

Measurement report : On the importance of nitrate for the number of Cloud Condensation Nuclei in stratocumulus in the North-Sea region

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Abstract. Anthropogenic aerosol particles serve as extra Cloud Condensation Nuclei (CCN), which increases the cloud droplet number concentration and thereby cloud properties. The influence of manmade aerosol is the highest in a clean
15 marine environment due to the limited number of natural CCN. Marine stratocumulus (SC) is the cloud type with the highest frequency of occurrence over the North Sea region. A general assumption is that sulphate particles govern the number of CCN. However, high levels of manmade nitrate in this region suggest a significant role for this component as well. This study is the first, according to the authors' knowledge, to experimentally assess the importance of nitrate on CCN. It was performed in a cloud chamber located at the seacoast in the Netherlands, in which the SC formation is simulated.
20 During a 6-week campaign in summer 2007 the number concentration and the size distribution of aerosol and CCN were assessed as well as the activated fraction of nitrate and sulphate in a number of submicron size classes. In a 9-day campaign in April 2009 the fraction of nitrate and sulphate activated as a detailed function of size was measured. Sorting the results as a function of wind-direction highlights two main marine situations: North-west and South-west air-flows. In air masses from the NW, sulphate was the dominant CCN-compound. In air masses coming from the SW, a similar result was found for air
25 arriving via the English Channel. When back-trajectories indicated that the air had passed over source areas in the UK or France/Belgium the impact of nitrate on CCN number concentration was as follows. Two situations applied: i) Nitrate prevailed in the larger CCN, but sulphate dominated the smaller and more numerous CCN (summer campaign); ii), nitrate was the dominant compound over the whole size range of the CCN (April campaign).
To generalise the observations in the short-duration campaigns, a longer-term monitoring study was conducted, in which the
30 ambient nitrate to sulphate ratio in two CCN size ranges (smaller than 150 and 150–250 nm) was monitored. In NW airflows the nitrate concentration was consistently negligible compared to that of sulphate. This was also the case for air masses arriving from the SW passing over the English Channel. In other air masses from the SW, travelling over polluted regions in

the UK or France/Belgium, nitrate was the most important compound in both CCN size range during winter / spring. This is consistent with what was observed in the April campaign. During summer, the nitrate to sulphate ratio in both CCN size range was, most of the time, close to zero, as in the summer campaign. This finding can be explained by the low stability of the semi-volatile nitrate, specifically in the smallest particle mode at the high temperatures of summer.

1 Introduction

Aerosol particles are well known to serve as cloud condensation nuclei (CCN). Extra CCN in the form of manmade aerosol particles modify clouds macro- and micro-properties. The full range of impacts of anthropogenic aerosol on clouds and its effect on climate, known as the Aerosol Cloud Interaction effects, is described in chapter 7 of the IPCC-AR5 report of WG1 Boucher et al., (2013) and by Carslaw et al. (2013). To date, this is the most uncertain of all climate effects exerted by manmade aerosols.

Stratocumulus (SC) is the most common (Wood, 2012) and the most frequent cloud type over the North Sea region. Together with stratus, it covers the North Sea nearly 50% of the time (Duynderke, 1988). SC generally forms at the top of the planetary boundary layer and is therefore a low altitude cloud in the form of a field. SC has imbedded patches of thicker clouds caused by convection/turbulence distinguishing it in this way from the more stable stratus. Within a stratocumulus field, different upward velocities coexist leading to a large range of supersaturations (up to 0.3%). The cloud chamber, previously described by Khlystov et al. (1996a), simulates these environmental conditions very well (see section S1 of the Supplementary Material).

Since the number concentration of natural cloud condensation nuclei (CCN) is low in marine stratocumulus, an increase of additional anthropogenic CCN makes a significant difference. Moreover, due to the limited atmospheric lifetime of aerosol, the aerosol/cloud interactions are a regionalised phenomenon. This effect should, therefore, be especially prominent in coastal marine regions with nearby anthropogenic aerosol sources, like the North Sea. As SC forms within the boundary layer, SCs are effectively influenced by manmade aerosols. Assuming a well mixed boundary layer, aerosol particles serving as CCN at the top of the boundary layer are the same as those observed at ground-level within the cloud chamber.

In literature, anthropogenic sulphate is considered to be the main component of cloud condensation nuclei (Boucher et al., 2013). However, the anthropogenic sulphate concentration is rapidly declining in the North-Sea region (Tørseth et al., 2012). Therefore, the importance of the regional Aerosol Cloud Interaction (ACI) rapidly decreases according to models (e.g., Bellouin et al., 2011). Tørseth et al. (2012) noticed that the concentration of nitrate in the region is of a similar magnitude as that of sulphate. Based on these data Bellouin et al. (2011) estimated that nitrate is an important CCN-compound and could become the dominant one in the course of this century. However, actual measurements in SC over the North Sea, by Crumeyrolle et al. (2013), show a very low ratio of submicron nitrate to sulphate. Another issue is that in modelling it is

assumed that nitrate and sulphate have the same size distribution (Bellouin et al., 2011; Li et al., 2009, Wang et al., 2014).
65 This assumption is not based on actual observations. The aim of the present experimental study is to obtain data on the actual composition of the CCN especially with respect to the contribution of nitrate in SC.
The study was performed in a cloud chamber, located on the coast of the North Sea in the Netherlands. In this chamber, the atmospheric conditions are controlled so that the typical microstructure of marine stratocumulus is simulated as assessed by Khlystov (1998) who determined in detail the size-distribution of the CCN. The chemical composition was not assessed; or
70 rather some data on the chemical composition of the aerosol, as a crude function of aerosol size, were collected using cascade impactors. The results indicated that for NW-air masses the nitrate concentration in the aerosol size range corresponding to the majority of the CCN (particles less than 300 nm) was small relative to that of sulphate. However, for two spells with air arriving from the SW, the nitrate concentration below 300 nm was close to those of sulphate, suggesting a possible equivalent role as CCN-compound.
75 An issue with the above measurements is that classical impactor measurements underestimate the concentration of small nitrate due to evaporative losses. For that reason in the present study artefact-free instrumentation was used to measure the nitrate fraction. The same cloud chamber was used to identify the CCN particle size range and to determine the activated fraction of nitrate and sulphate as a function of size. The importance of nitrate in the CCN size range and in marine air was further evaluated using long-term measurements of nitrate to sulphate ratio in ambient aerosol. The CCN size range was
80 based on the results in the intensive campaigns in the cloud chamber.

2. Experimental

The cloud chamber was operated during two intensive campaigns to assess the role of nitrate in regulating the number of CCN in stratocumulus. These two campaigns took place in summer 2007 (3 weeks) and April 2009 (9-days). Both campaigns were dedicated to better understand the chemical and physical properties of the cloud condensation nuclei. To
85 achieve this goal, ambient air is sucked throughout the instrumental system using a three steps method:
- First, the physical (total concentration and size distribution) and chemical properties of ambient aerosols are characterized.
- Then ambient air is guided into the cloud chamber, where environmental conditions are controlled (see section 2.1), to characterise Cloud Droplet (CD) physical properties, such as the concentration and the size distribution.
- Finally, droplets are removed and only interstitial aerosols remain in the airflow. These aerosols are then going though the
90 same instrument used at the first step to measure their physical and chemical properties
During the 2007 summer campaign, the ionic compositions of ambient and interstitial aerosols were monitored in three size bins with a “MARGA-sizer”. During the second campaign an Aerosol Mass spectrometer (AMS) providing the detailed size-distribution of the components relevant as CCN-compound. Unfortunately, data post-processing showed that aerosol sizing and the cloud droplet monitor had malfunctioned during the second campaign. Results from this campaign are therefore
95 more qualitative.

In between these two intensive campaigns, long-term monitoring of the nitrate and sulphate concentrations in the size range in which most of the CCN were observed in the campaigns (150-250nm) occurred in 2008 at the monitoring site for aerosol of CESAR in Cabauw, 90 km south of the site of the cloud chamber. The sodium concentration, measured with a classical MARGA, was used as tracer for seasalt to assess that air masses were of a marine origin.

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2.1 Cloud chamber and physical instrumentation

The cloud chamber, located in Petten (Figure 1), used in the study was described in detail by Khlystov (1998) and the flow scheme is described in Section 1 of the Supplementary Material. The chamber volume is 21 m³ and air is vented through the chamber at a flow rate of 0.5 m³ s⁻¹. The air is humidified and warmed in a humidifier at the entrance channel. The air then arrives in the cloud chamber where it cools due to contact with the cooler walls, which leads to super-saturation; the excess water condenses on particles whose size and composition allows them to serve as cloud nuclei. The air leaves the chamber via a measuring tunnel/channel in which the number concentrations and the size distribution of droplets, formed in the chamber, are measured. The Liquid Water Content (LWC) of the cloud was monitored with a LWC meter (PVM100). During the intensive period, the number concentration and size of the droplets were determined with an FSSP probe also used by Khlystov et al. (1996b).

Part of the exhaust air is withdrawn through a cyclone in which the droplets are removed while non-activated aerosols (i.e. interstitial aerosol) remain in the air-flow. The air is subsequently dried by mixing in with dry particle-free air to remove water taken up by interstitial aerosols in the chamber. The size spectra of ambient (entrance of the chamber, site B as depicted in fig. S1 with the filter removed) and interstitial (exit of the chamber) aerosol were determined with two identical SMPS (a combination of a TSI-DMA 3071 and a TSI CN-counter 3020). The difference between both measurements is representative of the CCN spectrum. Moreover, a LAS-X (PMS Inc.) optical particle counter was installed at the entrance to measure the complete size distribution of aerosol particles in the size range between 100 nm to 5 µm.

The efficiency of the cloud chamber to reproduce representative CDNC was tested during a specific day involving aircraft measurements over the site. The CDNC observed in the chamber were similar to those observed in the actual marine stratocumulus (Khlystov et al., 1999; Khlystov, 1998) at the standard setting of the chamber as discussed in section S1.

To assess the aerosol loss in the chamber, it was operated close to saturated humidity conditions (100% RH) for an extended period of time, see below. During this test, the observations showed similar concentrations and size distributions of sulphate and nitrate at the chamber entrance (ambient aerosols) and exit (interstitial aerosols).

2.2 Chemical composition measurements

A MARGA-sizer and an Aerosol Mass Spectrometer (AMS), described in the respective subsections below, were used during the first and second campaign respectively. During each campaign, only one instrument was available to measure

ambient and interstitial aerosol chemical composition. Therefore, a 2-way valve was used to alternatingly sample ambient and interstitial aerosols.

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2.2.1 MARGA-sizer

The MARGA-sizer has been described in detail before (ten Brink et al., 2007; ten Brink et al., 2009) and only some aspects relevant for the present study will be presented here. A measuring cycle, including two blanks, takes two hours. In this instrument, aerosols are separated into size fractions. The aerodynamic cut-off sizes of the impactors correspond to the following approximate mobility diameters: 0.15, 0.25 and 0.45 μm . A classical MARGA, with a size-cut at 10 μm , measured the concentration of coarse Na as a tracer for sea-salt. The performance of the MARGA-sizer was checked prior and after the campaign of 2007 and it was found that a fraction (about 7%) of the particles with a size larger than the cut-off diameter pass through the 150nm impactor. This interference is an issue due to low mass concentration in this bin and the issue was fixed after this campaign. The implications will be addressed in section 3.1.

The detection limit for nitrate was 15 ng m^{-3} ; respectively 30 ng m^{-3} for sulphate, chloride and sodium. The uncertainty associated with the difference in concentration at entrance and exit, defining the concentration of the components in the interstitial aerosol, was hence 20 ng m^{-3} for nitrate and 40 ng m^{-3} for the other ions.

During the 2008 monitoring campaign there were two additional impactor lines with cut-off sizes at 1 and 2 μm aerodynamic diameter. The detection limit, governed by variations in the blank, differed from batch to batch of the eluent of the chromatograph, as was observed in earlier monitoring (ten Brink et al., 2009). Therefore, the detection limit differs from period to period as further discussed in the section 3 on the monitoring.

Since only one MARGA-sizer unit exists, the interstitial aerosol chemical composition was measured two hours after the ambient aerosol chemical composition. Therefore, to compare ambient and interstitial aerosol composition, we used periods for which the aerosol characteristics were rather stable over a four-hour period. This was based on low variations of mass/volume as derived from the size-distribution of SMPS and LAS-X

A classical MARGA, with a size-cut at 10 μm , measured the concentration of coarse Na in ambient air as a tracer for sea-salt, in the chamber study of April 2009 and in the monitoring campaign of 2008.

2.2.2 AMS

The chemical characterization of non-refractory submicron particles (NR-PM₁), that is to say material vaporizing around 600°C under close-to-vacuum conditions, was performed on-line by an AMS (Aerodyne Research Inc.) during the 2009 campaign. A full description of the instrument used is given in Mensah et al. (2012). Mass concentrations of nitrate, sulphate, ammonium, chloride and organics are obtained with a detection limit of approximately 0.08 $\mu\text{g m}^{-3}$. The switching

frequency of the AMS between ambient and interstitial aerosol measurements was about 4 minutes. Almost simultaneous
160 compositional spectra were obtained for ambient and interstitial aerosols.

3. Results and discussion

165 In this section, results from both intensive campaigns will be explored to better understand the role of nitrate as cloud
condensation nuclei in comparison to sulphate. These results will then be compared to results from long-term monitoring
measurements of ambient aerosol in order to generalize the observations.

3.1 Summer 2007 campaign

The summer campaign was conducted at the end of July and the first half of August. Figure 2 shows the time series of the
170 main parameters: sulphate and nitrate (with a diameter smaller than 450 nm) concentrations, wind direction and number
concentrations of aerosol particles with a diameter larger than 100 nm (N_{100}). Generally, the nitrate concentration has a
higher variability than that of sulphate. Moreover, there were relatively long periods during which the nitrate concentration
in ambient air was at or below its detection limit of 15 ng m^{-3} . The sulphate concentration has a lesser variability and was
consistently well above the lower detection limit.

175 The wind directions (Figure 2b) were measured at a nearby airfield (KNMI, 2007) and coupled to multiday HYSPLIT back-
trajectories in order to determine the air mass origin. N_{100} is used as an indicator of the air mass degree of pollution. As an
example, one can see (Figure 2b and c) that air masses coming from the NW are associated with a low value of N_{100} , while in
air coming more from the SW N_{100} can be twenty times higher while the CDNC varies by a factor of two over time. In the
following section, we distinguish two types of air mass origin (clean: NW and polluted: SW).

180 3.1.1 Clean (NW) air masses

Two periods were highlighted (green area) with air masses coming from NW and high cloud coverage, around 6 on average
(Figure 3b), corresponding to the last days of July and 8-11 August. During these periods, the nitrate concentration was at or
close to the detection limit of 20 ng m^{-3} while the sulphate concentration was significantly higher and reached $1 \text{ } \mu\text{g m}^{-3}$. Such
concentrations were generally observed in the chamber prior to the intensive campaign and within actual stratocumulus
185 observed over the North-Sea (Crumeyroffe et al., 2013).

The CDNC in NW air masses varied between a minimum of 175 cm^{-3} on 29 and 30 July, associated with a minimum of N_{100}
of less than 200 cm^{-3} , to $250\text{-}300 \text{ cm}^{-3}$ on 8-11 August as can be seen in Figure 3a. Due to the low number concentration,

190 ambient and interstitial aerosol size distributions were averaged over the period from 29 to 30 July during which the CDNC was less than 200 cm^{-3} (Figure 2a). The resulting average spectra are shown in Figure 4a. By subtraction the size distribution of the CCN is obtained as depicted in Figure 4b. One can note that the smallest bins of the CCN spectra are rather uncertain due to the subtraction of two large values. The CCN size distribution is mono-modal with a broad maximum centred at 120 nm. The total CCN number concentration (180 cm^{-3}) is in good agreement with the CDNC observed during the same period. It should be mentioned that some ambient particles larger than 450 nm, and then possibly acting as CCN, were observed (3 cm^{-3}). Similar CCN spectra were measured for NW air masses at other periods but with higher total concentrations.

195 3.1.2 Polluted (SW) air masses

In SW air masses (grey areas) the concentration of nitrate is highly variable. On 27, 28 and 29 July and 15 August it was at or close to the detection limit, while, from July 31st to August 2nd, the nitrate concentration became measurable and reached a peak of $3.5 \text{ }\mu\text{g}/\text{m}^3$. This high variability could be explained by the air mass trajectory. Indeed, HYSPLIT 72-hr back-trajectories highlight two different paths: (i) over the English Channel corresponding to low nitrate concentrations and (ii) 200 over the Southern part of the UK or western France/Belgium associated with high nitrate concentrations.

Focusing on the July 31st to August 2nd period, nitrate and sulphate concentrations of ambient and interstitial aerosols are shown in Figure 5a in three size ranges: less than 150, 150-250, 250-450 nm. The interstitial nitrate concentration was at the detection limit of 20 ng m^{-3} for the whole period. This implies that virtually all (95% at least, depending on the size range of interest) nitrate is taken up in the cloud droplets. In contrast, sulphate is present in significant amounts ($0.2 \text{ }\mu\text{g m}^{-3}$) in the 205 interstitial aerosol in all three size classes (Figure 5b).

The ambient and interstitial aerosol spectra, averaged over the night of 1-2 August, are presented in Figure 6. From the difference of both size distributions, one obtains the CCN spectra (Figure 6b) and, once again, the uncertainties associated with the first bins of the CCN size distribution are high. The CCN size distribution has a rather sharp maximum around a diameter of 170 nm. The combination of ambient aerosol and CCN size spectra allowed us to calculate the aerosol activated 210 fraction shown in Figure 5c. Particles with a diameter between 250 and 450 nm essentially all serve as CCN. In this size range, the CCN comprised about 20% of the total number. The percentage of CCN in which nitrate or sulphate is the prevalent component was assessed via a combination of data as presented in Figure 5 and Figure 6.

In the size-range of 250-450 nm The CCN contain on average $2 \text{ }\mu\text{g m}^{-3}$ of nitrate while interstitial nitrate concentration, within the CCN size range, was at the detection limit of 20 ng m^{-3} . This result implies that close to 98% of nitrate 215 concentration is activated while at most 2% of the nitrate is not activated. The ambient sulphate concentration in this fraction is $0.5 \text{ }\mu\text{g m}^{-3}$, which is small in comparison to the nitrate concentration (Figure 5b). Therefore, nitrate is a main compound of the CCN in the size range 250 - 450 nm.

For aerosols smaller than 250 nm, at least 95% of the nitrate is taken up in the cloud droplets as deduced from the nitrate concentration of ambient and interstitial aerosols. Assuming nitrate and sulphate both behave similarly as CCN, the large 220 fraction of activated nitrate implies that it must be within a size range for which the activated fraction is high corresponding

to the 200-250 nm bin. Sulphate, in contrast, is only partly activated (about 30%) and may be within smaller (150-200 nm bin) particles that do not fully activate. The interval 150-250 nm corresponds to 45% of the total CCN number concentration of which two third (~70%) is in the smaller particles (150-200 nm) dominated by sulphate.

225 During the second period with quite persistent SW winds (14 August), the nitrate and sulphate fractions were similar but the concentrations were lower which makes evaluation of the percentages activated more uncertain but indicative of about equal contributions of nitrate and sulphate in the larger CCN ($D > 200$ nm).

3.2. April 2009 campaign

The campaign organised in the early half of April 2009 lasted for two weeks. The cloud chamber was operated on 9 days in that period. The physical probes did not operate properly and therefore only information on the size distributions of ambient and interstitial aerosol from the AMS measurement are available (section S2 of the Supplementary Material) with the MARGA-sizer measuring only the ambient aerosol. In addition the hourly Na concentration in PM10 served as a proxy for the marine character of aerosol and air mass. Figure 7 shows the time evolution of the concentration of nitrate in the submicron fraction, together with the Na concentration for the period that the cloud chamber was in operation. The data relevant for the present study are discussed below.

235 On April 5th nitrate concentrations were at the detection limit for most of the day (Figure 7a) and sulphate was at its lowest in the evening, with a concentration lower than during the 2007 campaign. In the evening of April 7th and 8th, high sodium concentrations evidenced a strong marine influence associated with an absence of measurable nitrate. According to the local wind-direction (Figure 7b), air masses were from the SW and more precisely from the English Channel according to the HYSPLIT back-trajectories.

240 On April 4th, a quite persistent episode occurred with a large concentration of submicron nitrate and a lower concentration of submicron sulphate. Air masses were from a SW direction and associated with the presence of seasalt (Figure 7a). Satellite images show a low cloud field in the region, extending from the Gulf of Biscay to the North Sea, also covering the Netherlands (fig. S5). On this day, 85% of the submicron nitrate was activated in comparison to the close to 100% during the summer campaign of 2007. The inactivated (15%) nitrate was in particles that were too small to serve as CCN (as deducible from Figure 8). The activated fraction of sulphate as a function of size was virtually identical to that of nitrate due to a fully similar distribution. This is exemplified in fig. S6 for the 2-day period (April 2^d -3^d) with low cloud fields over the North Sea (section S2.2).

250 With nitrate concentrations higher than sulphate over the full size range, nitrate must be the more abundant CCN-compound, even though we do not have the size distribution of the CCN. The finding that nitrate prevails over sulphate as CCN-compound is different from the situation in summer 2007 when the nitrate was preferentially present in the larger, less numerous, CCN in SW air masses passing over source areas of nitrate. This difference might be due to the volatile nature of the nitrate and the lesser stability of the smallest particles at the higher temperatures in summer. This issue is the specific subject of the investigation in the next section.

255 3.3 Seasonal difference in the importance of nitrate to sulphate as CCN-compound

For practical reasons, the large cloud chamber and the variety of instrumentation could only be operated during short intensive campaigns. To generalise the findings in the campaigns and especially to assess the importance of nitrate as CCN-compound in summer versus other seasons in the year we undertook long-term monitoring of the ambient nitrate to sulphate ratio in the CCN size range (100-250nm). The MARGA-sizer was deployed at the central monitoring site in the Netherlands, known as CESAR at Cabauw, in the year 2008, thus in-between the two campaigns of section 3.1 and 3.2. The relevant CCN size-range, i.e., the range in which the majority of the CCN reside is that of 100-250 nm, see Figure 4 and Figure 6. This range corresponds to two MARGA-sizer channels, previously mentioned: $D_p < 150$ nm and $150 < D_p < 250$ nm.

We briefly illustrate the approach to evaluate the results of the long-term monitoring with data from the cloud-chamber campaign of April 2009. The detailed size-dependent and time-dependent compositional data from the AMS can thereby serve as a reference. The PM10 sodium (Na) concentration was used as tracer for the marine origin of the air, as discussed in section 3.2. We present here the nitrate to sulphate ratio in the size range of 150-250 nm ($N/S_{150-250nm}$) in Figure 9a, together with the averaged 2hourly wind-direction in Figure 9b. One can see that only in some occasions the concentration of sodium is substantial and in those cases the $N/S_{150-250nm}$ ratio is near zero for winds from the NW, except for quite an extended period of April 12th to 13th. Then, a high $N/S_{150-250nm}$ ratio occurred in combination with a very large submicron nitrate concentration as compared to that in any situation during the two campaigns with NW-winds. This is due to a trajectory shift bringing continental air via a southbound curve over the North Sea back onto the continent (see section S2.3 for more details). This example served as a warning to check wind-direction with the associated back-trajectory.

The results of the longer-term monitoring, which took place at the CESAR observatory at Cabauw in the centre of the Netherlands, are presented in the Supplementary Material, section S3. We here evaluate the data, similar to the evaluation of the data in the summer campaign, thus according to wind-direction, respectively “NW” and “SW”.

3.3.1 Clean (NW) air masses

As observed during the intensive campaigns, NW air masses were almost always associated with high sodium concentrations and submicron nitrate concentrations at the detection limit. Submicron sulphate concentrations were 100 ng m^{-3} and higher, consistent with this finding submicron-nitrate was at the detection limit when winds were coming from the NW, as measured with an ACSM (Schlag, 2014), in a year-long monitoring project at the same measuring site of CESAR in Cabauw.

3.3.2 Polluted (SW) air masses

285 For air masses from the SW, two situations could be discerned according to back trajectory path (over the English Channel /
source regions), like during both intensive campaigns. Absence of measurable submicron nitrate occurred when the air
arrived via the direction of the English Channel. In case the air had travelled over the southern UK or western
France/Belgium there was a substantial concentration of nitrate. To sort the data, the following criteria were selected: (i) a
total nitrate concentration larger than 150 ng m^{-3} , (ii) sodium concentrations larger than twice the detection limit ($100 \text{ ng } \mu\text{g}$
290 m^{-3}). In this way a total of close to 600 points, corresponding to 2hr-data per point, were left for summer (150 points) and
winter (450 points). The marine origin of the air mass of each data-point entry was then visually checked via the respective
back-trajectory for that point.

Note: the criterion of a concentration of submicron nitrate larger than 150 ng m^{-3} meant that the average concentration of
nitrate in the “CCN” range for the relevant situations could be well above the detection limit of 15 ng m^{-3} .

295 For periods for which the conditions described in the previous paragraph were fulfilled, we evaluated the data for winter /
early spring (December/January/February/March) and summer (June/July/August) as separate categories. This is done in
order to highlight the seasonal difference in the ratio. The following was found with respect to the seasonality.

In winter, both $N/S_{Dp<150\text{nm}}$ and $N/S_{150-250\text{nm}}$ varied from 1 to 5, with an average value close to 3 clearly showing the
importance of manmade nitrate as CCN-compound in polluted air masses. In summer, for almost all events, $N/S_{Dp<150\text{nm}}$ was
300 close to zero, while only in a few (4 data point of 2hrs) occasions $N/S_{Dp<150\text{nm}}$ reached 2. It should be noted that $N/S_{150-250\text{nm}}$,
on average, was 0.4. Such low ratios were also observed during the summer campaign of 2007 (section 3.1) and can be
qualitatively understood from the semi-volatile nature of the nitrate. The stability of (ammonium) nitrate is limited when
ambient temperatures are larger than $20 \text{ }^\circ\text{C}$ (aan de Brugh et al., 2012). The lower concentration of nitrate in the smallest
diameter range can be explained by the preferential evaporation of nitrate from small particles. During spring (April/May),
305 the average $N/S_{Dp<150\text{nm}}$ as well as $N/S_{150-250\text{nm}}$ was just over 2.

We can summarise the results as follows. Most of the time (winter and spring) nitrate prevails over sulphate in the CCN.
This seasonal behaviour needs to be modelled to further explore the impact of nitrate on the cloud properties in the North
Sea region. An example of such a modelling study is that of Chen et al. (2016) made for the region, but for one particular
day only.

310 Finally we like to mention that stratus is the more common cloud type in SW airflows. Values and spread of the super-
saturation (0.05 to 0.1 %) in stratus are less than in SC (up to 0.3 %) and thus also lower than those in the cloud chamber. It
implies that preferentially the larger particles within the CCN size range (150 – 250nm) act as CCN and those particles
contain relatively more nitrate.

4. Conclusions

315 Based on the present measurements, the role of nitrate versus sulphate as CCN (Cloud Condensation Nuclei) and associated
CDNC (Cloud Droplet Number Concentration) in the regional stratocumulus was evaluated. The experiments occurred in a
cloud chamber, mimicking the supersaturation conditions within stratocumulus that allows measuring the concentration and
the chemical composition of ambient and interstitial aerosols and by difference the CCN concentration and chemical
composition.

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Two marine air flows could be discerned with respect to the composition of ambient aerosol and CCN: (i) North-West that
are characterized by a low aerosol concentration (N_{100}) and therefore called ‘clean’ air masses and (ii) South-West, passing
over European countries and characterized by high total aerosol concentration and then called “polluted” air masses.
Sometimes, under Southwest flows, the aerosol concentration was low due to the passage of the air mass over the English
325 Channel thereby avoiding polluted areas. These latter specific cases were sorted using HYSPLIT back trajectories.

In clean air masses (NW), the total ambient nitrate concentrations were always lower than the detection limit. In contrast, the
total ambient sulphate concentration was significantly in excess in comparison to its detection limit. In polluted air masses,
SW flows and travelling over aerosol sources, nitrate was a significant compound of the ambient aerosol as well as the CCN.
330 For air masses passing over the English Channel, ambient aerosol chemical composition is similar to those in clean air
masses. These results were confirmed using long-term (6 months) measurements at Cabauw site in 2008 and consistent with
those of Schlag et al. (2014) using ACSM measurements at the same site.

The CCN size range was estimated in the cloud chamber to be between 100 and 250 nm. The CCN sulphate and nitrate
335 concentrations were determined and the nitrate to sulphate ratio in this size range was used to evaluate the importance of the
nitrate vs. sulphate within polluted air masses. The results from both intensive campaigns (9-day campaign in April 2009 and
6-week summer campaign in 2007) are quite different. During the summer campaign, the activated fraction of nitrate was
virtually 100 % proving its high hygroscopicity. However, nitrate was only found in the larger particles (250-450nm) which
are the less numerous. Therefore, the main CCN compound in term of number concentration was clearly sulphate. During
340 the April campaign, nitrate was the main compound of the aerosol over the full size range. Therefore, nitrate was, this time,
dominating the CCN by a factor of two in comparison to sulphate. Concentrations of organics were less than those of nitrate
and moreover only 70% was activated, implying that organics had a limited role as CCN.

Long-term observations allowed us to calculate the nitrate to sulphate ratio within the CCN size range (100-250nm). The
345 observation highlights a seasonal trend of this ratio for marine aerosol striking over the polluted regions of Southern England
or the western part of the European continent. The average Nitrate/Sulphate ratio in the CCN size range was close to 3 in

winter, around 2 in spring and close to 0 during summer. The low values during summer could be explained by the instability of the semi-volatile nitrate at the elevated temperatures occurring during this season in combination with preferential evaporation of nitrate from the smallest particles. Therefore, in the CCN size range the nitrate is often close to the detection limit and nitrate then plays a minor role as a CCN in summer, even when marine air mass pass over polluted regions before arriving to the North-Sea region.

With the projected rapid decrease in the regional sulphate levels, nitrate will become a more dominant CCN-compound in “polluted” marine air in the moderate / cold seasons, which should be taken into account in modelling studies. We noticed that in winter/spring the size distribution of nitrate was highly comparable to that of sulphate which would simplify model calculations. The present data-set would be a good basis for modelling efforts on the role of nitrate in marine SC in our region.

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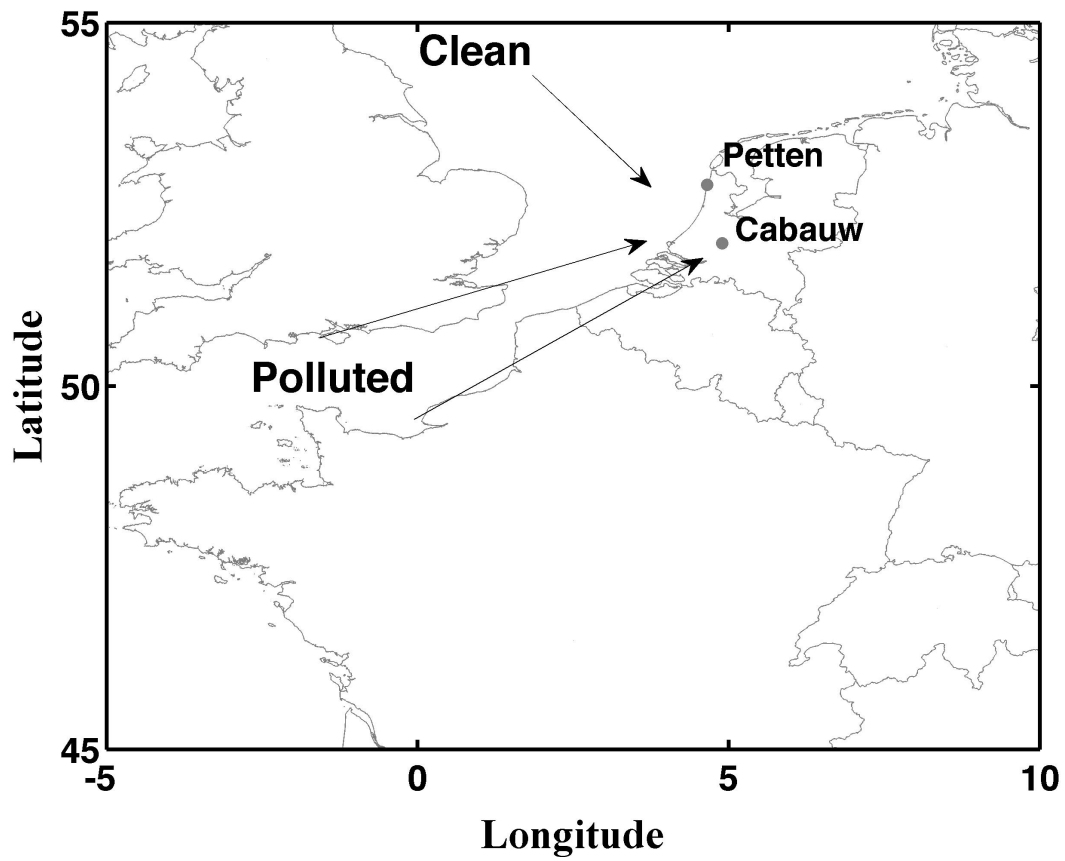


Figure 1 Petten and Cabauw locations as well as the main air mass flows reaching Petten (NW : clean air masses and SW : Polluted air masses)

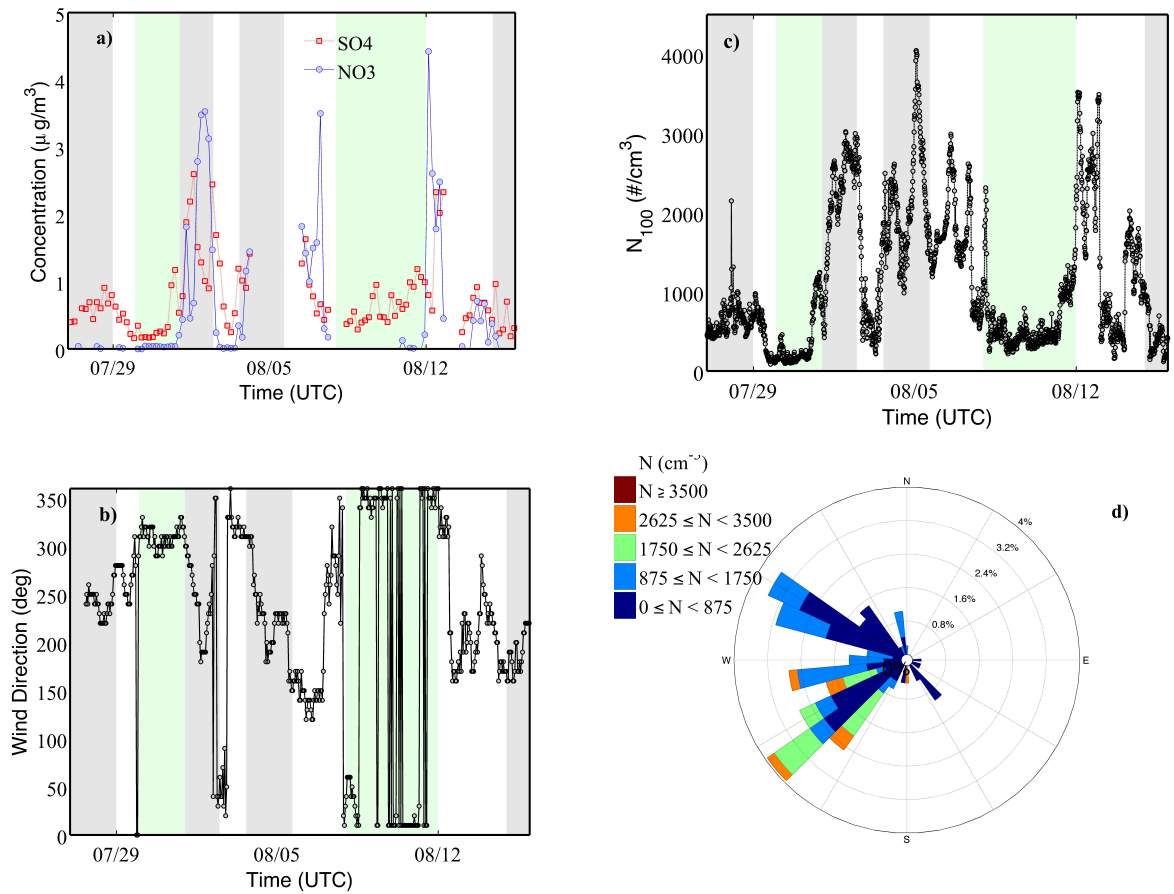


Figure 2: Total concentration of nitrate and sulphate (a), wind direction (b, in degrees) and the total number concentration of particles with a diameter larger than 100 nm (c, N_{100}) observed during the summer campaign in 2007. The grey and green areas corresponds to air masses coming from South west (North West) and considered as polluted and clean air masses, respectively. Wind rose of the relationship between aerosol number concentration and wind direction (d).

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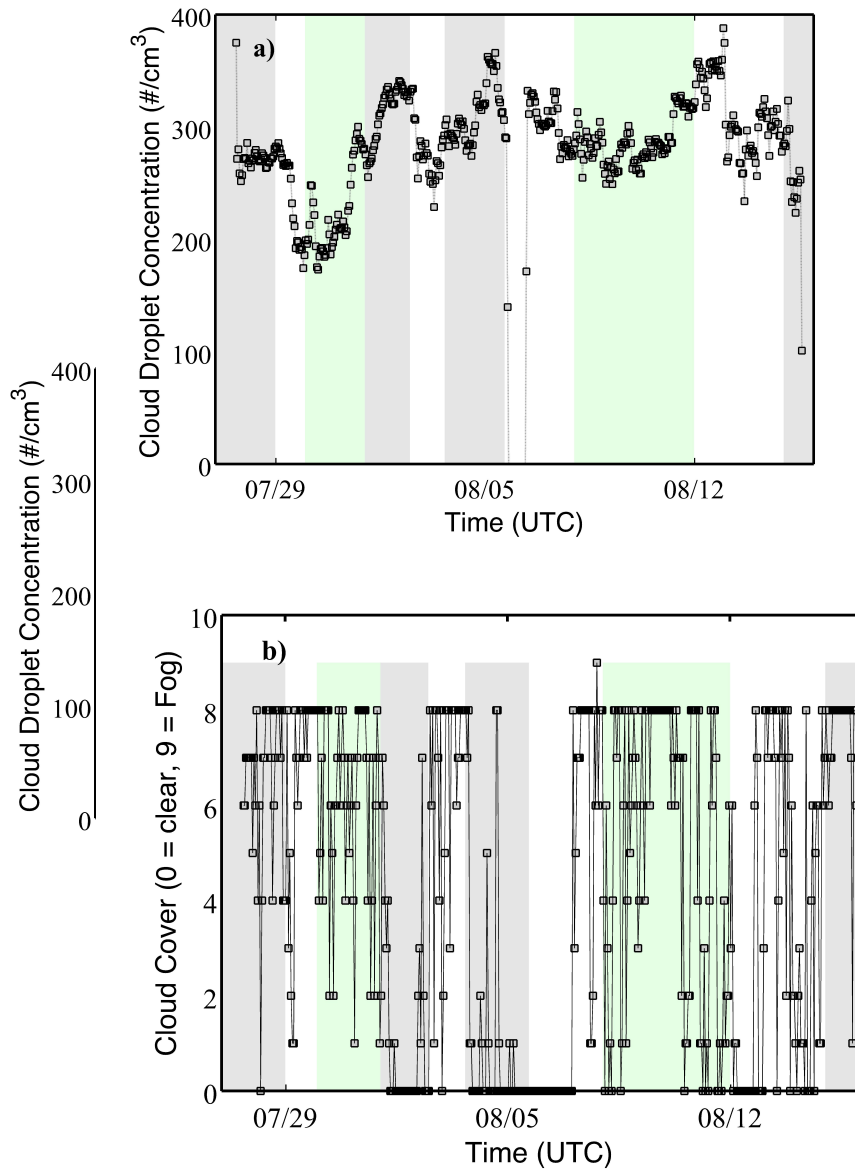


Figure 3 : Number concentration of cloud droplets and cloud cover in octants in the same period as in Figure 2. 0 octants corresponds to a clear sky and 9 to a fog situation. The data gap from 6-7 August correspond to a cloud chamber cleaning period.

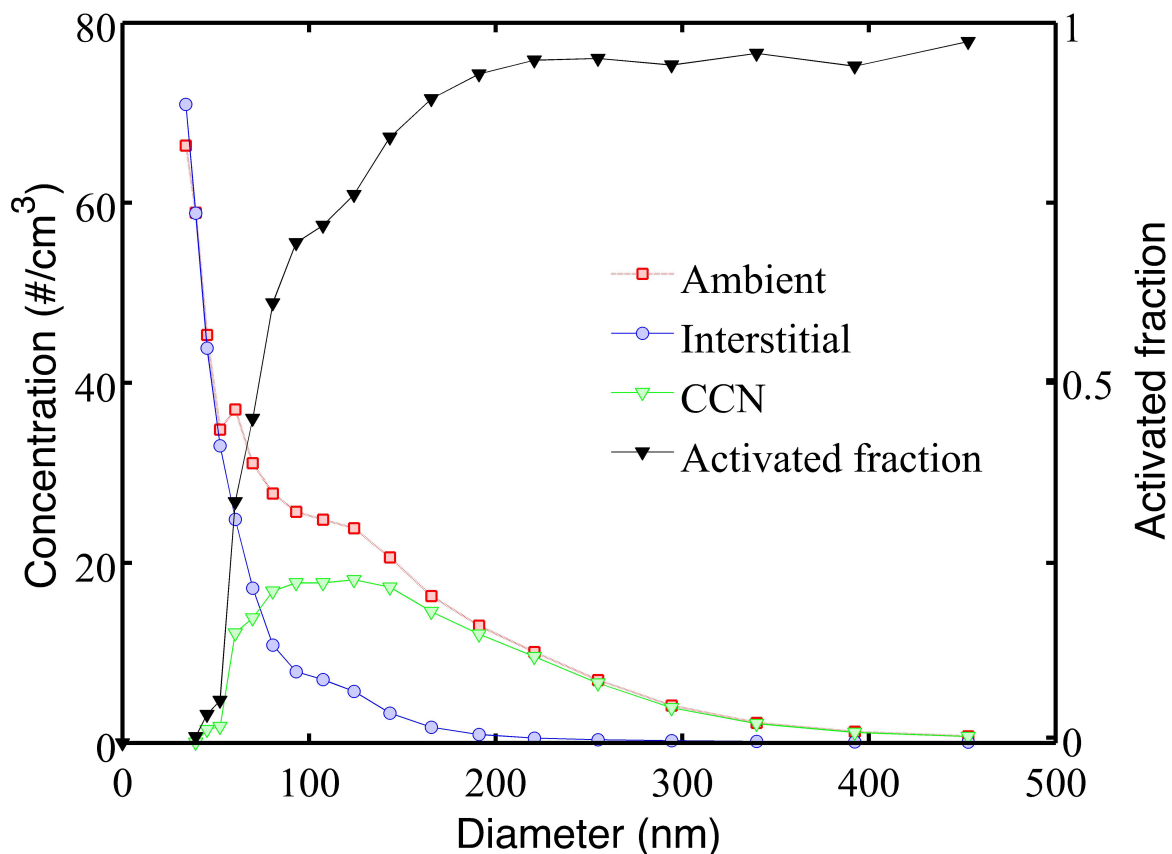


Figure 4: Average aerosol size distribution of ambient (red colour) and interstitial (blue colour) aerosols observed within north-west (clean) air masses and averaged from 29 to 31 July 2007. The CCN SD (green colour) was estimated by difference between ambient and interstitial SD. The total cloud number concentration was less than 200 cm^{-3} , see Figure 3a. The number concentration per logarithmic size-interval is represented by the dot at the midpoint of the interval. The concentrations in the size bins smaller than 40 nm are off-scale

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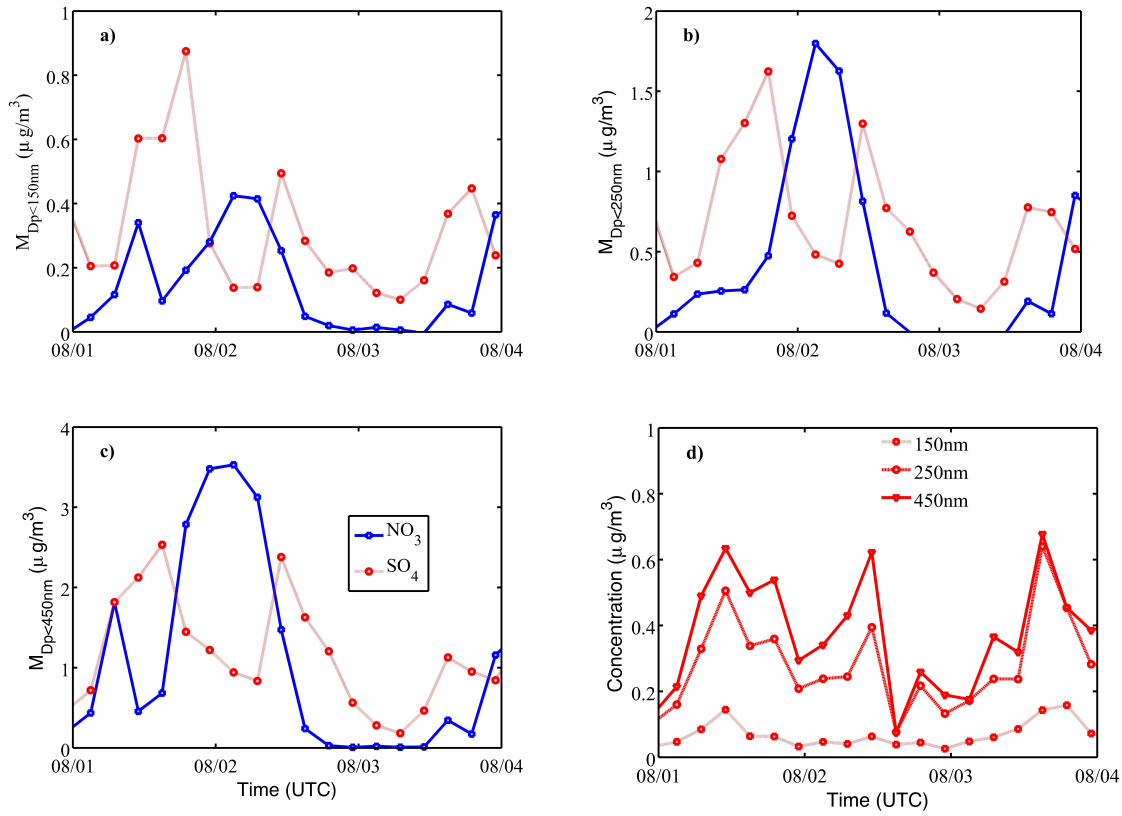


Figure 5: Evolution of the ambient mass concentrations of nitrate and sulphate with a diameter smaller than 150nm (a), 150-250nm (b), 250-450nm (c) in August 2007. The interstitial mass concentration of sulphate is given for all fractions as a function of time (d). The nitrate concentration in the interstitial aerosol is at the detection limit for the interstitial aerosol for all size classes.

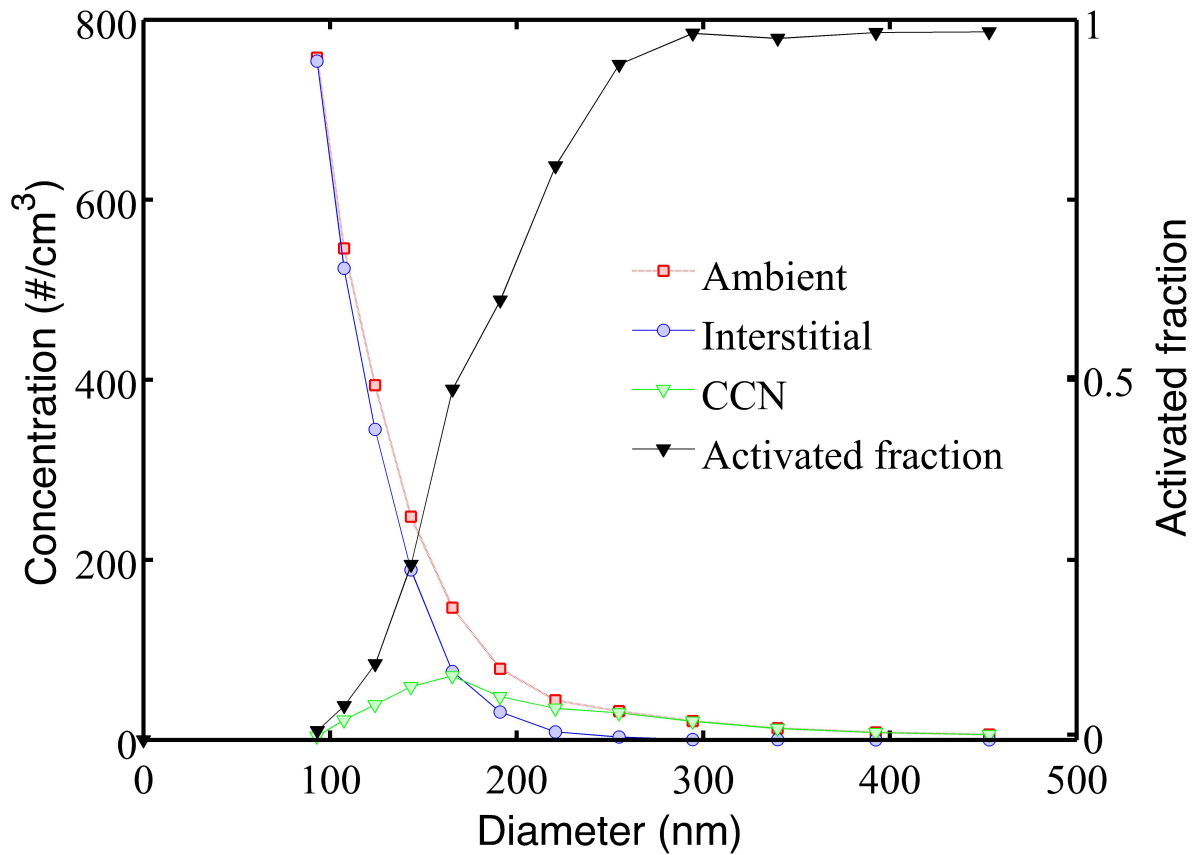


Figure 6 Average size distributions of ambient (red colour) and interstitial (blue colour) aerosol over the period 17:00 - 11:00 on 1-2 August, 2007. The number concentration per size-interval is represented by the dot at the midpoint of the interval. For clarity the high number concentrations of particles smaller than 90 nm are not shown. Difference between ambient and interstitial aerosol spectra is denoting the spectrum of the CCN (green color). Fraction of particles activated as a function of size over the same period.

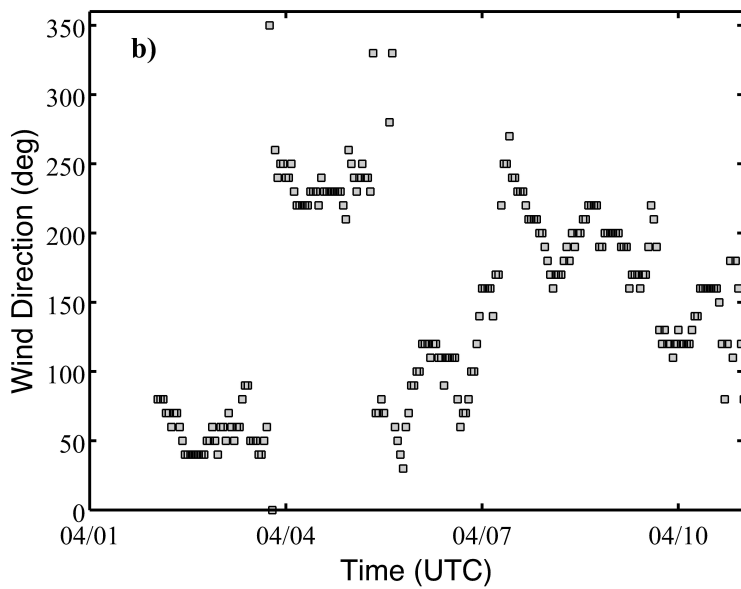
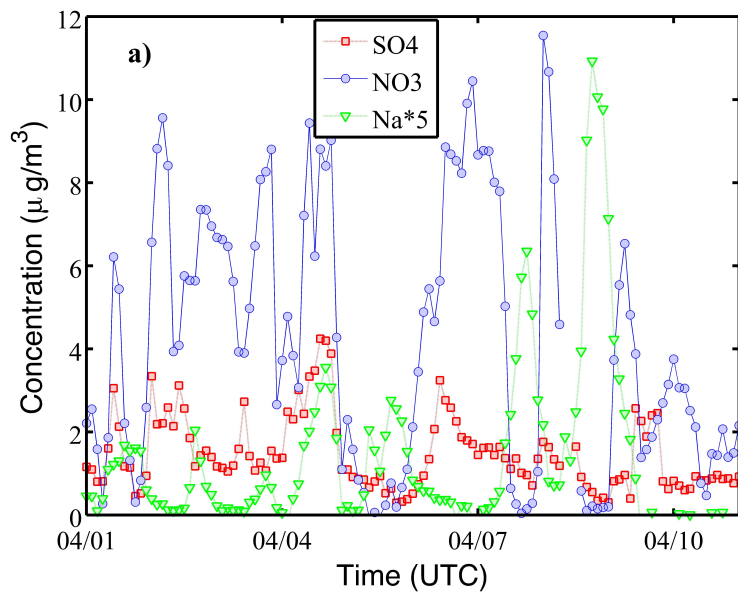
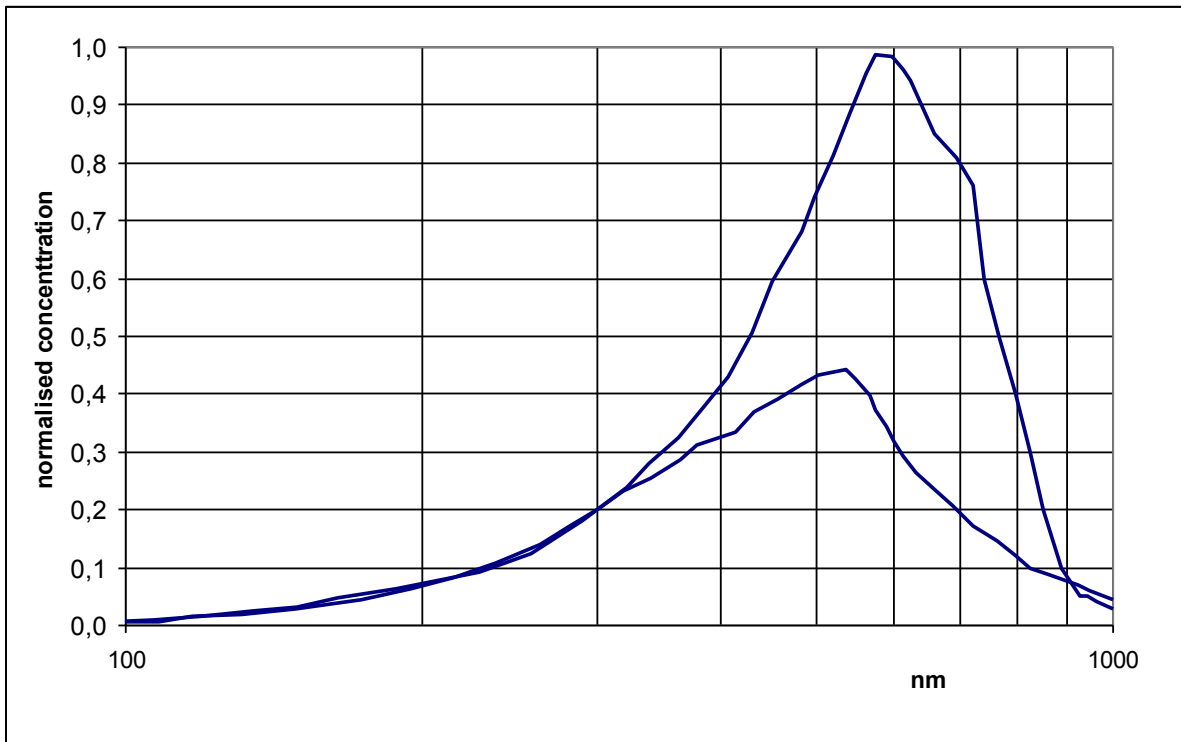


Figure 7: a) Concentrations of submicron nitrate (blue), submicron sulphate (red) during the intensive campaign of April 2009. Notice the very good comparability of these data with those of the AMS (fig. S2). Also the marine tracer sodium (green) in the PM10 fraction is given. b) Wind direction, in degrees, during the same period. Note that, to ease the view, the sodium concentration was multiplied by a factor of 5.



470 **Figure 8:** Activation of nitrate as a function of (the vacuum aerodynamic) diameter on April 4th. Upper graph: ambient aerosol. Lower graph: interstitial aerosol. The vacuum-aerodynamic diameter is the measuring unit in the AMS and a factor of 1.6 larger than the mobility diameter for the average aerosol in the Netherlands (Mensah et al., 2012).

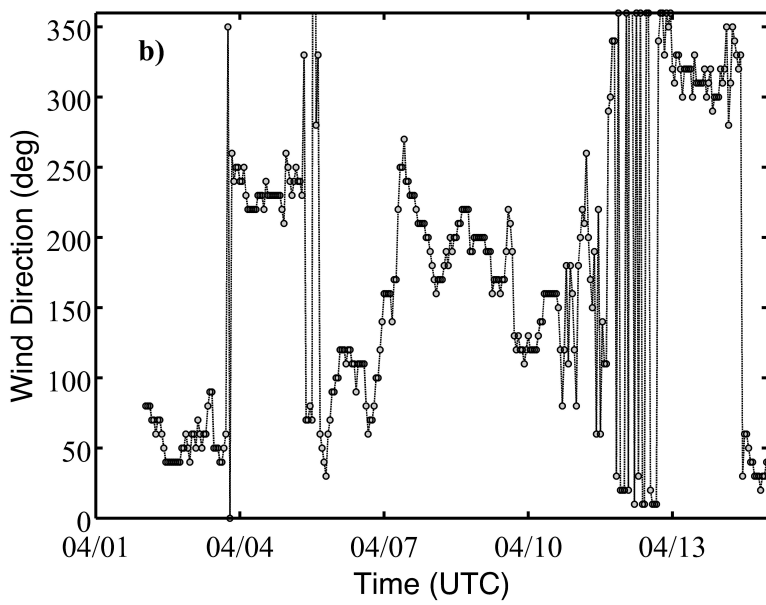
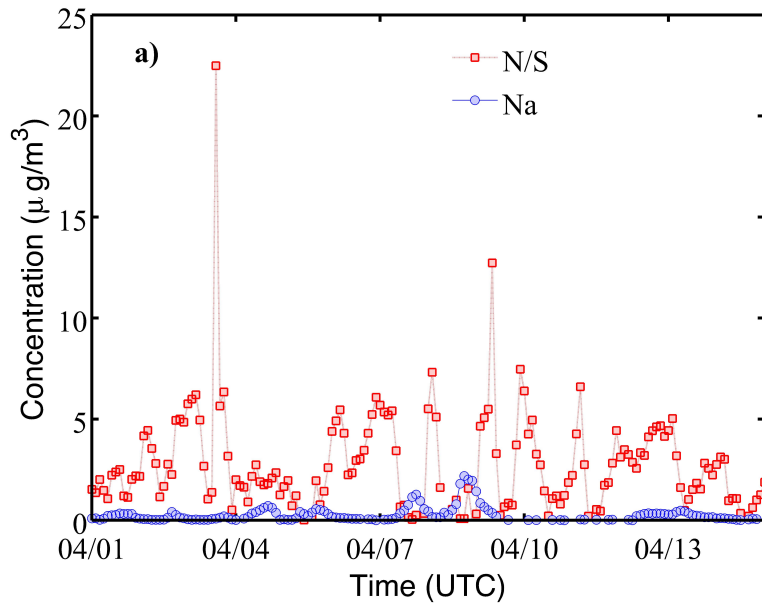


Figure 9: The CCN nitrate to sulphate ratio observed within the size range of 150-250 nm and the PM10 sodium concentrations (a) as well as the wind direction (b) during the indicated period in April 2009.

