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

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

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

ABSTRACT

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

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

1. Introduction

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

A Belgian Science Policy project ("Health effects of particulate matter in relation to physical-chemical characteristics and meteorology"), which this study was a part of, intended to investigate acute, short-term health effects of PM and its composition in the elderly part of the population (Jacobs et al. 2012). The sampling of air pollution was designed, so that there was a contrast in ambient PM concentrations between the first and second visit of a patient during which a set of clinical measurements was performed. More information may be found in Jacobs et al. (2012). This was possible thanks to the predictions of PM concentrations (4 days in advance) made by Ircel (Belgian Interregional Environment Agency). The air particulate matter was sampled both indoors and outdoors of the building. Since this part of the population spends most of their time indoors, monitoring the indoor air and close outdoor environment in place of the personal exposure seems justified. Brunekreef et al. (2005) found highly correlated time-series of pairs of personal, indoor and outdoor fixed site PM2.5 and black smoke concentrations in a small population of elderly cardiovascular patients. - The concentration of the PM inside of a building is mainly governed by indoor generation of particles, the concentration of the particles outside, the rate of air exchange and the depositional characteristics of the particles (Gemenetzis et al., 2006). For those reasons this study monitored both environments.

This paper is thus one of a handful reporting on the chemical (elemental composition and water-soluble ion concentrations, including secondary aerosols) and physical (mass concentrations) differences between ambient and indoor concentrations of PM2.5 and PM1 during periods of high and low pollution events in old-age home (Czagani Broechem, Belgium). We chose this location as it was characterised by the highest pollution event observed in Antwerp during the course of the project (2007-2010). The sampling campaign covers days before, during and after the event. Thus, in addition to investigation of the relationship between the outdoor and indoor pollutants, a comparison between days with "normal" PM concentrations or so-called non-episode days (NED's) and episode days (ED's) could be made.

A target value of 25 $\mu g\ m^{-3}$ for PM2.5 entered into force in 2010 under the Ambient Air Quality and Cleaner Air Act for Europe (Council Directive 2008/50/EC) and will enter into force as a limit value in 2015. Although a yearly average indoor PM2.5 guideline value of 15 $\mu g\ m^{-3}$ in Flanders, Belgium exists, we decided to use the 24-h PM10 indoor air quality guideline value (Stranger et al., 2007) of 40 $\mu g\ m^{-3}$. In this study, the PM10 concentration was not measured; however, based on our unpublished results from simultaneous PM10 and PM2.5 mass measurements in various indoor locations in Belgium, PM2.5 accounts on average for 73% of PM10 mass concentration. Therefore, the 24h PM2.5 indoor value higher than 29.2 µg m^{-3} stands for an ED in this study and lower than 29.2 µg m^{-3} stands for a NED. This value is not unreasonable taking into account that the WHO guideline values for short term PM2.5 exposure is 25 µg m^{-3} 24-h mean, and as recently as 2011, this value has also been adopted as an indoor air guideline value (WHO, 2011).

2. EXPERIMENTAL

2.1 Sampling location

Broechem is a village (12 km^2) located in the province of Antwerp, around 10 km to the east of the Antwerp city (N50º10’, E4º36’) with about 4000 inhabitants. The sampling was performed in the Czagani old-age home, with around 120 inhabitants and 100 workers at the time of the sampling. The old-age home has a surface area of about 6500 m^2 and three floors. The building, built in 1994, is both mechanically and naturally vented. The ground floor (where sampling was performed), was a carpeted open space, it served as a dining room, cafeteria and the reception; the cleaning thereof was performed 6 days per week. The building is situated about 1 km from the highway and 300 m from a major village road.

Local pollution sources include mainly traffic and domestic heating. Other potential sources include the harbour of Antwerp (located to the north of the city), a large petrochemical plant, a municipal waste incinerator, and a nonferrous plant to the south of Antwerp (Stranger, 2005).

2.2 Sampling methodology

PM was collected indoors and outdoors simultaneously by means of impaction (Harvard impactors from Air Diagnostics and Engineering Inc., Naples, ME, USA) and operated at a flow rate of 23 L min $^{-1}$ for PM1 collection and 10 L min^{-1} for PM2.5 collection. Membrane Teflon filters were used (2 µm pore size and 37 mm in diameter) to collect the particles over periods of 24 hours. Filter changing took place in the mornings, during which time the flow rate was checked. Indoor sampling took place in the ground floor dining room and the impactors were positioned so that the inlets were as close as possible to the breathing zone of people (about 1 m above the ground). Outdoor sampling was done at the back of the building in order to avoid direct influence from the automobile exhaust emissions originating from a small parking lot in front of the building. Since the building was only 3 storeys high, the ground floor concentrations are assumed representative for all floors. As shown by Gemenetzis et al. (2006) in the study conducted in university rooms in Greece, although a slight decrease in PM10 and PM2.5 mass concentrations was observed with an increase in the elevation level, it could be considered as negligibly small up to the 5th floor. The effect of elevation (up to the 40th floor) on indoor particulate concentrations was also studied by Chao et al. (2002), who reports no significant difference in the PM10 and PM2.5 mass concentrations at different levels.

Co-located duplicate samples of PM2.5 were collected both in indoor and outdoor sites, they were however used only for the determination of the mass concentration and were not subjected to further examinations for elemental and ionic measurements. Thus, the PM mass concentration values are the arithmetic mean of two measurements. The results of the duplicate sampling of PM2.5 agreed with each other to within 5%, exceeding this difference only four times, with the highest being 16%.

2.3. Analysis

The masses of the collected particulates were determined gravimetrically using a microbalance with a resolution of 1 μg (Mettler Toledo MX5, Mettler Toledo, Columbus, USA) in an environmentally controlled laboratory. Filters were conditioned at 20 °C and 50% relative humidity, for at least 24h before weighing, and stored in Petri dishes until sampling. After sample collection, they were conditioned again, weighed and stored at 4 °C until the analysis.

The filters were analysed firstly by means of X-ray fluorescence (Epsilon-5 XRF, PANAnalytical, The Netherlands) in order to determine the bulk elemental concentrations of selected elements (Al, As, Ca, Cd, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Sb, Se, Si, Sr, Ti, V, Zn) and afterwards subjected to Ion Chromatographic (IC) analysis (Dionex DX-120, Dionex, USA) for anion (Cl^-, NO_3^-, SO_4^{2-}) and cation (Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+) concentrations. Procedures followed have been described elsewhere (Avigo et al., 2008; Stranger et al., 2009). The IC detection limits (LODs) were estimated from blank filters (three standard deviations of the concentration found in blank) using the average air volume of PM2.5 and PM1 samples taken during the sampling campaign. LODs were ranging from 3 ng m^{-3} for magnesium to 72 ng m^{-3} for sodium cation in PM2.5, and from 1 ng m^{-3} to 30 ng m^{-3} in PM1 for the same cations, respectively. Magnesium and calcium ions were generally found in very low amounts. Magnesium was detected above its LOD in 63% of all samples, calcium, in 46%. All other ions were detected in significant amounts in all samples. The precision was better than 3.6% for all analytes (Bencs et al., 2008). For XRF analysis, the detection limits ranged from 0.7 for vanadium and 32 ng m^{-3} for aluminium in PM2.5 and from 0.3 ng m^{-3} for vanadium to 13 ng m^{-3} for aluminium in PM1. Cd, Se and Sb were below the detection limits in all samples, for other elements there were 11% of non-detects. The precision, expressed as relative standard deviation of three repetitions was generally below 5%. Quality check of these analyses was performed by calculating the correlation coefficients between elemental-sulphur with sulphate-sulphur. R^2 values of 1 and 0.99 were found for indoor and outdoor PM2.5, respectively. The PM1 correlation coefficients were 0.99 for both indoor and outdoor PM. For chloride the values were somewhat lower, in indoor PM1 two outliers had to be excluded, the correlations had the R^2 equal to 0.98 and 0.95 in PM2.5 indoors and outdoors, and 0.84 in indoor and 0.97 in outdoor PM1.

Identification of the origin of air masses was done for each day of the sampling using 5-day backward trajectories performed with Hysplit model (http://www.arl.noaa.gov/HYSPLIT.php). Initial heights of 2 m and 20 m above ground level were investigated.

All statistical calculations were performed using an IBM SPSS Statistics, version 22.0 software package (IBM Corp., Armonk, NY, USA).

3. RESULTS AND DISCUSSION

3.1 Mass concentrations

Descriptive statistics of daily PM2.5 and PM1 concentrations for the whole campaign, episode days and non-episode days are summarized in Table 1. Mean outdoor concentrations of 77.0μg m^{-3} and 36.7 μg m^{-3} for PM2.5 and PM1, respectively, are reported for episode days. Mean indoor concentrations were 43 % and 29 % lower for PM2.5 and PM1, respectively (Table 1). PM1 therefore constitutes 53% of PM2.5 on average (48±12 % for EDs and 55±11 % on NEDs) in outdoor air and 64 ±8 % (62±12 % for EDs and 65±9 % on NEDs) indoors.. Maximum PM2.5 concentrations reached 101 μg m^{-3} (46.1 μg m^{-3} for PM1) outdoors and 53.5 μg m^{-3} (31.9 μm m^{-3} for PM1) indoors. In context to the overall research project investigations, these values are considerably higher than any of those measured during five other campaigns, in different old-age homes in Belgium between years 2007-2010. These values are also much higher than some of the values published across the literature, for example: in Birmingham 7.9 µg m^{-3} was reported for residential indoor PM2.5 (Jones et al. 2000), and 9.1 µg m^{-3} in Oxford, England (Lai et al. (2004)). A maximum of 56 μg m^{-3} was observed for outdoor PM2.5 in Canada (Cheng et al., 1998), and 66 μg m^{-3} (PM2.5 12 h day sample) in a study of air quality in offices near a busy street in the centre of Antwerp (Horemans and Van Grieken, 2010). The outdoor values are also higher than those found in the study of Stranger et al. (2009) reporting on residential indoor air quality in Belgium, although the average indoor concentration and maximum values reported were similar to the ones reported here. Moreover, EDs' PM2.5 outdoor values exceeded those reported for PM10 during a yearly study at six different sites in Belgium (urban background to rural; 24-h samples taken once a week) (Vercauteren et al. 2011). However, literature also indicates much higher concentrations elsewhere, especially in Asia, for example, Ye et al. (2003), in a yearly study in Shanghai, reported weekly averages of PM2.5 equal to 156 μg m^{-3}. Chen et al. (2003) in their study of pollution episodes set the threshold value for ED's and NED's at 150 μg m^{-3}.

Figure 1 gives the average ambient daily temperature, wind speed and relative humidity during the study. Days with elevated PM concentrations (13, 18, 19 February) are characterized by the lowest temperatures (0.8-1.4°C) and wind speeds (1.6-2.5 m s^{-1}). The only exception is the 20th February where high concentrations of PM were measured despite a maximum temperature of 6.4 °C and a wind speed of 2.8 m s^{-1}. Vecchi et al.(2004), noticed typically an increase by 20-35% in both PM1 and PM2.5 on days when wind velocity was lower than 2 m s^{-1}. In this study the increase of PM concentration registered on episode days was much higher, on average 2.5 to almost 3 times higher, compared to non-episode days. Wintertime increases in ambient pollutant concentrations are frequently attributable to a combination of low level, persistent temperature inversions and increases in emissions related to heating (Ye et al., (2003)). Additionally, lower temperatures occurring during the winter season favour the persistence of particle phase with respect to the gas phase, e.g. NH_4NO_3 (Vecchi et al., (2004)). Inversion was evident on most days of high pollution events in our study (See Figure 1S in supplementary material). Additionally, backward trajectory analyses revealed that anticyclonic circulation of the air masses coincided with the episode days. On the 13th of February, the impact of 120h trajectories was almost entirely regional (Germany, The Netherlands and Belgium) and between 18th and 20th February the air masses originated in the arctic region, passing Norway, Sweden, Germany and finally creating an anticyclone over Belgium. As pointed out by Viana et al. (2007a), anticyclonic scenarios lead to the development of thermal inversions, air mass stagnation and accumulation of locally emitted pollutants. During NED's, air masses seemed to be impacted to a larger extent by cleaner air from the Atlantic Ocean and the North Sea before reaching the sampling location .This is especially visible during the third week of the study, in which air masses travelled very long distances over the Atlantic Ocean before reaching Belgium.

Table 1. Summary of the PM mass concentrations (µg m^{-3}) registered during the study.

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

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

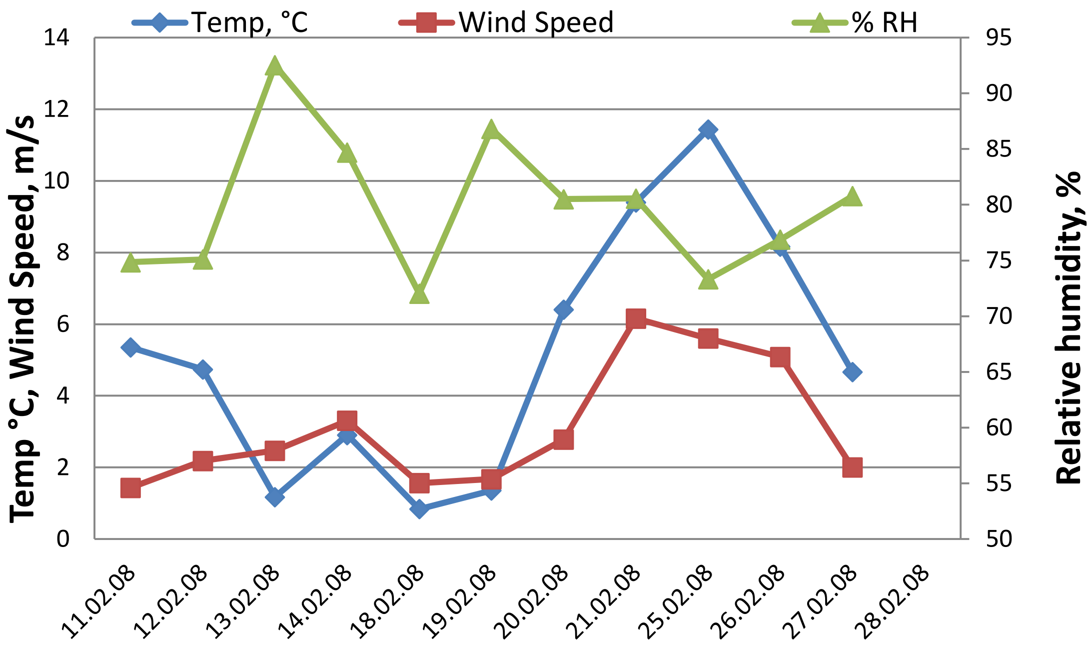


Figure 1. Ambient meteorological conditions during the sampling campaign

3.2 Indoor - outdoor correlations in PM

The degree of outside PM infiltration was gauged by determining straight-line indoor-outdoor correlations for two fractions PM2.5-1 and PM1, thus using the value of the correlation coefficient, R^2, as the indicator (Figure 2). PM2.5-1 fraction was obtained by subtracting the concentrations found in PM2.5 and PM1. Mass concentration profiles for PM2.5-1 match each other and this correlation is illustrated by an R^2 of 0.93. A lower R^2

of 0.74 was observed for PM1, but after removal of an outlier (13.02.08) the value was close to that of the PM2.5-1 as is seen in the insert of Figure 2. The coefficients for both fractions were considerably higher than those reported for PM2.5 in residences in California (Geller et al., 2002), where the correlation coefficient was equal to 0.37. This indicates that mass concentration increases on the outside are reflected on the inside and one could deduce that a substantial fraction of indoor particles in our study penetrated - from the outdoor environment.

The correlation between PM1 and PM2.5 (R^2) was equal to 0.86 when PM outdoors was compared, and 0.97 for the indoor concentrations. The I/O ratios for PM2.5 was always below 1, and for PM1, exceeded 1 only twice (thus 17% of cases, amounting to 1.08 and 1.36). This, together with high correlations of indoor to outdoor air reported above, suggest no major indoor sources of particulate matter in the studied old-age home. PM1 decreased indoors by 29 % on average compared to outdoors and the PM2.5-1 fraction by 57 %. These decreases were similar on EDs and NEDs. It thus suggests a more effective indoor penetration of fine particles than of supermicron PM2.5-1 particles. The building, hence, offers a relatively good protection against exposure to supermicron particles and to its components, although larger deposition velocities of these particles on window, door and furniture surfaces could also have played a role.

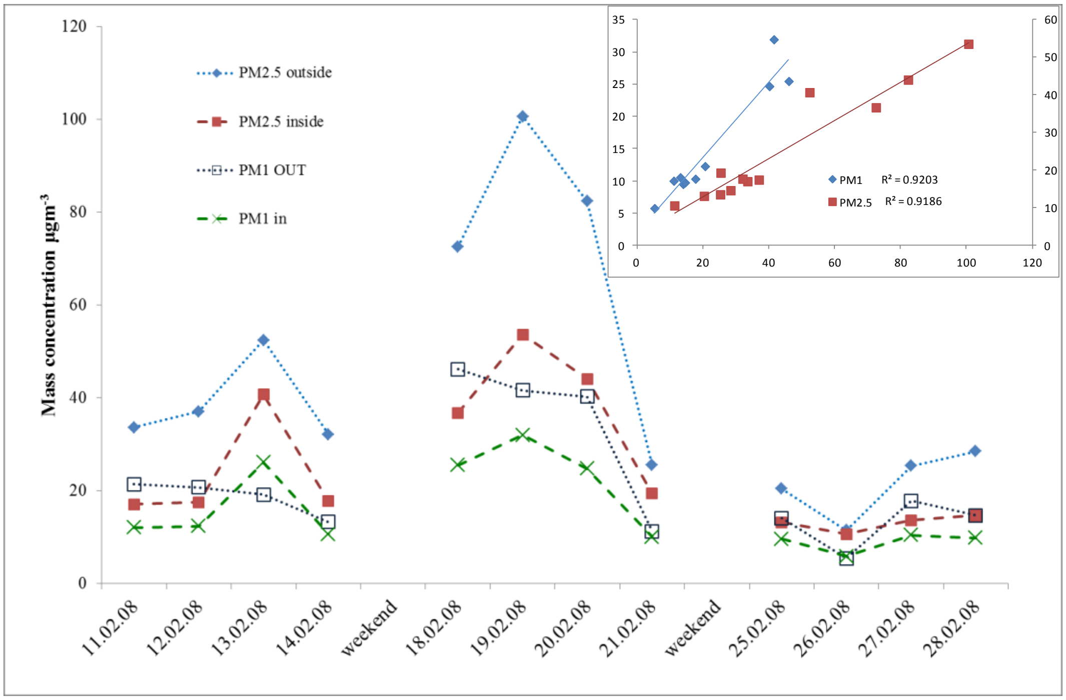


Figure 2. Indoor : Outdoor relationships for PM2.5 and PM1.

3.3. Chemical mass closure of PM

Chemical mass closure of the PM2.5, PM1 and PM2.5-1 was calculated using the results obtained from both the IC and XRF analyses (Table 2). PM2.5-1 composition was obtained by subtracting the concentrations found in PM2.5 and PM1; therefore larger uncertainties may be associated with this fraction. Subsequently, the relative contributions of PM components were calculated to illustrate the differences between ED's and NED's and outdoor and indoor environments (Figure 3). As pointed out already by Putaud et al. (2004), relative contributions reflect the differences in the sources and processes controlling the aerosol composition as they are independent of dilution. Additionally, outdoor-to-indoor transport of particles may modify the composition of PM. Meng et al. (2007) found distinct infiltration factors (fraction of ambient PM found indoors) for several components of PM2.5. For those reasons, the contributions of secondary inorganic aerosols, crustal matter, sea salt, smoke and other elements (including heavy metals) to collected PM size fractions was studied in detail.Crustal matter, sea salt, non-crustal K (smoke origin) non-sea salt (nss) SO_4^{2-} were assessed using the approaches published previously (Chan et al. (1997), Maenhaut et al. (2002), Sillanpää et al. (2006)). Sea salt content was calculated from Na^+ and Cl^- concentrations, nss-SO_4^{2-} from measured SO_4^{2-} and Na^+ and for both calculations, the composition of standard sea water was taken into account. The concentrations of inorganic secondary species (NH_4^+, NO_3^-) and "other" elements (As, Cr, Cu, Mn, Ni, Pb, Sr, V, Zn) were determined directly from measurements.

Substantial amounts of PM, named "unidentified", resulted from subtracting the reconstituted mass of each sample from total PM mass determined gravimetrically. Most likely it consists largely of organic (OC) and elemental carbon (EC), which were not measured in this study. Both, percentages of unidentified fraction and absolute values obtained for PM2.5 (30% on outdoor ED's corresponding to 24.6 µg m^{-3}, and up to 60% indoors on NED's, corresponding to 9.2 µg m^{-3}) are in agreement with the values obtained for OC and EC component in other studies conducted in Belgium and Europe, in which the major component of urban or regional background PM2.5 and PM10 appeared to be organic matter (Maenhaut et al. (2002), Putaud et al., (2004), Querol et al. (2004a), Sillanpää et al.(2006)). The OC+EC component is thought to originate mainly from traffic emissions, heating and other combustion related processes. The "unidentified" fraction prevailed in PM1 with concentrations twice that of the supermicron PM2.5-1 fraction.A fraction of an unaccounted PM mass may be as well water associated with hygroscopic aerosol components (Maenhaut et al. (2002), Querol et al. (2004b)). The relative contribution of unidentified species of particulate matter on ED’s is significantly lower than on NED’s for both indoor and outdoor PM. This component thus contributed less to the total PM on episode days than on non-episode days, although in absolute values, it was about two times higher on ED’s. The increase occurred both in PM1 and PM2.5-1 to a similar extent.

Table 2. Contribution of PM components to outdoor and indoor PM2.5, PM1 and PM2.5-1 on ED’s and NED’s. Concentration value (μg m^{-3}) is accompanied by 1σ.

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

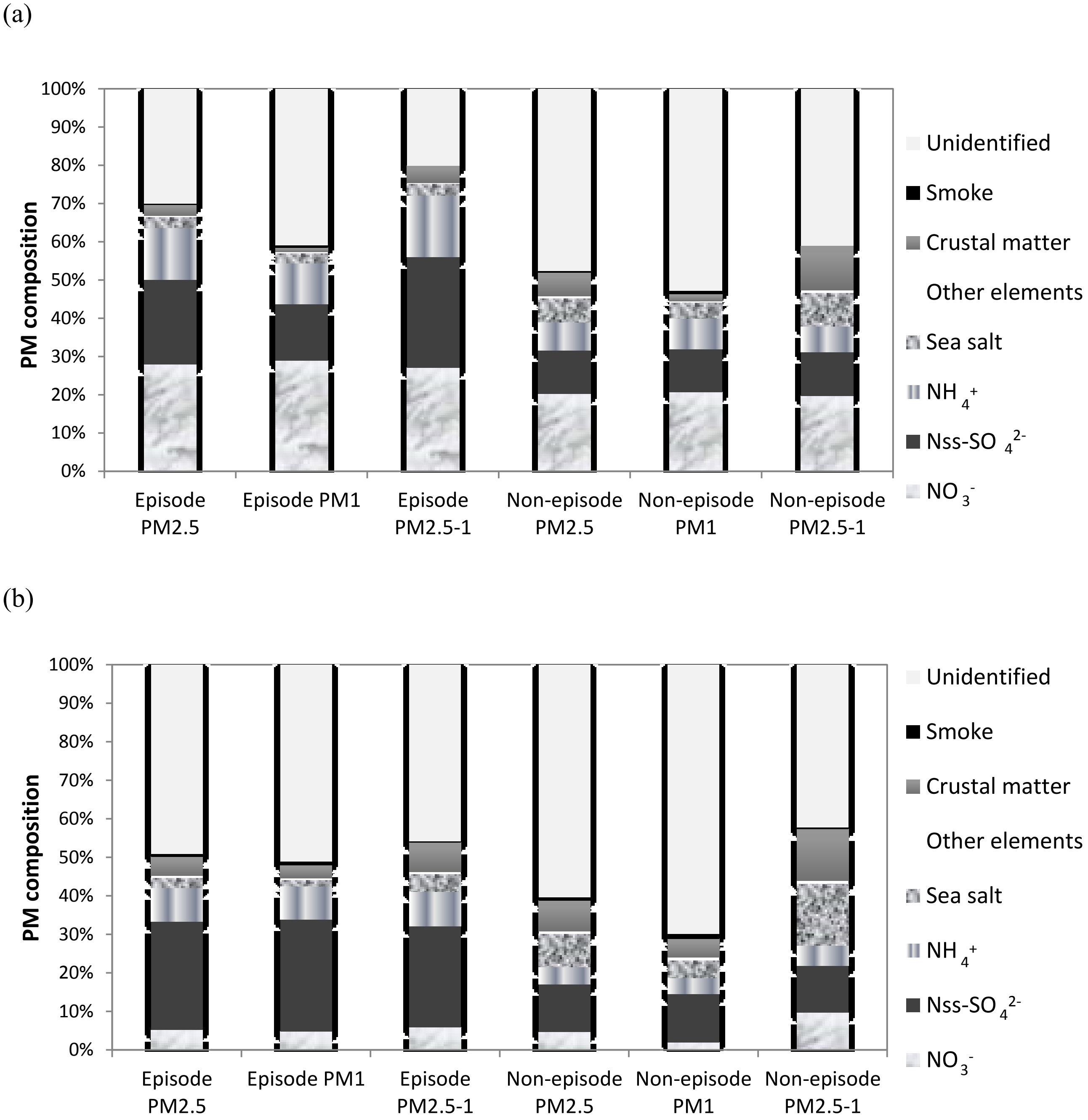


Figure 3. Relative contribution of PM components to outdoor (a) and indoor (b) PM2.5, PM1 and PM2.5-1 on ED's and NED's.

Secondary inorganic aerosol species (SIA)

Nss-sulphate constituted 99% of ambient PM 2.5 sulphate on ED's in all studied fractions and about 92% (96% of PM1 sulphate and 80% of PM2.5-1 sulphate) on NED's. In addition, on ED's the percentage range of nss-sulphate was very narrow - from 98% to 100%, on NED's, it was more variable. In PM1 it varied between 91% and 97% and in PM2.5-1, between 43% and 97%. The highest relative contribution of sea-sulphate was seen in the third week of the study, when the air masses passed a long distance over the Atlantic Ocean and it was preferably associated with fraction PM2.5-1.

Nss-sulphate, nitrate and ammonium, dominate the composition of PM, constituting 64% of PM2.5 during ED's (52 µg m^{-3}) and 39% on NED's (10 µg m^{-3}). Hence, not only an absolute increase in the concentration was seen but also the relative contribution increased by a factor of 1.6 on ED's compared to NED's. SIA absolute concentrations were 5-6 times higher during ED's compared to NED's both indoors and outdoors. Ram et al. (2012) reported an increase in concentration by a factor of 2 -3 in their study of SIA during fog and haze days . Although the percentage values reported by Ram et al. (2012) were much lower, the same tendency was seen, namely about a 2 fold increase in contribution from clear to foggy days. The episode days in our study were apparently not only influenced by a limited pollutant dilution connected to occurrence of temperature inversions, but also most probably by an increased formation of secondary species due to the preferable meteorological conditions. As stated by Ram et al. (2012) at lower ambient temperature and wind speed, high RH and SO_2 and in the presence of higher particle concentration the conversion of gaseous SO_2 to particle SO_4^{2-} is expected to be higher. Amongst secondary species, nitrate prevailed mostly in ambient air, whilst nss-sulphate, was the dominant ion in the indoor air. The nitrate indoor/outdoor (I/O) ratio was only

0.14 on the average while the nss-sulphate ratio was equal to 0.66 for PM2.5. For PM1, these values were 0.10 and 0.96 for nitrate and nss-sulphate, respectively. The trend of fine particles showing higher I/O ratios for sulphate was also observed by Jones et al. (2000).

The low I/O nitrate ratio indicates a significant decrease of nitrate concentration indoors due to the higher temperature compared to the outdoor air and thus transformation of particle ammonium nitrate to ammonia and nitric acid gasses (Parker et al. (2008)) (NO_3^- conversion between particle and the gas phase is strongly temperature dependant). Nitrate appears to be evenly distributed between PM1 and PM2.5-1 on ED's, both in absolute values and relative contributions in ambient (29% and 27%, respectively) and indoor (5% and 6%) concentrations. On NED's the nitrate prevails in PM1 but its relative contribution is the same in ambient PM1 and PM2.5-1 (20%); in indoor air it constitutes only 2% of PM1 and 10% of PM2.5-1.

Nss-sulphate on the other hand, during episode days is preferentially associated with the supermicron fraction (PM2.5-1), and so is ammonia; the concentration of nss-sulphate in this fraction is 2 times higher than in PM1 and in case of ammonia 1.6 times higher. The relative contribution follows a similar trend. Indoors, both nss-sulphate and ammonia have a higher concentration in PM1 than PM2.5-1 which could be attributed to lower infiltration capacity of supermicron particles. As demonstrated earlier, the I/O for sulphate in PM1 was close to 1 on average for all days and much lower in PM2.5. The relative contributions indoors are similar in both size fractions (29% and 26% for EDs and 12% during NEDs). On NED's slightly higher concentrations of nss-sulphate and ammonia are found in PM1 than PM2.5-1 in indoor as well as ambient air.

The NH_4^+ / SO_4^{2-} molar concentration ratios were calculated and were found to be 1.8 and 1.9 for PM2.5 and PM1, respectively, for outdoor concentrations and 0.9 and 0.8 for indoor PM2.5 and PM1 concentrations..The maximum ratio was 3 in PM2.5 and 2.8 in PM1 during one of the episode days. Scatter plots (not shown) of μequivalent concentrations of NH_4^+ versus SO_4^{2-} showed a significant correlation for both outdoor and indoor fractions (R^2 = 0.80 and 0.72 for outdoor PM2.5 and PM1, and 0.98 for indoor PM2.5 and 0.99 for indoor PM1). Generally, at low ammonia concentrations, neutralization of sulphate is favoured over nitrate; nitrate is stabilized by ammonium at NH_4^+ / SO_4^{2-} >1.5; this threshold was set at 2 in the study of Squizzato et al., (2013) (Squizzato et al., (2013) and references therein). In our study, nitrate dominates over sulphate in ambient air. When the sum of the μequivalent concentrations of NO_3^- and SO_4^{2-} concentrations were plotted against that of NH_4^+ (Figure 4) the R^2 for outdoor values were in the range of 0.97 - 0.99. The ED's are indicated in red to illustrate their significantly higher concentrations. The slopes of the linear regression lines in all cases suggest an ammonia deficit; therefore invoke the possible role of mineral neutralisation. However, the calcium and magnesium concentrations were very low and one may conclude that an acidic aerosol prevailed. Although Querol et al. (2001) has found the slope value close to 1 for PM2.5 in Barcelona, Spain (1.5 for PM10), others reported ammonium deficits similar to our study, for e.g. Yao et al. (2002) found the slope equal to 1.2-1.4. Taking into account that the average molar concentration ratios, also referred to as a neutralization ratio (NR) (Bencs et al. (2008), Squizzato et al., (2013)), for NH_4^+ / NO_3^- + nss-SO_4^{2-} are 0.8 and 0.7 outdoors and indoors for PM2.5, and 0.8 for PM1 indoors and outdoors, one can conclude that the ammonium deficit is similar for both environment.

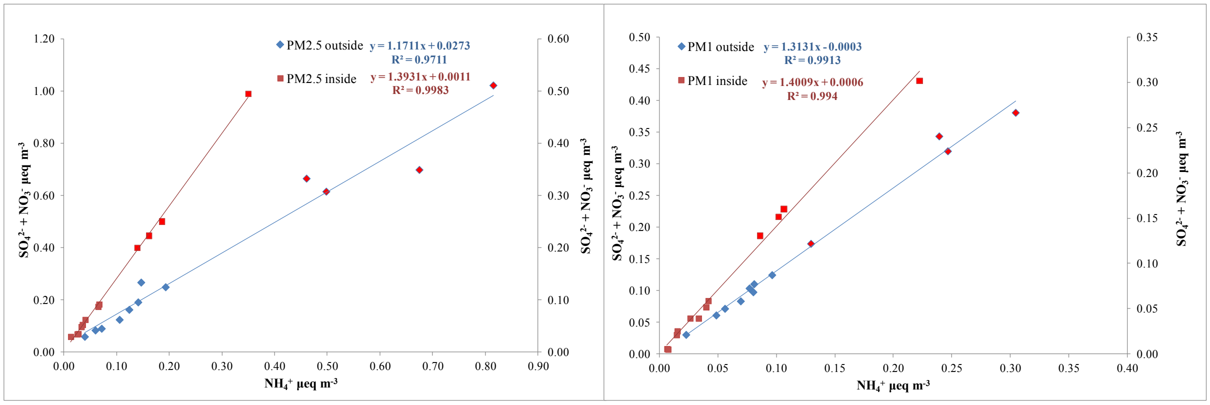


Figure 4. Correlations between ammonium and the sum of nitrate and sulphate ions in PM1 and PM2.5 (expressed as micro equivalents per m^3)

Crustal matter

Crustal matter was calculated using the equation 1.16 (1.90Al+2.15Si+1.41Ca+1.67Ti +2.09Fe) (Chan et al. (1997), Maenhaut et al. (2002), Sillanpää et al. (2006)). Additionally, enrichment factors were calculated for all elements. Enrichment factor analysis is based on comparison of the specific element’s concentration (Fe in this case) to the concentration of a so-called reference element in air relative to their concentration ratio in Earth’s crust (Mason, 1966). The enrichment factor close to one indicates that the crust is the likely source of the element whilst very high EF, points to origin other than crustal. All the above mentioned elements, have enrichment factors close to 1 (0.1-2.4), confirming their natural origin. Crustal matter contributes to about 3% (2.3 µg m^{-3}) of the total PM2.5 mass outdoors during episode days and up to 6% (1.6 µg m^{-3}) on non-episode days. These values are similar to those found for mineral fraction in Ghent, Belgium, namely 3% for winter PM2.5 and 4% for summer (Viana et al. (2007a)).

The mineral fraction is enriched in the supermicron PM2.5-1 particles by a factor of about 4-5, compared to PM1. Indoors, this prevalence decreases to a factor of 1.5. Hence, it constitutes 5% of the indoor PM2.5 on episode days and 8% on NED's. It is mostly derived from wind-blown soil dust in the outdoor environment or from re-suspension of the floor dust from human activities indoors. It is worth mentioning that the concentration of this fraction in PM2.5-1 is lower indoors than outdoors (I/O=0.7), whilst in PM1 it is higher (I/O=2, with the exclusion of one detected ($p<0.05$) outlier of 8). All days were taken into account. Amongst the crust elements analysed, Al outdoors in the PM1 fraction was often found below the detection limit (9 days out of 12), in indoor PM1, only 1 day was below this limit. It may thus lead to some inaccuracies in estimating the contribution of crustal matter outdoors. Other four elements (Ca, Fe, Si, Ti) taken into account for "crustal matter" calculation had concentrations between 2 and 165 times above their respective detection limits in both environments. The inaccuracies are thus not expected to be large. The elevated ratios for indoor PM1 could be attributed to re-suspension by movement of people. This was not seen for PM2.5-1, perhaps due to much lower outdoor contribution to indoor levels in this fraction than in PM1. The indoor PM is a sum of particles generated indoors and those which infiltrated from the outdoor environment. Similarly, Horemans and Van Grieken (2010), found the contribution of soil dust (calculated in the same manner) in PM1, collected in offices in Antwerp (Belgium), higher indoors than outdoors during the day and slightly lower during the night, and was explained as being a result of daily office activities, which prevent gravitational settling.

Sea salt

Sea salt content was calculated using the concentrations of Cl^-, Na^+ and a standard composition of sea water. As this approach may have a disadvantage of attributing a part of Cl^- which may originate from urban/industrial activities to sea salt., an alternative approach was also tested, which assumes that sea salt contains 30.8% of Na (Maenhaut et al. (2002)). The latter approach may on the other hand overestimate the salt content, since Cl^- may be lost from sea salt particles in the atmosphere, especially from the fine PM fraction (Maenhaut et al. 2002, Bencs et al. 2008). Interestingly, during NED's (and one of the episode days, 13th February, which was influenced by solely regional anticyclonic air masses), the approach using both ions estimated the content of sea salt to be 40% less than the other approach, confirming thus the loss of Cl^- ions and overestimation of sea salt content using Na^+ content only. This did not seem the case during the other episode days, where the approach using both the content of Cl^- and Na^+ ions estimated the salt content to be about 40% higher than when using Na^+ only. An increase in Cl concentration (both as soluble Cl^- and total Cl) was visible during the episode days (except for the 13th of February), in all PM fractions outdoors, whilst Na^+ concentration remained constant through the whole campaign, with minimal changes confirming that the increased chloride concentration could not be attributed to sea salt. This can possibly mean that a part of Cl^- originated from other sources than sea salt on most days with high pollution and that the sea salt content might be overestimated during those days. Another possibility is as stated by Ye et al. (2003); that the chloride might have originated from the sea salt in large particles but has been displaced by the reaction with nitric acid, followed by the reaction with ammonia to form smaller particles. Higher concentration of pollutants on ED's might have enhances this process. The fact that the molar ratio of Cl^-/Na^+ is not close to unity (if close to one, according to Ye et al. (2003), it may indicate sea salt origin of chloride) further suggests the possible presence of ammonium chloride, which would result in an even more acidic aerosol. Indoors, the chloride concentration was largely reduced compared to respective outdoor values, especially on episode days.. I/O ratios of such calculated sea salt were thus 0.5 on EDs and 0.8 on NEDs in both PM2.5 and PM1. Sodium is the only ion that shows the I/O ratio of 1 in both PM fractions. The sea salt contributes to about 3% (2.3 µg m^{-3}) of the total ambient PM2.5 on ED's and 6% on NED's (1.6 µg m^{-3}). It is enriched in the supermicron fraction PM2.5-1, having about 2 times higher concentration than in fraction PM1 during NED's. During ED's these differences are less prounced (Table 2). Generally, the contribution of this fraction is similar in our study to the results obtained for ambient Ghent PM, where it constituted about 5% (1.2 µg m^{-3}) of winter PM2.5 (Viana et al. (2007a)).

Other elements

The fraction "other elements", was calculated, similarly to Sillanpää et al. 2006, by summation of the Sr, Cr, Ni, Mn, Cu, Zn, As, Pb and V concentrations. For samples below the detection limit, random numbers below the detection limits were generated for the calculation of the averages. This fraction contributes negligibly to the sampled PM, namely 0.3-0.8% of various size ranges (Table 2). Amongst these elements, Sr had the lowest EFs (1.7-2.6), comparable with other soil derived elements. Mn and Cr show medium enrichment, therefore displaying both natural and anthropogenic origin and are followed by slightly higher values for V and Ni. Cu, Zn, As, Pb, are highly enriched (EFs

>100), implying mainly anthropogenic origin of those species. The results of concentration measurements and EFs calculations are presented in Table 3.

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

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

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

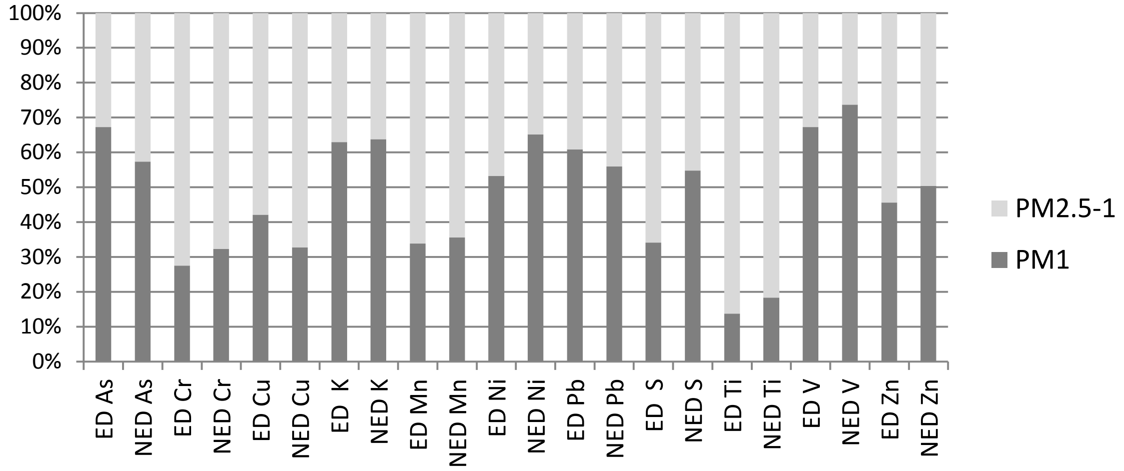
*the average value without the one elevated point of 812 ng m^{-3}

The "other elements" are mostly heavy metals that were present in relatively low concentrations in the outdoor environment and only as trace quantities in the indoor air. A few remarks concerning these elements are however of importance. In general, Pb had one of the highest concentrations in this class, ranging from 15 ng m^{-3} (NED's indoor PM1) to 51 ng m^{-3} (ED's ambient PM2.5). The National Ambient Air Quality Standard (NAAQS) for Pb (3 month rolling 0.15 µg m^{-3}) is therefore not exceeded, neither was it exceeded under the New European Directive (Directive 2008/50/EC-http://ec.europa.eu/environment/air/quality/legislation/directive.htm) where the standard is 0.5 μg m^{-3} based on a yearly average. The new directive that came into play on 31.12.2012 (http://ec.europa.eu/environment/air/quality/standards.htm) for As (6 ng m^{-3}) was exceeded during ED's for PM2.5, but it should be noted that our concentrations are reported as 24-h averages and the standard is an annual average. Other elemental concentrations regulated by the new directive are Ni and Cd, both of which were well below the standard. Except for Cu and Cr, all other minors and traces in general exhibited increases in concentration on ED's, ranging from 1.1 to 2.5 times higher than on NED's. It is also noticeable that V, Fe and Ni showed on average a 1.9 increase in concentration during ED's. These three metals are of interest as Jacobs et al. (2012) reported a significant association between their concentrations and the systolic blood pressure and pulse pressure of the elderly in this (and 5 other) old age homes. During non-episode days the concentration levels of elements in this group are comparable with the levels reported in other studies of outdoor PM2.5 in Antwerp, Belgium (Götschi et al.(2005), Stranger et al. (2009)). On ED's only Cu and Zn exceeded levels reported as winter average for Antwerp (Götschi et al.(2005)) by 1.4 times. In another work by Horemans and Van Grieken, (2010), 12h (both day and night) PM1 and PM2.5 averages calculated for those elements inside offices in Antwerp, were much higher than our NED's indoor levels. On ED's, Zn, Ni and V were elevated in our study by 1.5-3.5 times.

Elements such as: As, Ni, Pb, V and Zn accumulate to a large extent in the fine fraction as opposed to for example Ti; Figure 5 shows the fractional distributions (PM1 and PM2.5-1) of these elements with Ti given for comparison. They are characterized by high PM1/PM2.5 ratios of 0.5-0.7 in ambient air and 0.6-0.7 in indoor air. These ratios generally increase for indoor air compared to outdoor air as expected due to the ease of infiltration of fine particles. Additionally, in Figure 5, sulphur was shown as it exhibits the largest difference in the fractional distribution between ED's and NED's (about 20%). For other elements variation below 10% can be seen.

Pearson correlation coefficients (not shown) were calculated for these elements to investigate which elements may originate from a common source. Cr was excluded from correlation analyses as it was detected in about 50% cases only. Among *other elements*, V correlated very well with Ni ($r = 0.92$, $p<0.001$ for PM2.5 outdoors) both are considered as originating in Europe from oil combustion (Swietlicki and Krejci, (1996)). Their concentration was two times higher on ED's compared to NED's. Cu did not correlate with other elements from this group, it is fairly correlated with Ca, Si and Ti in ambient PM1 ($r=0.66\text{-}0.72$, $p=0.008\text{-}0.020$) what may suggest some contribution of re-suspended road dust source as Cu is a known tracer for break wear (Viana et al., (2007b), Cyrys et al. (2003)). In PM2.5 these correlations are weaker ($r=0.43\text{-}0.63$) and are only significant for Ca ($r=0.62$, $p=0.028$). Other anthropogenic origin elements (Zn, As, Pb) correlated very well with each other ($r>0.71\text{-}0.95$, $p<0.01$) both in PM1 and PM2.5. Of interest is a very high correlation between Zn, K and Cl ($r=0.97 - 0.99$, $p<0.001$) in ambient PM1. In PM2.5, the correlation between Zn and K is still high ($r=0.99$, $p<0.001$) but with Cl it is slightly weaker ($r=0.74 - 0.77$, $p<0.01$), probably because of higher contribution of sea salt Cl in this fraction. K is generally associated with biomass combustion (Götschi et al. (2005)) and waste incinerators (Maenhaut et al. (2002)) whilst Zn, is considered to originate from traffic and/or industrial activities such as non-ferrous smelters. Cl, apart from its natural sea salt origin, is thought to originate from industrial emissions of hydrochloric acid and from waste incineration (Götschi et al. (2005)). As already mentioned, the air masses influencing the high pollution days created an anticyclone over the territories of Belgium, The Netherlands and Germany, favouring the accumulation of pollutants not only from local traffic emissions and local industrialized areas (Antwerp) but also from more distant locations such as for example highly industrialized Ruhr region (Stranger, 2005) in Germany.

(a)



(b)

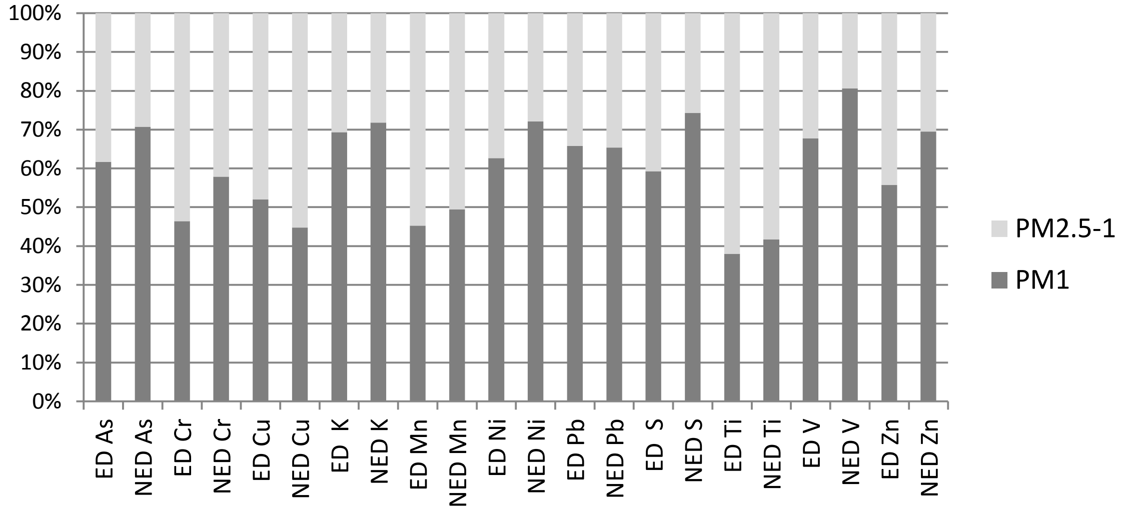


Figure 5. Partitioning of various elements between PM1 and PM2.5-1 fractions outdoors (a) and indoors (b) during EDs and NEDs.

Smoke

The contribution of smoke (or non-crustal K) was calculated as concentration of K - 0.6 of that of Fe (Maenhaut et al., (2002)). This fraction contributes to about 0.5 % of PM2.5 (0.3 µg m^{-3}), it is preferentially associated with PM1, ranging from 0.7 % in ambient PM1 on ED's to 1.2% of indoor PM1 during NED's.The indoor concentration equals outdoor, as already mentioned elsewhere, due to the high efficiency of fine particles to penetrate the building envelope. The average concentration of this fraction during episode days is twice as high as that on normal days.

3.4. Ion balance

In order to evaluate the acid-base balance of aerosols the ion balance equations (Shen et al., 2009; Zhang et al., 2002) were calculated in both PM fractions according to equations (1) and (2) for cations (C) and anions (A), respectively, whereby the concentration for each ion is in µg m^{-3}. The contribution of Mg^{2+} and Ca^{2+} were very low, in agreement with Stranger, 2005, thus random numbers were generated for samples which exhibited levels lower than LODs.

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

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

The C/A ratios were subsequently calculated. On average, during the episode days all fractions, except for PM2.5 indoors, were slightly acidic (C/A = 0.9), whilst on normal days the aerosol particles were on average slightly basic with the C/A values between 1 and 1.3 for different fractions. Statistically significant differences between ED's and NED's were, however, only found indoors in PM2.5 (p=0.009) and PM1 (p=0.022). During ED's the C/A values in outdoor PM2.5 ranged between 0.82 and 1.08, whilst in PM1, between 0.80 and 0.91. During NED's in outdoor PM2.5 variation between 0.74 and 1.30 was found and in PM1 between 0.93 and 1.33. Indoors, during ED's PM2.5 C/A values were between 0.90 and 1.02 and in PM1 between 0.89 and 0.91, on NED's these values ranged from 0.96 to 1.58 in PM2.5 and 0.98 to 1.47 in PM1 (in this fraction two values above 3 were seen). Neutral to alkaline aerosols coincided with the minima's of the registered PM mass (third week of the study, Figure 2), thus both anions and cations showed lower concentrations than during other days of the study. The highest sea salt content was registered (2 days out of 4) on those days, and a direct influence of North Sea and Atlantic Ocean air masses was noticed.

4. Conclusions

A comprehensive insight into the composition of PM 2.5 and PM1 on high and low pollution days and outdoor to indoor comparisons of PM sampled in old-age home was provided. This paper is complementary to a study by Jacobs et al. 2012, which investigated acute, short-term health effects of PM and its composition in the elderly part of the population. Extremely high ambient PM2.5 and PM1 values were registered during some days of this study. The investigation of PM composition revealed that although all components were found to be considerably higher during episode days than during non-episode days, it was the secondary inorganic aerosols that contributed the most towards an increase in the PM pollution as their relative contribution was higher by a factor of 1.6. Therefore, the episode days were not only influenced by a limited pollutant dilution connected to occurrence of temperature inversions, but also most probably by an increased formation of secondary inorganic pollutants due to preferable meteorological conditions. The 120h air mass backward trajectories influencing the high pollution days showed an anticyclonic scenarios with no or less direct influences of the North Sea or Atlantic Ocean air masses than during the low pollution days. The anticyclone was formed over the territories of Belgium, The Netherlands and Germany thus facilitating the accumulation of both local and regional pollutants. Natural contribution (mineral dust and sea salt) was relatively less important on ED's than NED's, the same was true for the "other elements" which included mostly heavy metals and for unaccounted mass which is in our study most probably composed of OC, EC and water. An ammonium deficit for PM was deducted in this study, especially on ED's. On average, the PM fractions on ED's were then slightly acidic (C/A = 0.9), whilst on normal days more variation was seen, and C/A ranged from acidic to alkaline (C/A>1-1.3) in ambient air. Neutral to alkaline aerosols coincided with the minima's of the registered PM mass. Amongst heavy metals Zn and Pb were found at the highest concentrations in both PM2.5 and PM1. No significant sources of indoor pollutants could be identified inside the old-age home. Generally, the PM1 mass concentration decreased indoors by 29 % compared to outdoors, whilst PM2.5-1 fraction by 57 %; this decrease was similar on ED's and

NED's. This is in agreement with the fact that fine mode particles penetrate the building envelope easier than supermicron mode. High correlations were found between outdoor and indoor PM, confirming the mainly outdoor origin of air pollution inside the Czagani old-age home.

Acknowledgements

The work reported in this paper was financed by the Belgian science policy under the Science for Sustainable Development program (SD/HE/01), Flemish Scientific Fund (FWO:G.0873.11). We thank the direction and staff of the elderly homes for their support. The authors are thankful to the partners of the project Lotte Jacobs, Tim Nawrot and Benoit Nemery for taking care of project organization, Andy Delcoo, Jo Dewulf and Hugo De Backer from Royal Meteorological Institute, Brussels, Belgium for supplying the meteorological data. We acknowledge Dr. Laszlo Bencs for assistance regarding backward trajectories analyses and two reviewers for their constructive comments. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication.

References

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

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

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

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

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

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

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

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

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

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

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

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

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

Hu, M., He., L.Y., Zhang, Y.H., Wang, M., Kim, Y.P., Moon, K.C., 2002. Seasonal variation of ionic species in fine particles at Qingdao, China. Atmospheric Environment 36, 5853-5859.

Jacobs, L., Buczynska, A., Walgraeve, C., Delcloo, A., Potgieter-Vermaak, S., Van Grieken, R., Demeestere, K., Dewulf, J., Van Langenhove, H., De Backer, H., Nemery, B., Nawrot, T.S., 2012. Acute changes in pulse pressure in relation to constituents of particulate air pollution in elderly persons. Environmental Research 117, 60 – 67.

Jones , N.C., Thornton, C.A., Mark, D., Harrison, R.M., 2000. Indoor/outdoor relationship of particulate matter in domestic homes with roadside, urban and rural locations. AtmosphericEnvironment 34, 2603-2612.

Krupinska, B., Worobiec, A., Rotondo, G, G., Novakovic, V., Kontozova, V., Ro, C., Van Grieken, R., De Wael, K., 2009. Assessment of the air quality (NO2, SO2, O3 and particulate matter) in the Plantin-Moretus Museum/Print Room in Antwerp, Belgium, in different seasons of the year. Microchemical Journal 102, 49 – 53.

Lai, H.K., Kendall, M., Ferrier, H., Lindup, I., Alm, S., Hänninen, O.,2004. Personal exposures and microenvironment concentrations of PM2.5, VOC, NO2, CO in Oxford, UK. Atmospheric Environment 38, 6399–410.

Mason, S., 1966. Principles of Geochemistry. Wiley, New York, p.45-46.

Maenhaut, W., Cafmeyer, J., Dubtsov, S., Chi, X., 2002. Detailed mass size distributions of elements and species, and aerosol chemical mass closure during fall 1999 at Gent, Belgium. Nuclear Instruments and Methods in Physics Research B 189, 238-242.

Meng, Q.Y., Turpin, B. J., Lee, J.H., Polidori, A.,, Weisel, C.P., Morandi, M., Colome, S., Zhang, J., Stock, T., Winer, A.,2007. How Does Infiltration Behavior Modify the Composition of Ambient PM 2.5 in Indoor Spaces? An Analysis of RIOPA Data. Environmental Science and Technology 41, 7315-7321.

Parker, J.L., Larson, R.R., Eskelson, E., Wood, E.M., Veranth, J.M., 2008. Particle size distribution and composition in a mechanically ventilated school building during air pollution episodes. Indoor Air 18, 386-393.

Putaud,J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, C., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H.T., Tørseth, K., Wiedensholer, A., 2004. A European aerosol phenomenology—2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmospheric Environment 38, 2579-2595.

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C.R., Cots, N., Massague, G., Puig, O., 2001. PM10 and PM2.5 source apportionment in the Barcelona Metropolitan area, Catalonia, Spain. Atmospheric Environment 35, 6407-6419.

Querol, X., Alastuey, A., Ruiz, C.R., Artiñano, B., Hansson, H.C., Harrison, R.M., Buringh, E., ten Brink, H.M., M. Lutz, Bruckmann, P., Straehl, P., Schneider, J., 2004a. Speciation and origin of PM10 and PM2.5 in selected European cities. Atmospheric Environment 38, 6547-6555.

Querol, X., Alastuey, A., Viana, M.M., Rodriguez, S., Artiñano, B., Salvador, P., Garcia do Santos, S., Fernandez Patier, R., Ruiz, C.R., de la Rosa, J., Sanchez de la Campa, A. , Menendez, M., Gil, J.I., 2004b. Speciation and origin of PM10 and PM2.5 in Spain. Aerosol Science 35, 1151-1172.

Ram, K., Sarin, M. M., Sudheer, A. K., Rengarajan, R., 2012. Carbonaceous and secondary inorganic aerosols during wintertime fog and haze over urban sites in the Indo-Gangetic plain. Aerosols and Air Quality Research 12, 359-370.

Rattigan, O.V., Reilly, J., Judd, C.D., Moore, K.F., Das, M., Sherman, D.E., Dutkiewicz, V.A., Collett, J.L., Jr. and Husain, L., 2001. Sulfur dioxide oxidation in clouds at Whiteface Mountain as a function of drop size. Journal of Geophysical Research 106, 17347–17358.

Shen, Z., Cao, J., Arimoto, R., Han, Z., Zhang, R., Han, Y., Liu, S., Okuda, T., Nakao, S., Tanaka, S., 2009. Ionic composition of TSP and PM2.5 during dust storms and air pollution episodes at Xi'an, China. Atmospheric Environment 43, 2911-2918.

Sillanpää, M., Hillamo, R., Saarikoski, S., Frey, A., Pennanen, A., Makkonen, U., Spolnik, Z., Van Grieken, R., Braniš, M., Brunekreef, B., Chalbot, M.-C., Kuhlbusch, T., Sunyer, J., Kerminen, V.-M., Kulmala, M., Salonen, R.O., 2006. Chemical composition and mass closure of particulate matter at six urban sites in Europe. Atmospheric Environment 40, S212-S223.

Squizzato, S., Masiol, M., Brunelli, A., Pistollato, S., Tarabotti, E., Rampazzo, G., Pavoni, B., 2013. Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy). Atmospheric Chemistry and Physics 13, 1927-1939

Strak, M., Janssen, N.A.H., Godri, K.J., Gosens, I., Mudway, I.S., Cassee, F.R., Lebret, E., Kelly, F.J., Harrison, R.M., Brunekreef, B., Steenhof, M., Hoek, G., 2012. Respiratory health effects of airborne particulate matter: The role of partical size, composition, and oxidative potential. Environmental Health Perspectives 123, 1183-1189.

Stranger, M., 2005. Characterisation of health related particulate and gas-phase compounds in multiple indoor and outdoor sites in Flanders. PhD dissertation, University of Antwerp.

Stranger, M., Potgieter-Vermaak, S.S., Van Grieken, R., 2007. Comparative overview of indoor air quality in Antwerp, Belgium. Environment International 33, 789-797.

Stranger, M., Potgieter-Vermaak, S.S., Van Grieken, R., 2009. Particulate matter and gaseous pollutants in residences in Antwerp, Belgium. Science of the Total Environment 407, 1182 – 1192.

Swietlicki, E. and Krejci, R., 1996. Source characterisation of the Central European atmospheric aerosol using multivariate statistical methods. Nuclear Instruments and Methods in Physics Research B 109/110, 519-525.

Vecchi, R., Marcazzan, G., Valli, G., Ceriani, M., Antoniazzi, C., 2004. The role of atmospheric dispersion in the seasonal variation of PM1 and PM2.5 concentration and composition in the urban area of Milan (Italy). Atmospheric Environment 38, 443-4446.

Vercauteren, J., Matheeussen, C., Wauters, E., Roekens, E, Van Grieken R, Krata, A, Makarovska, Y, Maenhaut, W, Chi, X, Geypens, B., 2011.Chemkar PM10: An extensive look at the local differences in chemical composition of PM10 in Flanders, Belgium. Atmospheric Environment 45, 108-116.

Viana, M., Maenhaut, W., Chi, X., Querol, X., Alastuey, A., 2007a. Comparative chemical mass closure of fine and coarse aerosols at two sites in south and west Europe: Implications for EU air pollution policies, Atmospheric Environment 41, 315-326.

Viana, M., Querol, X., Götschi, T., Alastuey, A., Sunyer, J., Forsberg, B., Heinrich, J., Norbäck, D., Payo, F., Maldonado, J., Künzli, N., 2007b. Atmospheric Environment 41, 1395-1406.

Wang, Y., Zhuang, G., Sun, Y.,An, Z., 2006. The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing. Atmospheric Environment 40, 6579–6591.

Yao, X., Chan, C.K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., Ye, B. 2002. The water-soluble ionic composition of PM2.5 in Shanghai and Beijing, China. Atmospheric Environment 36, 4223-4234.

Ye, B., Ji, X., Yang, H., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P.A., 2003. Concentration and chemical composition of PM2.5 in Shanghai for a 1-year period. Atmospheric Environment 37, 499-510.

Zhang, X.Y., Cao, J.J., Li, L.M., Arimoto, R., Cheng, Y., Huebert, B., Wang, D., 2002. Characterization of Atmospheric Aerosol over XiAn in the South Margin of the Loess Plateau, China. Atmospheric Environment 36, 4189-4199.