Major ionic species in size-segregated aerosols and associated gaseous pollutants at a coastal site on the Belgian North Sea

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Received 1st September 2008, Accepted 24th November 2008
First published as an Advance Article on the web 24th December 2008
DOI: 10.1039/b815059a

The chemical composition of airborne particulate matter (PM) was studied at a coastal region near De Haan, Belgium, during a winter–spring and a summer campaign in 2006. The major ionic components of size-segregated PM, *i.e.* NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}, and related gaseous pollutants (SO_2, NO_2, NH_3, HNO_2, and HNO_3) were monitored on a daily basis. Air mass backward-trajectories aided in evaluating the origin of the diurnal pollution load. This was characterised with high levels of fine secondary inorganic aerosols (NH_4^+, NO_3^-, and non-sea-salt SO_4^{2-}) for continental air masses, and sea-salts as the dominant species in coarse maritime aerosols. Seasonal variations in the level of major ionic species were explained by weather conditions and the release of dimethyl sulfide from marine regions. This species was responsible for an increased sea-salt Cl^- depletion during summer (56%), causing elevated levels of HCl. Neutralisation ratios for the coarse fraction (0.6–0.8) suggested a depleted NH_4^+ level, while that for the fine fraction (1.1–1.3) had definitely an excess of NH_4^+, formed by the neutralisation of HCl. The results of factor analysis and the extent of SO_2 oxidation indicated that the major ionic species originated from both local and remote sources, classifying the Belgian coastal region as a combined source–receptor area of air pollution.

1. Introduction

The growth of anthropogenic activities on terrestrial areas triggers enhanced nutrient deposition, and eliminates the natural limitations for phytoplankton growth. This can cause extensive phytoplankton blooms, which decreases the oxygen concentration in coastal waters, resulting in fish mortalities.[1,2] The major limiting nutrients for phytoplankton growth are biologically available (fixed) nitrogen and phosphorus compounds. The levels of these nutrients in water bodies are enhanced by anthropogenic activities. Phosphorus is mainly loaded into marine eco-systems through riverine sources, whereas nitrogen compounds have an additional, atmospheric source, which may represent 10–50% of the anthropogenic N flux to water surfaces.[3]

Because of the growing human population and the corresponding increase in the need for energy, the natural nitrogen-cycle is strongly affected. It has been predicted that the extent of anthropogenic nitrogen-fixation would increase by 60% till the year 2020.[4] NO_x (NO and NO_2) is emitted by different sources, but it is mainly formed during the combustion of fossil fuels. Lee *et al.*[5] estimated the global NO_x emission (both natural and anthropogenic) around 44 Tg N per year with an uncertainty ranging from 23 to 81 Tg N per year. They have also calculated that fossil fuel combustion would account for a NO_x emission of almost 47 Tg N per year by the year 2025. The global emission of NH_3 was estimated to be as high as 75 Tg N per year of which more than 50% could be attributed to animal husbandry and the use of fertilisers.[6]

Deposition of atmospheric gases occurs through both wet and dry mechanisms, but the major sink process is the formation of secondary aerosols, which are rapidly removed from the atmosphere. Therefore, these aerosols are very important when atmospheric nutrient loading of a water body is considered. For example, NH_3 is rapidly converted to NH_4^+ at a rate of 30% h^{-1},[7] while NO_2 is oxidised to HNO_3 *via* radical mediated reactions,[8] and sub-sequentially neutralised to give NO_3^- aerosols.

The North Sea is located in the North West of Europe and covers a total area of around 750000 km^2. It is surrounded by heavily industrialised countries and connected in the North with the Atlantic Ocean. Every year, around 140 kt N of NH_3 and NH_4^+ is deposited to the North Sea, while NO_x and its reaction products are deposited around 200 kt N per year.[9] Tamm and Schulz made a fifteen-month-long survey on the inorganic composition of aerosols collected over the open North Sea,[10] and observed a strong impact of Western European emissions on the pollution load of this regional sea. Surprisingly, the amount of pollution was hardly different between the middle of the North Sea and the coastal areas.

At marine areas, the formation and chemical behaviour of aerosols in the atmosphere differs strongly from those over continental areas. Sea-salt aerosols can, for example, affect the amount of secondary aerosol formation, since they provide a surface for heterogeneous reactions with all kinds of gaseous species.[11] Reaction of sea-salt with H_2SO_4 or HNO_3 results in the

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formation of SO_4^{2-} and NO_3^- aerosols, respectively, while Cl^- escapes as HCl.[12,13] Moreover, SO_4^{2-} aerosols do not always originate from anthropogenic sources, but they are brought to the atmosphere by sea-spray, or the release of dimethyl sulfide (DMS) from oceans.[14,15]

The present research provides information on the major ionic species in various size fractions of aerosols and their related gaseous air pollutants sampled at a coastal site on the Belgian North Sea. Temporal and spatial variation in the pollutant concentrations were evaluated on the base of daily and seasonal data, weather information, and air mass backward trajectories (BWTs). The emission sources of major ionic species were attempted to assign on the base of factor analysis and by evaluation of gas–aerosol phase conversion factors (*i.e.* sulfur oxidation ratios (SORs)).

2. Experimental

2.1. Description of the sampling site and meteorological data

Samples were collected some 2 km northeast of the seaside resort De Haan (lat. 51°17′13″N, long. 3°3′40″E), Belgium, and at about 13 km from the nearest cities Oostende and Zeebrugge. The sampling equipment was installed at less than 5 m above sea level some 0.5 km from the national road (N34) which is parallel to the Belgian coast. Two sampling campaigns were performed on a diurnal (24-hour) basis in 2006 from February 14th till April 30th (late winter–spring) and from June 12th till August 8th (mid-summer), respectively.

During the late winter–spring campaign, the average of the daily temperature ranged from −1.3 °C to 14.3 °C. During this campaign, a high level of relative humidity (RH) was observed, ranging from 59 to 97%. The prevailing wind directions were from south-southeast and southwest with a wind speed ranging from 0.8 to 4.5 m s^{-1} with an average of 2.3 m s^{-1}. The extent of precipitation was sometimes as high as 11.6 mm day^{-1} with a mean value of 1.5 mm day^{-1}. During the summer campaign the air temperature was considerably higher compared to winter (13–26 °C), while the RH was comparable with the former campaign (55–83%). Wind-speeds were sometimes as high as 11 m s^{-1}, averaging around 3.2 m s^{-1}. During this campaign, the winds blew mainly from south, southeast, and southwest. The amount of precipitation was significantly lower than in winter–spring, ranging up to 12 mm day^{-1} (0.5 mm day^{-1} on average).

2.2. Sampling procedures

Passive sampling of NO_2 and SO_2 was made with Radiëllo diffusion tubes (code 166, Radiëllo, Padova, Italy). To ensure the quality of the data, six diffusion tubes were installed simultaneously in specially designed shelters for a total period of seven days. An URG 2000-01-K annular denuder (URG, Chapel Hill, NC, USA) equipped with a PM_{10} inlet and a sharp $PM_{2.5}$ cyclone was used at an airflow rate of 14 m^3 day^{-1}. The denuder tubes were coated with a 1% citric acid/methanol solution and a 2% sodium carbonate 2% glycerine/methanol solution (analytical grade) for selective sampling of NH_3 and HNO_x, respectively. PM was collected at a height of 1.8 m above the ground level during 24 hours with a stacked filter-unit (SFU)[16,17] fitted with an additional (third) stage. The pump (Becker VT 4.4, Wuppertal, Germany) was set at 24 l min^{-1}, corresponding to a sampling face velocity of 23 cm s^{-1}. Nuclepore membrane filters (Whatman, Brentford, UK) with diameters of 47 mm and pore sizes of 10, 2 and 0.4 μm were used at the three stages of the SFU. Sampled air volumes were registered with standard gas meter units. Under the present sampling conditions the filters have a 50% collection efficiency for particles with an equivalent aerodynamic diameter (EAD) of 4, 0.8, and 0.16 μm, respectively.[18] In this way, aerosols are segregated in a fine (< 0.8 μm), medium (0.8–4 μm), and coarse (> 4 μm) fraction. Although this size segregation looks quite unconventional at first sight, the authors would like to emphasize that this sampling protocol divides aerosols more or less in super (> 0.8 μm) and sub (< 0.8 μm) micrometer particles, a split up that is made more and more in environmental aerosol research.

All the samples were stored at 4 °C until sample processing. Denuder and diffusion tubes were leached in 5 ml ultra-pure water of 18.2 MΩ cm resistivity (MilliQ, Millipore, Billerica, MA, USA) for 10 and 30 minutes, respectively, during which they were frequently stirred. Filters were leached in 5 ml ultra-pure water for 10 min with an ultrasonic bath (Bransonic 2210, Branson, Danbury, CT, USA). Unexposed diffusion tubes were used to estimate the background level of the analytes, while blank filters and coated denuder tubes were brought to the field for passive exposure during 24 hours.

2.3. Analytical procedure

Sample leachates were analysed by ion-chromatography with conductivity detection (Dionex DX-120, Dionex, Sunnyvale, CA, USA). NO_2, SO_2, HNO_x and NH_3 were determined by the content of NO_3^-, SO_3^{2-} + SO_4^{2-}, NO_x^- and NH_4^+ in the leachates, respectively, while PM was analysed for water-soluble species (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}). More details on the instrument and the analytic procedure are described elsewere.[19] Limits of detection (LODs) of 1, 10, 1, 4, 5, 1, 5, and 3 ng m^{-3} were observed for NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}, respectively, with relative standard deviations generally lower than 5%.

2.4. Evaluation methods

The BWTs were calculated with the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model.[20,21] Data were treated with the SPSS software (version 13.0, SPSS Inc., Chicago, IL, USA) and sorted according to the corresponding air mass trajectory and season. The reported averages are indicated with their standard error, *i.e.* the standard deviation divided by the square root of the number of samples. For factor analysis, concentration data were normalised according to Kaiser's method and the correlation matrix was rotated according to the orthogonal Varimax criterion.

3. Results and discussion

3.1. Evaluation of pollutant levels on the base of BWTs

On the base of the BWTs one may divide the air masses arriving to De Haan into three major groups: (1) continental, (2) North

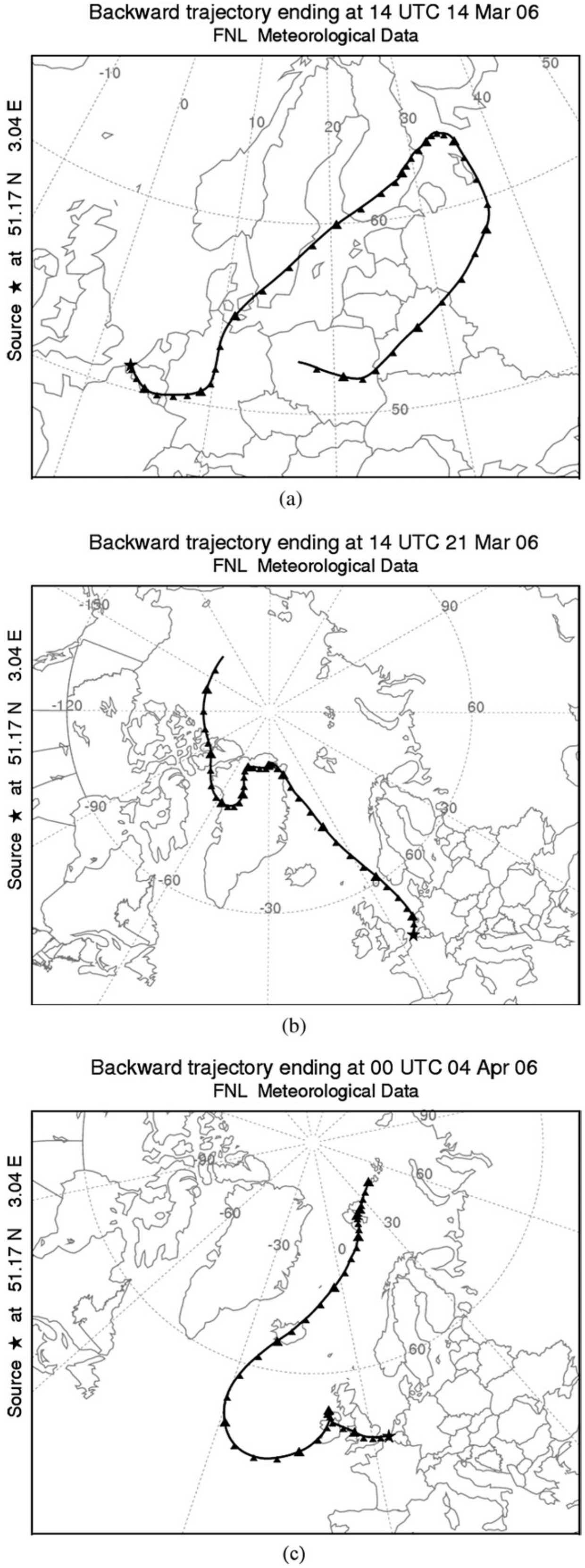

Fig. 1 Typical air mass backward trajectories for the three major air masses: (a) continental, (b) North Sea, and (c) Atlantic passing the Channel, United Kingdom, and/or North France.

Sea, and (3) Atlantic passing the Channel, the United Kingdom, and/or North France (Fig. 1).

The average NH_3 content in continental samples was 5 ± 2 and 4.2 ± 0.9 $\mu g\ m^{-3}$ during winter and summer, respectively (Table 1). HNO_2 and HNO_3 were present at much lower levels, together accounting for a continental concentration of 1.9 ± 0.1 and 2.7 ± 0.3 $\mu g\ m^{-3}$, respectively. The concentrations of gaseous species were generally lower when Oceanic air masses arrived to the site (Table 1). The daily average concentrations of NH_3 for the North Sea air masses were found to be relatively high, reaching up to 4.8 ± 0.7 $\mu g\ m^{-3}$ during summer, which could be due to the coastal pollution from the Netherlands and Belgium, a region well-known for its intensive animal husbandry activities. Average concentrations of major ionic species in PM are presented in Fig. 2. Distribution of NH_4^+ and NO_3^- in aerosols is in favour of the fine fraction. For continental air masses, the daily average concentrations of NH_4^+ in the coarse fraction was significantly lower (91%) compared to the fine fraction, though for the marine air masses the concentration drop was less pronounced, *i.e.*, 66 and 75% for Atlantic and North Sea samples, respectively.

Mg^{2+} and Ca^{2+} are the most abundant in the coarse fraction of marine air masses (Fig. 2.). These elevated levels could be due to the ablation of Mg^{2+} and Ca^{2+} containing sea-salts and the suspension of local soil dust. Na^+ and Cl^- were most abundant in the coarse fraction from air masses coming over sea (Fig. 2). Sea-salt is one of the primary sources for SO_4^{2-}, providing the coarse fraction with a SO_4^{2-} content. Additionally, oxidation of SO_2 gives SO_4^{2-} salts in fine PM.[22] Differentiation between sea-salt SO_4^{2-} (SSS) and non sea-salt SO_4^{2-} (NSSS) can be calculated as follows:[23]

$$SO_4^{2-}{}_{NSS} = SO_4^{2-}{}_{total} - 0.231 \times Na^+ \qquad (1)$$

$SO_4^{2-}{}_{NSS}$ represents the NSSS, $SO_4^{2-}{}_{total}$ the total SO_4^{2-}, and Na^+ the sodium concentration (all in $\mu g\ m^{-3}$). The factor 0.231 is the average molar ratio of SO_4^{2-} to Na^+ in bulk sea-water. As can be seen in Fig. 2, NSSS is the major contributor to the medium and fine fractions. The highest NSSS concentration (1.0 ± 0.1 $\mu g\ m^{-3}$) was found in the fine fraction of air masses coming from the North Sea, though it didn't differ significantly from levels found for continental and Atlantic samples (Fig. 2). For SSS, the highest contribution was found in the coarse fraction of Atlantic samples (0.18 ± 0.02 $\mu g\ m^{-3}$), as one can expect.

3.2. Seasonal variation

Seasonal comparison of the average daily contribution of each species to the total amount of ionic species in aerosols clearly shows a higher abundance for SO_4^{2-}, Na^+, Mg^{2+}, NH_4^+, and Ca^{2+} during summer, while NO_3^- and Cl^- were found to be more abundant during winter–spring (Fig. 3). Although the NH_3 levels are generally higher during summer since the warmer atmosphere favours its evaporation from fertilized agricultural fields, no significant seasonal difference could be observed (Table 1). In contrast, the NH_4^+ contribution to the total amount of major ionic species during summer was 7 ± 2% higher compared to winter–spring (Fig. 3). Since the temperature for the summer season was higher compared to winter–spring and the observed

Table 1 Descriptive statistics for the concentrations of gaseous species (µg m^{-3}) during winter–spring and summer according to the different air masses

	Winter–spring				Mid-summer			
	n^a	Min–max	Median	Mean ± SE [b]	n	Min–max	Median	Mean ± SE
Continental								
NH_3	11	n.d.[c]–19	3	5 ± 2	14	n.d.–9.0	5.0	4.2 ± 0.9
HNO_2	11	0.56–1.88	1.0	1.0 ± 0.1	14	n.d.–1.9	0.7	0.8 ± 0.1
HNO_3	11	0.2–1.9	1.0	0.9 ± 0.1	14	n.d.–3.8	1.9	1.9 ± 0.3
Atlantic/UK								
NH_3	17	n.d.–7.3	2.7	2.7 ± 0.5	19	n.d.–9.1	3.0	3.4 ± 0.6
HNO_2	17	n.d.–1.19	0.33	0.44 ± 0.08	19	n.d.–1.9	0.4	0.5 ± 0.1
HNO_3	17	n.d.–2.2	0.4	0.7 ± 0.1	19	n.d.–2.8	1.0	1.0 ± 0.2
North Sea								
NH_3	9	2–11	3	4 ± 1	11	2.1–8.9	3.9	4.8 ± 0.7
HNO_2	9	n.d.–1.4	0.3	0.5 ± 0.1	11	0.03–1.4	0.1	0.3 ± 0.1
HNO_3	9	0.5–1.9	1.2	1.1 ± 0.2	11	0.6–2.1	1.0	1.3 ± 0.2
Total								
NH_3	37	n.d.–19.4	1.8	2.8 ± 0.6	44	n.d.–9.1	3.9	4.0 ± 0.4
HNO_2	37	n.d.–1.88	0.56	0.63 ± 0.08	44	n.d.–1.93	0.44	0.53 ± 0.07
HNO_3	37	n.d.–2.23	0.73	0.85 ± 0.09	44	n.d.–3.76	1.14	1.3 ± 0.1
NO_2	9	0.18–1.4	0.5	0.6 ± 0.1	8	0.1–1.1	0.4	0.5 ± 0.1
SO_2	9	0.08–0.44	0.17	0.21 ± 0.04	8	0.3–1.5	1.1	1.0 ± 0.1

[a] n = number of samples. [b] SE = standard error. [c] n.d. = not detected.

levels of RH were comparable, the air-masses arriving to the sampling area during winter–spring were generally drier. This drier atmosphere could be the main reason for the lower NH_4^+ contribution during winter–spring, since NH_4^+-salts such as NH_4NO_3 decompose more rapidly under dry conditions.[24] As a consequence, NH_4NO_3 particles hardly grow to large particle sizes during winter (Fig. 4). NO_x is mainly produced during combustion of fossil fuels, by both stationary and mobile sources. During the past century, the increased fossil fuel combustion resulted in an increase of the NO_x emission by an order of magnitude.[25] Although NO_x levels are generally believed to be elevated during winter due to the increased domestic heating and the higher electricity demand, the observed NO_2 levels do not show any seasonality (Table 1). The contribution of NO_3^- to the total amount of ionic species during winter was on average 8 ± 2% higher compared to summer (Fig. 3), which could be explained by the low winter temperatures, that favour NO_3^- formation.[26] The use of S-rich fossil fuels has been decreased drastically during the last two decades, at least for Europe and North America,[27] showing moderate contributions of SO_2 during the winter–spring campaign (Table 1). In contrast, the SO_2 budget is observed to be around 5 times higher during summer. This is not unusual for maritime regions, where the total atmospheric S budget is elevated by the oceanic release of DMS, which rapidly oxidises to H_2SO_4 *via* OH radical mediated reactions. Both DMS and the OH radical have a strong seasonal variability with maximum fluxes during the summer months.[28] The influence of DMS on the levels of NSSS is supported by the air-masses, which show maximal NSSS levels for air-masses coming from the Atlantic Ocean during summer (Table 2). Therefore, one can see in Fig. 3 that the contribution of SO_4^{2-} during summer is 6 ± 2% higher compared to winter. Apart from SO_4^{2-} formation, H_2SO_4 reacts with sea-salt during which Cl^- escapes as HCl.[13] Therefore, one could observe a strong decrease in the contribution of Cl^- during summer (10 ± 3%, Fig. 3) which is maximal for the medium particle fraction (Fig. 4). Despite the increased loss of Cl^- in summer, Na^+ showed elevated summer levels compared to winter (9 ± 2%), because the higher wind speeds during this season create more freshly generated sea spray. Usually, these fresh sea-salts are fine particles, especially compared to aged sea-salt particles coming from more remote areas. That is why, Na^+ in summer is more present in the fine fraction, while winter shows maximal Na^+ levels in the coarse fraction. Ca^{2+} and Mg^{2+} were more abundant during summer (1.8 ± 0.4% and 0.8 ± 0.3%, respectively). These elevated concentrations could be due to the increased level of sea spray for the summer season, though, in contrast to Na^+, the maximal summer loadings were found for the coarse fraction (Fig. 4). Therefore, it is believed that these species were suspended in air by the ablation of coarse carbonaceous soil dust, which is suspended more easily during periods of low precipitation and strong wind bursts (summer).

3.3. Chloride replacement and aerosol acidity

The Na^+ and Cl^- concentrations are significantly higher in air masses originating from the Atlantic Ocean and North Sea compared to those coming from the continent, indicating sea-salt as their source. Assuming that all Na^+ in the atmosphere originates from sea-salt, one may calculate the sea-salt Cl^- as follows:

$$Cl_{sea} = 1.8 \times Na^+ \quad (2)$$

The factor 1.8 represents the average molar Cl^- to Na^+ ratio in bulk sea-water. During atmospheric aerosol transport, the sea-salt Cl^- is released from PM as HCl due to reaction, for example, with HNO_3 or H_2SO_4.[12,13] The percentage of Cl^- lost during transport/transformation can be derived as follows:[29,30]

$$Cl_{loss} = (Cl_{sea} - Cl^-)/Cl_{sea} \quad (3)$$

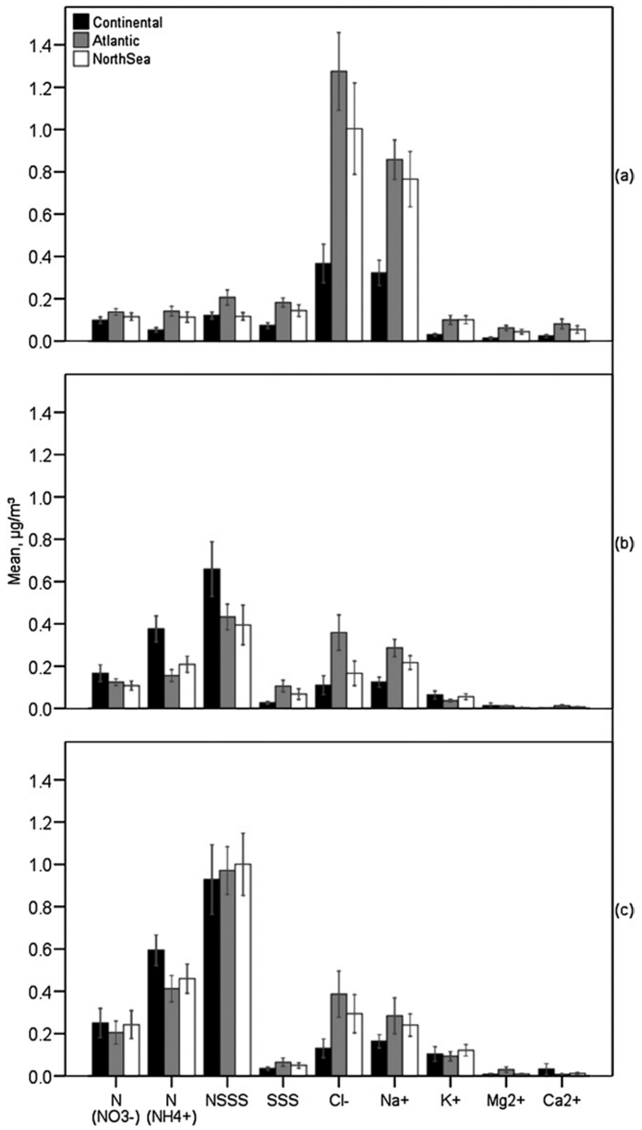

Fig. 2 Daily average concentrations (± standard error) of major ionic species in the (a) coarse, (b) medium, and (c) fine fractions of airborne particulate matter for the different air masses ($n = 81$). NSSS = non-sea-salt SO_4^{2-}, SSS = sea-salt SO_4^{2-}.

The calculated data for Cl_{sea}, and Cl_{loss} are listed in Table 2. The highest sea-salt Cl^- concentration has been found in the coarse fraction (0.7–1.5 µg m^{-3}) with higher values for air masses coming from the Atlantic Ocean and the North Sea. The highest Cl_{loss} is observed for continental air masses, *i.e.*, 43, 74, and 71% for the coarse, medium, and fine aerosol fractions, respectively, due to the longer residence time of sea-salts between the source and the sampling site. For the city of Ghent (Belgium), Viana *et al.* observed a three times higher Cl_{sea} concentration during winter than summer, while the opposite seasonal trend was found for Barcelona.[31] This observation accounted for the long-range air mass transport from the Atlantic Ocean, which is predominant during winter for the North Sea region. Nevertheless, in the present research there was no significant difference between the amount of Cl_{sea} in PM during the winter–spring and summer campaign (Table 2). Indeed, the number of days with winds

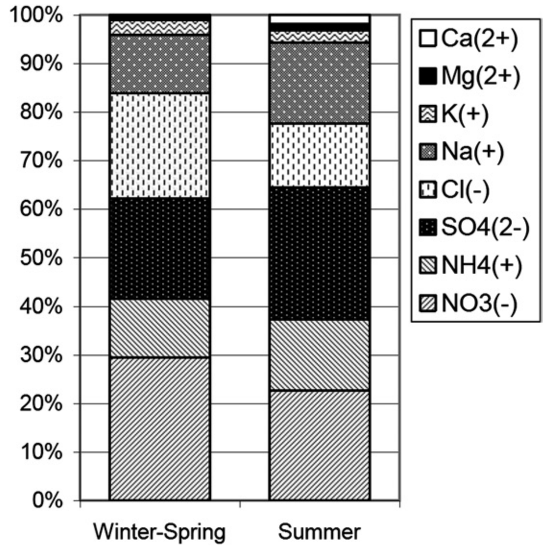

Fig. 3 Average relative contribution for each ionic species to the amount of major ionic species in PM for the winter–spring and the summer campaign ($n = 81$).

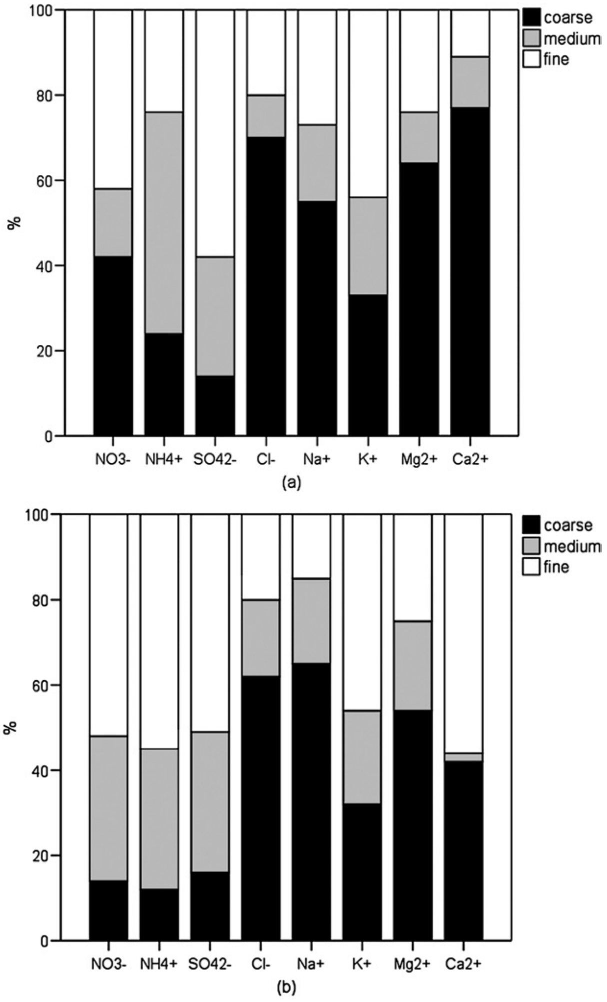

Fig. 4 Average distribution of each ionic species (%) over the three size fractions of PM (coarse, medium, and fine) for the (a) mid-summer ($n = 44$) and (b) winter–spring ($n = 37$) campaign.

Table 2 Average of daily sea-salt chloride concentrations (Cl_{sea}, μg m^{-3}), lost sea-salt chloride (Cl_{loss}, %), and neutralisation ratios (NRs) for each PM size fraction and for total PM averaged according to the three main air mass origins (± standard error)

	NSSS (μg m^{-3})	Cl_{sea} (μg m^{-3})	Cl_{loss} (%)	NR
Coarse[a]				
Continental	0.12 ± 0.02	0.7 ± 0.1	43 ± 9	0.8 ± 0.1
Atlantic/Channel/UK	0.21 ± 0.04	1.5 ± 0.2	18 ± 8	0.8 ± 0.1
North Sea	0.12 ± 0.02	1.38 ± 0.2	30 ± 8	0.6 ± 0.1
Medium[a]				
Continental	0.6 ± 0.1	0.30 ± 0.05	74 ± 7	1.35 ± 0.06
Atlantic/Channel/UK	0.43 ± 0.06	0.52 ± 0.07	47 ± 9	1.2 ± 0.3
North Sea	0.40 ± 0.09	0.39 ± 0.06	70 ± 8	0.9 ± 0.1
Fine[a]				
Continental	0.9 ± 0.2	0.38 ± 0.07	71 ± 4	1.33 ± 0.05
Atlantic/Channel/UK	1.0 ± 0.1	0.5 ± 0.2	58 ± 7	1.1 ± 0.1
North Sea	1.0 ± 0.1	0.43 ± 0.09	60 ± 8	1.2 ± 0.1
Total PM[b]				
Winter–spring				
Continental	0.46 ± 0.08	1.3 ± 0.2	48 ± 9	0.94 ± 0.04
Atlantic/Channel/UK	0.56 ± 0.06	2.6 ± 0.4	19 ± 4	0.7 ± 0.1
North Sea	0.42 ± 0.09	2.5 ± 0.6	10 ± 6	0.76 ± 0.03
Average	0.49 ± 0.04	2.2 ± 0.2	27 ± 5	0.80 ± 0.05
Mid-summer				
Continental	0.52 ± 0.09	1.0 ± 0.3	61 ± 7	2.2 ± 0.4
Atlantic/Channel/UK	0.8 ± 0.1	2.5 ± 0.3	51 ± 7	1.0 ± 0.2
North Sea	0.5 ± 0.1	1.9 ± 0.3	61 ± 8	0.82 ± 0.09
Average	0.59 ± 0.06	1.9 ± 0.2	56 ± 4	1.4 ± 0.2

[a] Data averaged for the winter–spring and the mid-summer campaign ($n = 81$). [b] Seasonal data (winter–spring: $n = 37$, summer: $n = 44$).

originating from the continent, North Sea, or the Atlantic Ocean was almost exactly the same for both seasons.

The amount of sea-salt chloride lost during atmospheric transport was significantly higher during summer due to the considerably elevated levels of SO_2 (Table 1). Similar observations were made by Wakamatsu *et al.*, who reported a minimum Cl^- to Na^+ ratio in August that was half of that observed in February.[32] The elevated HCl concentrations during summer have a profound effect on the composition and acidity of aerosols. The neutralisation ratio (NR), *i.e.*, the molar ratio of the amount of reacted alkaline species (mol m^{-3}) to the total amount of acidic species (mol m^{-3}), can give useful information concerning the composition and acidity of aerosols (Eqn. 6).

$$\mathrm{NR} = \mathrm{eq}_{\mathrm{NH4+}}/(\mathrm{eq}_{\mathrm{Nitrate}} + \mathrm{eq}_{\mathrm{NSSS}}) \qquad (6)$$

An NR value close to unity suggests that ammonium sulfate is predominantly present as $(NH_4)_2SO_4$, while lower NR values indicate the presence of NH_4HSO_4 particles.[33] As can be seen in Table 2, NRs were lower than unity for coarse aerosols, suggesting the presence of acidic sulfates, while fine and medium aerosols were found with an excess of NH_4^+ (NR > 1). The excess of NH_4^+ is most probably present in the form of NH_4Cl due to the neutralisation of HCl. Indeed, while the average NR values during winter were below unity, NH_3 was substantially neutralised by elevated HCl levels during summer (Table 2).

3.4. Chemical conversion of gaseous species

The extent of conversion from SO_2 to SO_4^{2-} and from NO_2 to NO_3^- can be given by the sulfur (Eqn. 4) and the nitrogen (Eqn. 5) oxidation ratios, respectively.

$$\mathrm{SOR} = \mathrm{S}_{\mathrm{NSSS}}/(\mathrm{S}_{\mathrm{NSSS}} + \mathrm{S}_{\mathrm{SO_2}}) \qquad (4)$$

$$\mathrm{NOR} = \mathrm{N}_{\mathrm{Nitrate}}/(\mathrm{N}_{\mathrm{Nitrate}} + \mathrm{N}_{\mathrm{NO_2}}) \qquad (5)$$

All units in Eqns. 4 and 5 are expressed in μg S m^{-3} and μg N m^{-3}, respectively. NOR values for total PM were calculated to be 0.54 ± 0.03 and 0.59 ± 0.07 on average for the winter and the summer season, respectively, with higher levels for the fine and medium fractions (Table 3). According to Ohta and Okita, SO_4^{2-} originates only from primary sources if the observed SOR values are < 0.1, while higher SOR values indicate the formation of SO_4^{2-} *via* photochemical oxidation of SO_2.[30] From Table 3, it is clear that SO_4^{2-} is substantially formed by photochemical oxidation, especially, in the smaller size fractions. Shaw and Rodhe developed a way to classify a monitoring site either as a source, or a receptor area on the base of SOR data.[34] They reported SOR between 0.05–0.35 and 0.15–0.49 in winter and 0.09–0.48 and 0.30–0.63 during summer, for source and receptor areas, respectively. In this study, the high SOR value (0.72 ±

Table 3 Weekly average sulfur/nitrogen oxidation ratios (SORs/NORs) for each PM size fraction and total PM (± standard error)

	SOR	NOR
Coarse[a]	0.14 ± 0.03	0.17 ± 0.04
Medium[a]	0.29 ± 0.06	0.31 ± 0.05
Fine[a]	0.40 ± 0.06	0.33 ± 0.04
Total PM[b]		
Winter–spring	0.72 ± 0.04	0.54 ± 0.03
Mid-summer	0.30 ± 0.06	0.59 ± 0.07

[a] Data averaged for the winter–spring and the mid-summer campaign ($n = 16$). [b] Seasonal data (winter–spring: $n = 8$, summer: $n = 8$).

0.04) for the winter–spring season suggests that the coastal sampling site acts as a receptor area, while according to the summer value (0.30 ± 0.06) the site could be classified as a source area. Increased domestic heating on the continent and the UK during winter could indeed increase the SO_4^{2-} content arriving at the site, resulting in high SOR values, while algal blooms during summer are paired with increased SO_2 levels (Table 1), thereby reducing the SOR values significantly (Table 3). Therefore, one may classify the sampling site as a combined source–receptor area, for its behaviour being dependent on the seasonal conditions.

3.5. Factor analysis

Factor analysis was performed on the size segregated major ionic species in order to classify them in groups of similarity. Since Mg^{2+} and Ca^{2+} are not actively involved in the major atmospheric processes, they were not taken into account. Major ionic species seemed to correspond to four major aerosol types (F1–F4), which together explained more than 80% of the total variation (Table 4). The elements belonging to the first factor (F1) were Na^+ and Cl^- of the coarse and medium aerosol fractions, as well as NO_3^-, NH_4^+, and SO_4^{2-} of the coarse fraction. This factor clearly represents aged sea-salt, *i.e.*, sea-salt that is transported over long distances, during which it reacts with gaseous species[12,35,36] and coagulates with secondary aerosols. F2 corresponded to NO_3^-, SO_4^{2-}, and NH_4^+ of the fine fraction, and K^+ of the fine and medium fraction. This factor represents freshly formed secondary and K^+ aerosols. The latter is probably emitted in the form of K_2CO_3 during the combustion of fossil fuels. F3 shows high loadings for sea-salt compounds, *i.e.* Na^+ and Cl^- of the fine fraction and K^+ of the coarse fraction, which are freshly formed at the coastal site. The last factor (F4) is highly loaded with NO_3^-, NH_4^+, and SO_4^{2-} in the medium fraction, and represents coagulated secondary continental aerosols. Summarising, one can group the major ionic species into 'local' or 'remote' aerosols, which are either coming from the North Sea/Atlantic Ocean or from the coast/continent. Freshly formed sea-salts (F3) and aged secondary aerosols from the continent (F4) had a relative constant contribution, representing only 10% and 7% of the total variability. On top of this pollution 'background', local anthropogenic emissions (21%) and the arrival of aged sea-salts (42%) determine the content of major ionic species at the Belgian coastal area (Table 2).

Table 4 Results of factor analysis for size segregated major ionic species in airborne particulate matter $(n = 81)$[a]

	Factor			
	1	2	3	4
Coarse				
NO_3^-	0.514[b]	0.510	0.325	0.395
NH_4^+	0.636[b]	−0.069	0.473	0.310
SO_4^{2-}	0.771[b]	0.069	0.541	0.234
Cl^-	0.905[b]	−0.08	0.268	−0.036
Na^+	0.789[b]	0.064	0.518	0.072
K^+	0.340	0.105	0.839[b]	0.002
Medium				
NO_3^-	0.108	0.339	0.094	0.878[b]
NH_4^+	−0.90	0.263	0.069	0.903[b]
SO_4^{2-}	0.207	0.216	0.102	0.865[b]
Cl^-	0.796[b]	0.127	0.000	−0.065
Na^+	0.890[b]	0.025	0.128	0.237
K^+	0.214	0.816[b]	0.120	0.081
Fine				
NO_3^-	−1.42	0.866[b]	0.069	0.262
NH_4^+	−0.96	0.837[b]	0.133	0.416
SO_4^{2-}	0.253	0.715[b]	0.143	0.503
Cl^-	−0.002	0.342	0.728[b]	−0.047
Na^+	0.069	0.349	0.781[b]	0.170
K^+	0.113	0.789[b]	0.344	0.106
% of variance	42.3	21.0	10.1	7.2
% cumulative	42.3	63.3	73.4	80.6

[a] Extraction method: principal component analysis; Rotation method: Varimax with Kaizer normalisation. [b] Highest loading.

4. Conclusions

BWTs are very useful for the classification of air pollutants and their daily variation. Secondary inorganic aerosols (NH_4^+, NO_3^-, and non-sea-salt SO_4^{2-}) were the most abundant under a continental influenced air with higher levels for the smallest size fraction, while marine air masses contained mainly sea-salt components and non-sea-salt SO_4^{2-} in the coarse and fine aerosol fraction, respectively.

Seasonal variations of ionic species were mainly caused by differences in meteorological conditions such as air temperature, humidity and wind speed, while the amount of non-sea-salt SO_4^{2-} was affected by the biogenic release of DMS. This compound was thought to be responsible for the elevated SO_2 levels during summer, which reacted with sea-salt Cl^- to form HCl. This process was found to have a profound influence on the composition and acidity of aerosols.

Factor analysis and calculated SOR data have shown that ionic species at the Belgian coastal area originated from both local and remote sources, *i.e.*, the site acted as either a source or a receptor area for atmospheric pollution.

Acknowledgements

The authors gratefully acknowledge the financial support of the Belgian Office for Scientific, Technical and Cultural Affairs (OSTC–EV/06/39A), the Hungarian Scientific Research Fund (OTKA–F67647, L. Bencs), and an EC grant within the Marie Curie program (HPMT-CT-2001-00310, A. Dirtu). They also thank the NOAA Air Resources Laboratory for the provision of the HYSPLIT model and the READY website. Special thanks go to Jan Van Loock (UA), André Cattrijsse and Frank Broecke (VLIZ) for their help in the sampling, and to Francisco Hernandez (VLIZ) for the supply of meteorological data.

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