. [43, 47]

The molar cation-to-anion ratios for NH_4^+ and the major anions exceeded unity and highly varied for all sites, indicating that a part of NH_4^+ probably exists in the gas phase by vaporization. In the gas phase, first, NH_3 neutralizes H_2SO_4 to form sulfate aerosols. After then, the excess NH_3 reacts with HNO_3 to form NH_4NO_3.[45] Hence, it seems that aerosol particles appeared mostly in the forms of $(NH_4)_2SO_4$ and NH_4NO_3

salts over Flanders. Small, but still significant amounts of anions missing for the charge compensation of the excess of cations observed at few sites (Table 4) is likely due to the presence of carbonaceous and/or organic anions in $PM_{2.5}$, which could not be detected with the IC methodology applied.

3.6 Sea-salt particle contribution

The average molar Na^+ to Cl^- ratios for $PM_{2.5}$ ranged from 2.0 to 11 over the sites/campaigns. The ratio of sea-salt in $PM_{2.5}$, calculated according to Maenhaut et al.[14] was found to be 7.0 and 8.1 % for the first and second campaigns, respectively. These values are a bit higher than the literature values for Ghent, i.e., 4 and 5 % for summer 2004 and winter 2004-2005, respectively.[2] However, they are close to the values (4.2 and 5.0 %) found for the urban site of Borgerhout (Table 2). The enhanced sea-salt input to Flanders observed during this study can be explained with the prevailing marine winds over the sampling period (Table 1).

As a first approach to estimate the sea-salt Cl-loss, suspended Na^+ was assumed to be derived only from sea-salt particles.[42] Considering that Cl_{sea} is the amount of Cl^- originally present in sea-salt,

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

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

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

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

For the first and second campaigns, Cl_{sea} ranged from 0.7-1.5 and from 0.8-2.2 μg/m^3, respectively, while Cl_{loss} varied between 0.5-1.4, and 0.8-2.1 μg/m^3, respectively (Table 4), corresponding to 69-95 % and 92-96 % sea-salt Cl-loss with average values of 79 and 93 %, respectively. Most of these values are comparatively higher than those observed at coastal cities,[32] suggesting a more limited transport of fine sea-salt particles from the marine environment to terrestrial areas, due to more intensive atmospheric removal processes (e.g., reaction of sea-salt with secondary aerosols).

Other possibility for Cl-loss is the conversion of fine sea-salt to coarse, "aged" particles with a short atmospheric life-time, due to rapid deposition. The Cl-loss from sea-salt particles has been found to be higher for fine particles.[48] In this study, sites situated further from the sea (e.g., Hasselt) and/or possessing strong anthropogenic influence (e.g., Petroleumkaai) showed higher Cl-loss in $PM_{2.5}$. It followed, therefore, that the rural Wingene, as the closest (~30 km) site to the coast, experienced the lowest Cl-loss.

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

3.7.1 Correlation analysis – SO_4^{2-} and NH_4^+ was reported as the most abundant species in $PM_{2.5}$, while NO_3^- and Na^+ were found in both fine and coarse particles of 2.5-100 µm size.[38] NO_3^- mainly exists in coarse mode together with alkaline ions, such as Ca^{2+} and K^+.[39,40] In this study, a strong correlation of NO_3^- was found with NH_4^+ ($r=0.95$, $p=0.01$), and also with Ca^{2+} ($r=0.73$, $p=0.01$) and K^+ ($r=0.78$, $p=0.01$) in $PM_{2.5}$. Moreover, correlation of NO_3^- was observed with Na^+ ($r=0.4$). Particulate NO_3^- is mainly formed by oxidation of NO_x to HNO_3, which then forms particles through the reaction either with NaCl, or NH_3.[41] SO_4^{2-} was weakly correlated with other ions of $PM_{2.5}$, indicating its widespread presence and formation from SO_2 over Flanders.

However fluoride could be of natural (crustal) origin but it seems primarily from anthropogenic sources (e.g., steel/aluminum smelters, coal fueled power plants, and super-phosphate fertilizer manufacture). Oravisjarvi et al.[50] have also suggested that particles between 2.5 and 10 µm in size are more related to a soil source instead of

$PM_{2.5}$. The level of F^- was significantly anti-correlated with that of Na^+ (r=-0.66, p=0.05), and weakly with that of SO_4^{2-} (r=-0.55). The level of Cl^- was strongly correlated with those of Mg^{2+} (r=0.85, p=0.01) and Ca^{2+} (r=0.62, p=0.05), but weakly correlated with that of F^- (r=0.53, p=0.05). These findings suggest the local, anthropogenic origin of F^-, given that the high levels of Na^+ imply transport of aerosols from the sea, and therefore, a lower influence of local anthropogenic sources of particulate. The strong correlation of Cl^- with both Mg^{2+} and Ca^{2+} suggests their origin in $PM_{2.5}$ mostly from aerosols produced over the sea.

3.7.2 Cluster analysis – HCA revealed three dominating groups of compounds in MICs 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. Mixtures of these groups were also present, certainly, with a lower abundance. The first group represents aerosols that originate mostly from combustions of coal/wood and secondary aerosol formation. The second is Na_2SO_4, which is formed in reaction of sea-salt with H_2SO_4. The third group is assumed to be the reaction-products of sea-salt with anthropogenic (mainly combustion) aerosols and/or soil-dust.

3.7.3 Source apportionment by PCA

To enhance the accuracy of emission sources identification and their relative contribution, the method of PCA was also applied. Normalized levels of gaseous, ionic, and fine particles were used for PCA and subsequent results are shown in Table 5. The factor loading correlates these variables and they represent the most important information on which interpretation of the factors is based. However, it has to be noticed that Table 5 shows only factors having an eigen value above 1 with a variance of more than 10% and this results in two main factors for each site. First factor is generally more correlated with the variables than the second factors because these factors are extracted successively, each one accounting for as much of remaining variables as possible.

For all the sites, factor 1 shows high factor loadings for N- and S-species, which indicates the formation of secondary aerosols, and supports the conclusions for SOR and NOR. Both NO_3^- and SO_4^{2-} are largely produced as secondary aerosols during coal combustion, biomass burning and vehicular emission.[45] They seem to be also dominant sources of MIC of $PM_{2.5}$ in Belgium, which is a similar result to that found for Beijing.[46] Factor 1 also has high factor loadings of Cl^- and F^- at Petroleumkaai and for factor 2 at Hasselt, respectively. Both sites have significant ship-traffic and also influenced by industrial emissions. Hence, Cl^- at these sites may also originate from anthropogenic activities. At Hasselt a nearby paper industry may also explain the factor loading for Cl^-. These sites also show high factor loadings of F^-, the source of which could be associated with steel/aluminum smelters [50], coal fueled power plants and super-phosphate fertilizer manufacture. K^+ has high loading for factor 1 at Hasselt and Mechelen and for factor 2 at Borgerhout and Wingene. SO_4^{2-} has also high factor loadings for Hasselt and Mechelen. Several studies have used high loading of these species as an indication of coal/wood burning.[34,49] Moreover, at Borgerhout the domestic heating (likely coal/wood burning) during the cold season and at Hasselt the emission from the movement of ships have also an influence on the factor loading.

The factor 1 also shows high factor loadings for NH_3 and NH_4^+. The former is the most abundant gaseous alkaline component of the atmosphere. The major sources of NH_3 include in animal farming, fertilizers and decomposition of organic matter. Generally, NH_3 is not transported over long distances,[37] as it is rapidly converted into NH_4^+ aerosols at a rate of 30 % h^{-1}. Consequently, the results of factor analysis also confirm the uniform distribution of these activities in Belgium.

4. Conclusions

The water-soluble, ionic compounds have been found to be representing a significant part of $PM_{2.5}$ aerosols with a varying composition over six locations in Belgium. Their contribution sometimes reached 80-90 % of the total mass of $PM_{2.5}$ aerosols, and showed rather alkaline chemical characteristics. This observation also raises more questions about the health related effects and human risks for this aerosol fraction. Fine particles are formed primarily by combustion and/or secondary chemical reactions in the atmosphere. The fairly high SO_4^{2-} and NO_3^- concentrations in Belgium suggest that photochemical oxidation occurs, and more secondary aerosols can be produced in the atmosphere. This is also confirmed by the present calculations for SOR, NOR, and NR ratios. A part of the secondary aerosols of ammonium salts likely decompose by releasing NH_3, according to the shift in the compensation point of NH_3, for example, by fast changing weather conditions. The resultant acidic decomposition products are readily neutralized with other common salts of the atmosphere.

This study indicates the contribution of sea-salt particles from the sea to the urban areas. Particles of sea-salt origin showed a considerable decrease in $PM_{2.5}$ with an increasing distance from the coast. Moreover, their level in $PM_{2.5}$ was very dependent on the meteorological conditions and atmospheric removal processes. PCA shows the existence of mixed sources of vehicular emissions, coal/wood burning, industrial activities and animal farming in Belgium. The present study also provides an aid in the implementation of the new European $PM_{2.5}$ air quality standard, and also, the accessed data can be useful to evaluate the human health risk of $PM_{2.5}$ aerosols.

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References

1. R. M. Harrison, J. Stedman, and D. Derwent, Atmos. Environ. 2008, **42**, 603-606.

2. M. Viana, W. Maenhaut, X. Chi, X. Querol, and A. Alastuey, Atmos. Environ. 2007, **41**, 315-326.

3. X. Querol, A. Alastuey, C. R. Ruiz, B. Artiñano, H C. Hansson, R. M. Harrison, et al., Atmos. Environ. 2004, **38**, 6547-6555.

4. Van Dingenen R, Raes F, Putaud JP, Baltensperger U, Charron A, Facchini MC, et al., Atmos Environ 2004; **38**: 2561-2577.

5. J. P. Putaud, F. Raes, R. Van Dingenen, E. Brüggemann, M.C. Facchini, S. Decesari, et al., Atmos. Environ. 2004, **38**, 2579-2595.

6. C. A. Pope, and D. W. Dockery, J. Air Waste. Manage. Assoc. 2006, **56**, 709-742.

7. A.Y. Ali-Mohamed, and A. H. Jaffar, Chemosphere 2000, **2**, 85-94.

8. M. Raizenne, L. M. Neas, A. I. Damokosh, D. W. Dockery, J. D. Spengler, P. Koutrakis, et al., Environ. Health Persp., 1996, **104**, 506-514.

9. S. J. Chen, S. Y. Cheng, M. F. Shue, K. L. Huang, P. J. Tsai, and C. C. Lin, Sci. Total Environ., 2006, **354**, 20-27.

10. P. Michelozzi, F. Forastiere, D. Fusco, C. A. Perucci, B. Ostro, C. Ancona, and G. Pallotti, Occup. Environ. Med., 1998, **55**, 605-610.

11. M. C. Jacobson, H. C. Hansson, K. J. Noone, and R. J. Charlson, Reviews of Geophysics 2000, **38**, 267-294.

12. V. Ramanathan, M. V. Ramana, G. Roberts, D. Kim, C. Corrigan, C. Chung, et al Nature 2007, **448**, 575-578.

13. M. Z. Jacobson, J. Geophys. Res. 2004, **109**, D21201 1-15 doi:10.1029/2004JD004945

14. W. Maenhaut, J. Cafmeyer, S. Dubtsov, and X. Chi, Nucl. Instrum. Meth. Phys. Res. 2002, **B189**, 238-242; W. Maenhaut, Atmos. Environ., 2008, **42**, 1070-1072.

15. P. A. Siskos, E.B. Bakeas, I. Lioli, V.N. Smirnioudi, and P. Koutrakis, Environ. Technol., 2001, **22**, 687-695.

16. E. Manoli, D. Voutsa, and C. Samara, Atmos. Environ., 2002, **36**, 949-961.

17. M. Schaap, K. Mueller, and H. M. ten Brink, Atmos. Environ., 2002, **36**, 1323-1335.

18. T. W. Andreae, M. O. Andreae, C. Ichoku, W. Maenhaut, J. Cafneyer, A. Karnieli, and L. Orlovsky, J. Geophys. Res., 2002, **107**, AAC 3-1 - AAC 3-18.

19. A. Chaloulakou, P. Kassomenos, N. Spyrellis, P. Demokritou and P. Koutrakis, Atmos. Environ. 2003, **37**, 649-660.

20. S. Rodriguez, X. Querol, A. Alastuey, M. M. Viana, M. Alarcon, E. Mantilla, and C. R. Ruiz, Sci. Total Environ., 2004, **328**, 95-113.

21. F. Karaca, O. Alagha, and F. Erturk, Chemosphere, 2005, **59**, 1183-1190.

22. E., Gerasopoulos, E. Koulouri, N. Kalivitis, G. Kouvarakis, S. Saarikoski, T. Mäkelä, R. Hillamo, and N. Mihalopoulos, Atmos. Chem. Phys., 2007, **7**, 2551-2561.

23. M. Kocak, N. Mihalopoulos, and N. Kubilay, Atmos. Environ., 2007, **41**, 7351-7368.

24. S. D. Glavas, P. Nikolakis, D. Ambatzoglou and N. Mihalopoulos, Atmos. Environ., 2008, **42**, 5365-5373

25. K. Ravindra, M. Stranger, and R. Van Grieken, J. Atmos. Chem. 2008, **59**, 199-218.

26. K. Eyckmans, J. Zhang, J. de Hoog, P. Joos, and R. Van Grieken. Int. J. Environ. Anal. Chem., 2001, **80**, 227-243.

27. J. D. Spengler, P. Koutrakis, D.W. Dockery, M. Raizenne, and F. E. Speizer, Environ. Health Persp., 1996, **104**, 492-499.

28. D.E. Day, W.C. Malm, and S.M. Kreidenweis. J. Air Waste Manage. Assoc. 1997, **47**, 411-418.

29. H. S. Lee, and B. W. Kang, Atmos. Environ. 2001, **35**, 739-746.

30. J. Cyrys, K. Gutschmidt, M. Brauer, T. Dumyahn, J. Heinrich, J. D. Spengler, and H. E. Wichmann, Atmos. Environ. 1995, **29**, 3545-3557.

31. N. Kaneyasu, S. Ohta, and N. Murao. Atmos. Environ., 1995, **29**, 1559-1568.

32. J. J. Lin, Environ. Int. 2002a, **28**, 55-61; J. J. Lin, Atmos. Environ., 2002b, **36**, 1911-1920.

33. A. Laskin, D. J. Gaspar, W. H. Wang, S. W. Hunt, J. P. Cowin, S. D. Colson, and B. J. Finlayson-Pitts, Science 2003, **301**, 340-344.

34. Z. B. Yuan, A. K. H. Lau, H. Y. Zhang, J. Z. Yu, P. K. K. Louie, and J. C. H. Fung, Atmos. Environ. 2006, **40**, 1803-1815.

35. R. M. Harrison and C. A. Pio, Atmos. Environ. 1983, **17**, 2539-2543.

36. J. Stutz, B. Alicke, and A. Neftel, J. Geophys. Res., 2002, **107**, 8192; J. Stutz, B. Alicke, R. Ackermann, A. Geyer, S.H. Wang, A.B. White, et al. J. Geophys. Res. 2004, **109,** D03307.

37. W. Asman, and H. Van Jaarsveld, Atmos. Environ. 1991, **24A**, 445-464; W. Asman, M. A. Sutton, and J.K. Schjørring, New Phytol., 1998, **139**, 27-48.

38. S. M. Wall, W. John, and J. L. Ondo, Atmos. Environ., 1988, **22**, 1649-1656.

39. P. M. Wu, and K. Okada, Atmos. Environ. 1994, **28**, 2053-2060.

40. H. Hayami, and G. R. Carmichael, Atmos, Environ, 1998, **32**, 1427-1434.

41. M. Claes, K. Gysels, R. Van Grieken, and R. M. Harrison. In: R. M. Harrison, and R. Van Grieken, Atmospheric Particles, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, Wiley, New York, 1998, pp. 95-145.

42. S. Ohta S, and T. Okita, Atmos. Environ .1990, **24A**, 815-822.

43. Y. I. Tsai, and M. T. Cheng, Sci. Total Environ., 1999, **231**, 37-51.

44. I. Colbeck, and R.M. Harrison, Sci. Total Environ., 1984, **34**, 87-100.

45. J. H. Seinfeld, and S. N. Pandis. Atmospheric Chemistry and Physics, Wiley, New York, 1998.

46. R. W. Shaw, and H. Rodhe, Atmos. Environ. 1982, **16**, 2879-2888.

47. Y. Wang, G. S. Zhuang, A.H. Tang, H. Yuan, Y. L. Sun, S. A. Chen, and A. H. Zheng, Atmos. Environ., 2005, **39,** 3771-3784.

48. V. M. Kerminen, R. Hillamo, K. Teinila, T. Pakkanen, I. Allegrini, and R. Sparapani, Atmos, Environ, 2001, **35**, 5255-5265.

49. M. A. K. Khalil, and R. A. Rasmussen, Atmos. Environ., 2003, **37**, 1211-1222.

50. K. Oravisjarvi, K. L. Timonen, T. Wiikinkoski, A. R. Ruuskanen, K. Heinanen, J. and J. Ruuskanen, Atmos. Environ., 2003, **37**, 1013– 1022.

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 $PM_{2.5}$ (µg/m³)***		***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 µg/m³) 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

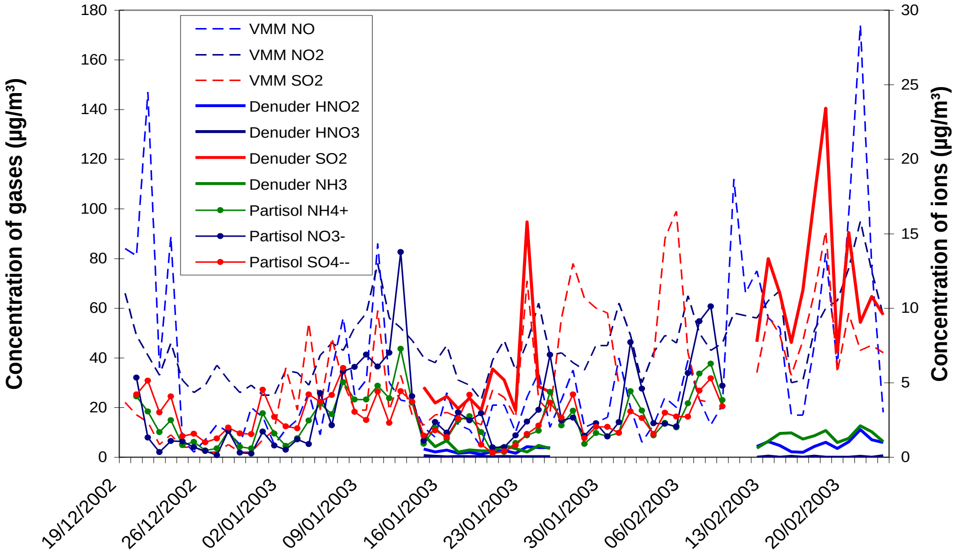
[c] Number of diurnal data used for the calculation

Table 5 Factor analyses of the major ionic components, $PM_{2.5}$, PM_{10} and gaseous pollutants for various locations.

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

[*] Direct gas monitoring (a) or denuder sampling and IC analysis (b)

Figure 1. Map showing sampling location in the northern part of Belgium (Source: Google Earth).



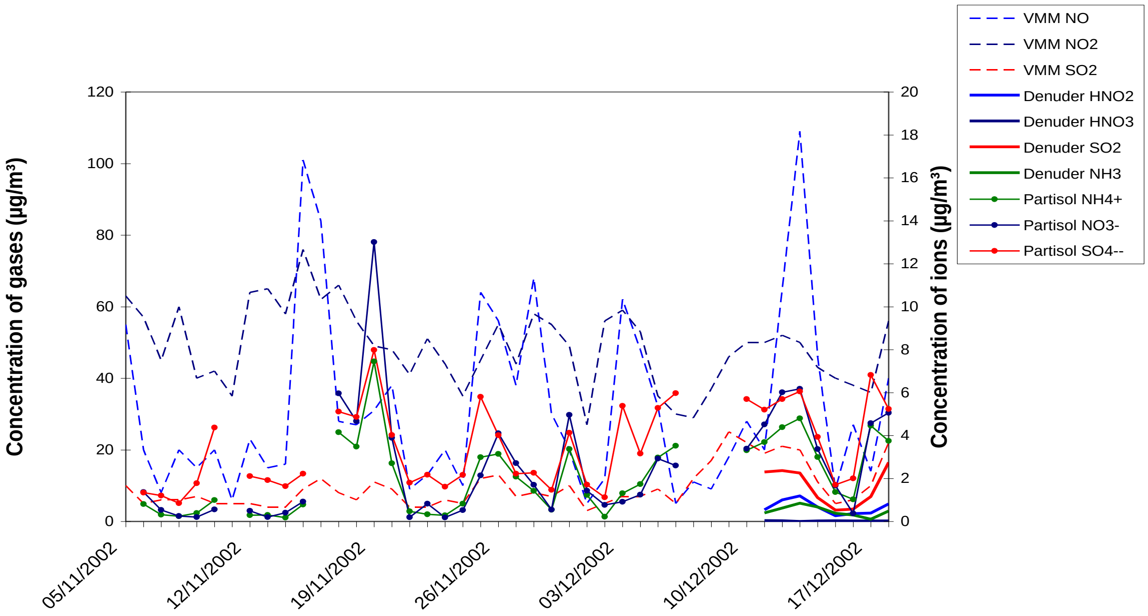


Figure 2. Temporal variation in the levels of gases and related ionic species in $PM_{2.5}$ at the industrial site of Petroleumkaai (above) and at the suburban Mechelen (below)