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## 3.2. Marine boundary layer studies

The marine boundary layer (MBL) is especially important part of the atmosphere to consider, as 70 % of the earth's surface is covered by water and at any one time, around half of this is covered by stratus clouds. As discussed in section 1.1.1.2., the number, size and chemical nature of the particles present in the atmosphere profoundly affect the lifetimes and optical properties of these clouds, so MBL aerosols are of paramount importance when considering global climate issues.

In addition to those originating from land-based sources, the MBL contains particulate matter that originates from sources over the open ocean, which consists of two major types [Katoshevski *et al.*, 1999]; sea salt particles that are created mechanically on the surface of the ocean due to wave action and bubble bursting and non sea salt (nss) particles which are predominantly sulphate-based particles created from gas to particle conversion. The sea salt particles tend to be much larger than the nss variety, being mainly in the coarse regime as opposed to the nss particles, which tend to be of fine sizes. The particle numbers are greatly reduced compared to terrestrial environments, ranging from around  $10^3 \text{ cm}^{-3}$  in polluted conditions to of the order of  $10^2 \text{ cm}^{-3}$  in clean conditions [Raes *et al.*, 2000]. This is in contrast to urban areas, where particle number concentrations can be of the order of  $10^4 \text{ cm}^{-3}$  or higher. A distinct Aitken mode is frequently not observed in the marine environment.

One of the main sources of the sulphur in nss particles is from the biogenic production of dimethyl sulphide (DMS) from phytoplankton and subsequent oxidation to sulphur dioxide and ultimately sulphuric acid. These particles readily act as CCN so this is conceptually an important factor when considering climate forcing [Charlson *et al.*, 1987]. However, it must be stressed that this is a complex process involving other oxidation products such as methylsulphonic acid (MSA) and is not completely understood at this stage. This oxidation can take place entirely in the gas phase but as with the terrestrial boundary layer, oxidation of  $\text{SO}_2$  to sulphate can take place much faster in the aqueous phase, in activated cloud drops or aqueous sea salt particles.

While sulphate deposition onto preexisting particles is an important source of particulate mass, the initial source of the nss particles is also an important, as this will dictate the number density of particles and therefore the number of CCN and the magnitude of any indirect cloud effects. Suggested mechanisms include binary nucleation from sulphuric acid and water in the gas phase [Covert *et al.*, 1992], but

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another important factor may be the formation of particles from halogen compounds, released into the atmosphere from algae species [McFiggans *et al.*, 2004a; O'Dowd *et al.*, 2002a]. Particles may also enter the MBL from the free troposphere, which can carry particles from other sources over large distances [Covert *et al.*, 1996; Raes *et al.*, 2000]. There may also be significant organic contributions to the particles from biological activity in the seawater [Middlebrook *et al.*, 1998; O'Dowd *et al.*, 2004].

The UMIST AMS has participated in three MBL field studies, the results of which are presented here. All three were ground-based deployments in remote coastal areas, where local terrestrial influences were expected to be low. The deployments were all in the northern mid-latitudes and located in sites in the western and eastern Pacific and western Atlantic Oceans.

### 3.2.1. ACE-Asia, Jeju-Do, South Korea, April 2001

#### 3.2.1.1. Deployment

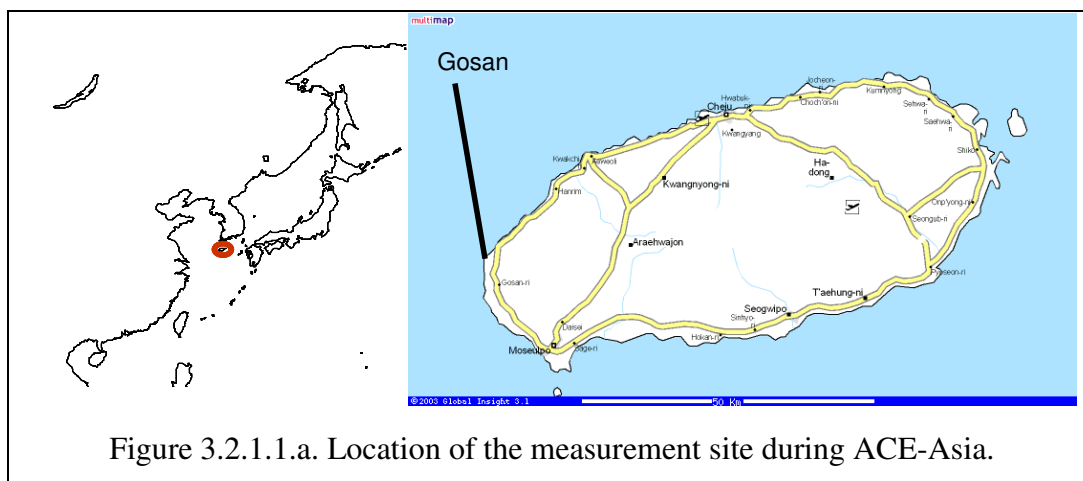


Figure 3.2.1.1.a. Location of the measurement site during ACE-Asia.

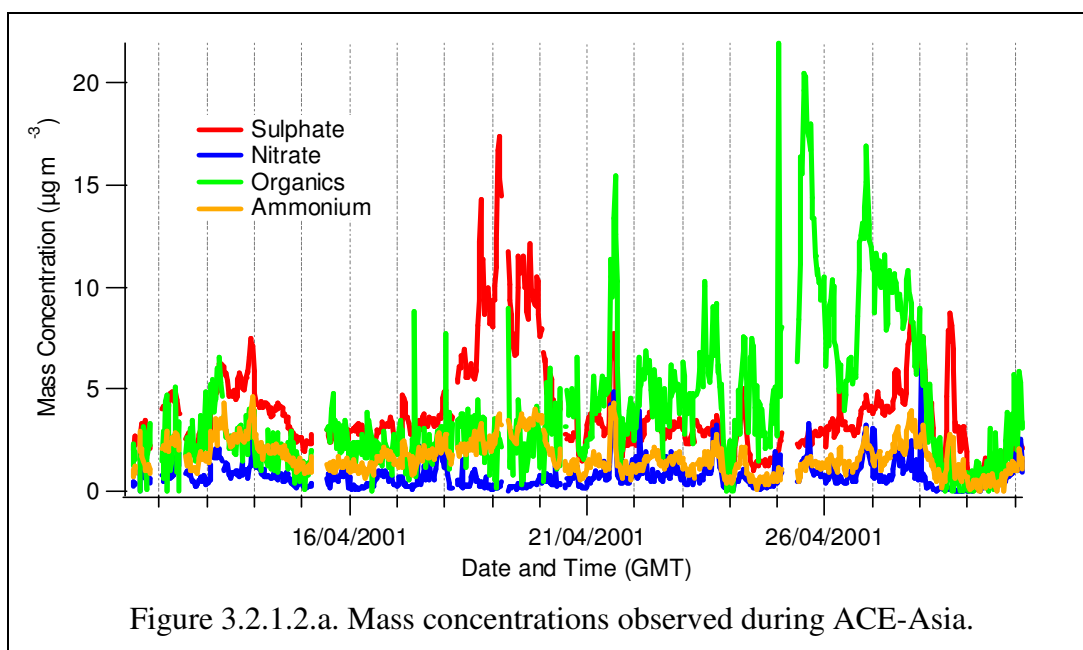
The overall goals of ACE-Asia, the fourth Aerosol Characterisation Experiment, were to characterise the particulate matter in the East Asian and Yellow Sea areas and assess what effects it may have on the radiative properties and chemical processes in the atmosphere [Huebert *et al.*, 2003]. This is generally seen as an important region of the globe to consider, as there are many major sources of atmospheric pollution. For instance, China is known to be a major source of SO<sub>2</sub> (an estimated 20.8 Tg were emitted during 2000 [Carmichael *et al.*, 2002]). Also of interest are the dust storms in Asia, which in part due to agricultural practices in the area, suspend large amounts of mineral particles in the air. These ‘yellow sand’ events are known to cause serious visibility and health problems regionally, but the material is also known to persist in the troposphere for some time, occasionally travelling as far as North America. The

experiment involved research groups from several countries and sites were operated in many places including South Korea, China, Japan and Taiwan. There were also ship and aircraft based measurement platforms as well.

The AMS was deployed at the Gosan supersite on the South Korean island of Jeju-do during the ACE-Asia experiment in April and May 2001. The site was on a coastal cliff top (33.29 °N, 126.16 °E, 60 m elevation) on the western tip of the island (figure 3.2.1.1.a). The island of Jeju-do is located in the Yellow Sea, approximately 100 km south of the Korean mainland, 250 km west of Kyushu Island, Japan, 500 km east-northeast of Shanghai, China and 1000 km north-northeast of Taichung, Taiwan. As it has few major industrial sources itself [Carmichael *et al.*, 1997] it is in a good position to characterise the pollution originating from East Asia.

The instrument was operated in the standard configuration, although the experiment occurred before most of the upgrades had taken place, so the signal to noise ratios were less than ideal. For this reason, it was operated with a thirty-minute averaging period. The AMS sample flow was sub-sampled from a 10.5 m mast equipped with a standard PM<sub>10</sub> impactor inlet. The results from this study were first published by Topping *et al.* [2004a].

### 3.2.1.2. Results



Unlike the urban studies, all the results presented in this MBL chapter (3.3.) have assumed that all particles have a collection efficiency ( $CE$ ) of 0.5. This is because this value has proved robust for some external comparisons (2.4.2.), so it is assumed

that, on average, this gives a good reflection of the true accumulation mode mass concentrations. This also includes the organics because as discussed later, they are assumed to be internally mixed in the accumulation mode. A caveat is the coarse mode; as well as the collection efficiency, there is also the problem of lens transmission in that regime which cannot be accurately accounted for, so it is not possible to be absolutely quantitative in this regime.

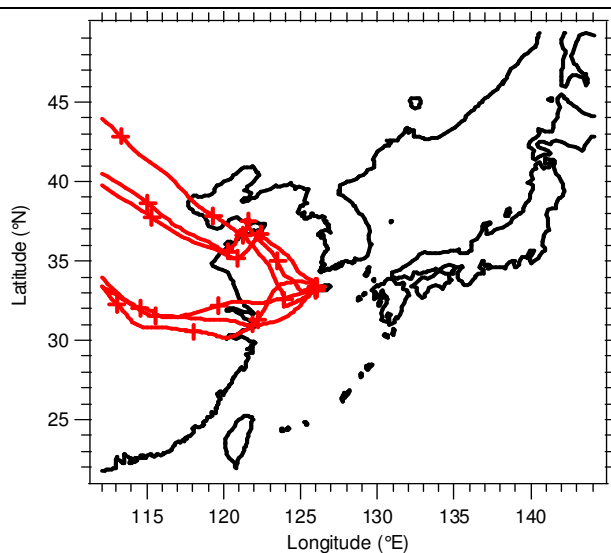


Figure 3.2.1.2.b. Back trajectories from the 'Chinese' period of ACE-Asia. Check marks are placed at 1 day intervals.

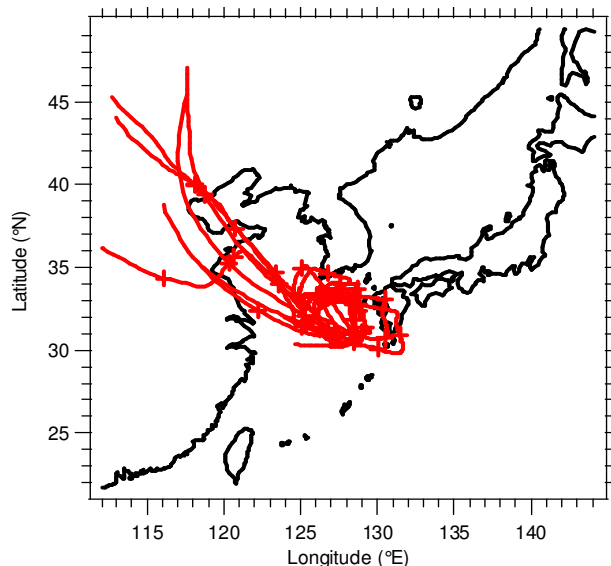


Figure 3.2.1.2.c. The 'marine' period of ACE-Asia.

The mass concentrations shown in figure 3.2.1.2.a can be separated into four periods, characterised by both the air histories (as shown by the back trajectory analyses) and particulate chemical composition. Generally, there were particles present at all times except for after the 28<sup>th</sup> of April, when it was raining. From the 13<sup>th</sup> to the

15<sup>th</sup> of April, the air sampled had come directly from the west, over China (figure 3.2.1.2.b), and the aerosol were dominated by a fairly stable sulphate concentration, although some organics were present and the loadings were generally fairly low at less than  $5 \mu\text{g m}^{-3}$ . Between the 16<sup>th</sup> and the 20<sup>th</sup> of April, the air again passed over China prior to sampling but instead resided for a period of days within the boundary layer above the yellow sea in the intervening time (figure 3.2.1.2.c). This has a profound effect on the chemical mass concentrations, especially on the 18<sup>th</sup> and 19<sup>th</sup> of April, where the sulphate loading increases to over  $10 \mu\text{g m}^{-3}$ . As mentioned above, China is known to be a major source of  $\text{SO}_2$  and it is likely that the difference between these two periods highlights the time needed to convert this to sulphate.

In a marked change to the aerosol behaviour, from the 21<sup>st</sup> onwards organics dominated the particulate mass and showed a much more episodic behaviour, which may indicate the sampling of diffuse emissions from point sources. This is a reflection of a change to the air mass histories, which according to the back trajectories originated from the East and North, gathering material from Japan and the Korean peninsula. Japan and South Korea are overall more industrialised than China, and while they do not emit as much  $\text{SO}_2$ , they do export more atmospheric organic carbon and this is reflected in the particulate compositions. This is especially pronounced during the period of the 25<sup>th</sup> to the 27<sup>th</sup>, where the air persistency came from the north, along the west coast of South Korea (figure 3.2.1.2.d), where there are many urban and industrial sources, including the capital, Seoul.

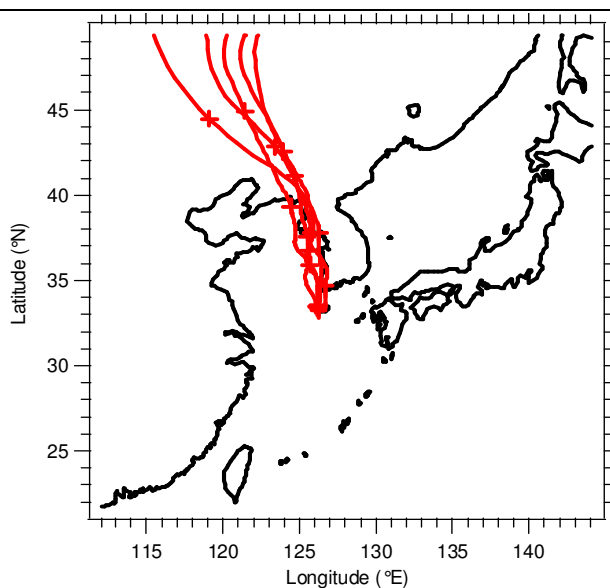
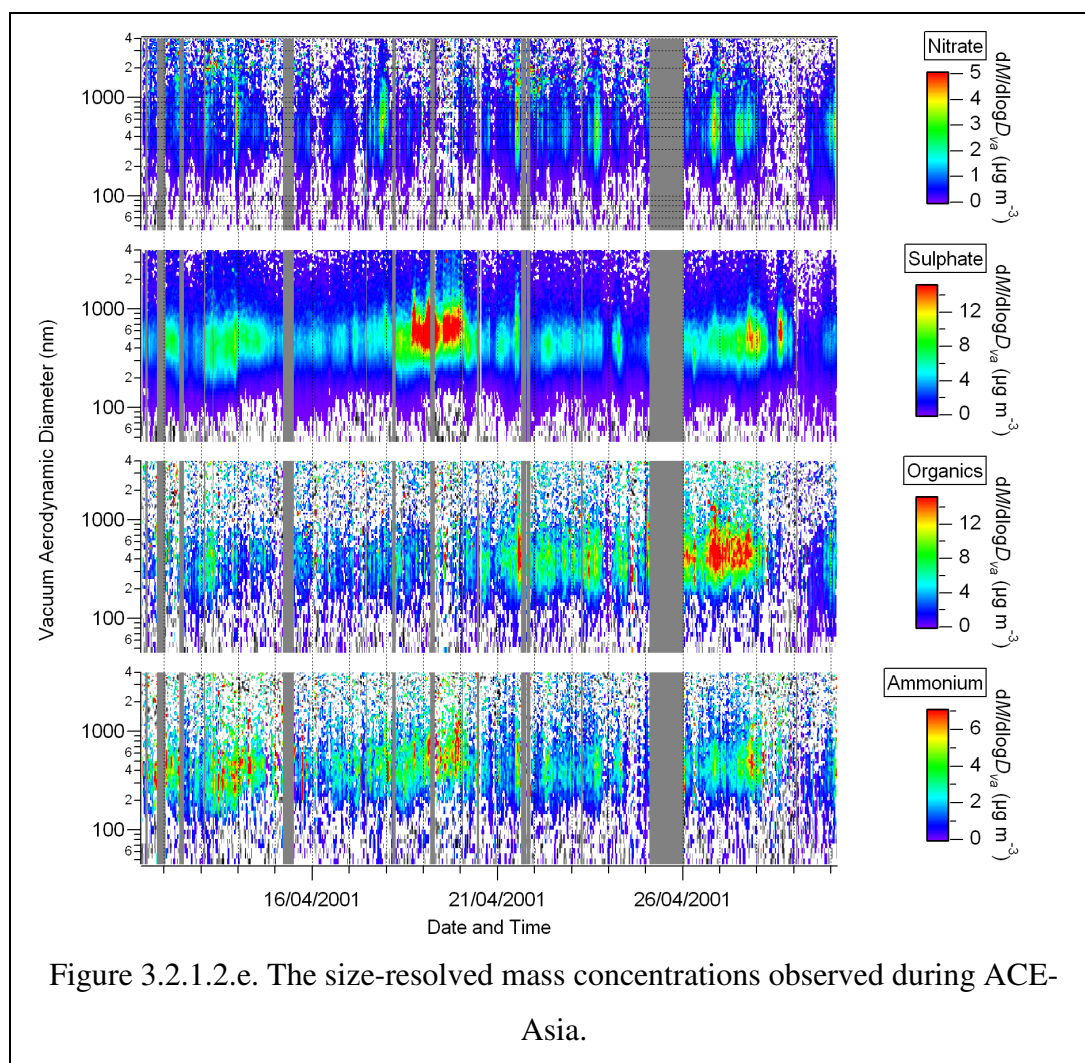


Figure 3.2.1.2.d. The 'Korean' period of ACE-Asia.

In terms of the size distribution, most chemical components existed within a single mass mode, with a vacuum aerodynamic diameter that varied between about 200 to 400 nm (figure 3.2.1.2.e). Additionally, the nitrate sometimes exhibited a coarse mode at around 2-3  $\mu\text{m}$ , occasionally accompanied by small amounts of sulphate (e.g. 19<sup>th</sup>-20<sup>th</sup> April) or organics (e.g. 26<sup>th</sup> April). It is difficult to compile any reasonable statistics about this mode, as the detected mass in this regime is distributed among a small number of relatively large particles. Also, the actual size of the particles cannot be determined with much confidence, as the instrument's sizing capability in this regime is based on an extrapolation of the velocity calibration curve described in section 2.3.3.2. There are technical difficulties associated with suspending and sampling sufficient numbers of PSL spheres of this size that prevent these being used for calibration purposes.



### 3.2.2. ITCT 2K2, Trinidad Head, California, April 2002

### 3.2.2.1. Deployment

The Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) was a National Oceanographic and Atmospheric Administration (NOAA) experiment, part of the International Global Atmospheric Chemistry (IGAC) project. It was designed to study the composition and processes of the atmosphere as it arrived at North America over the Pacific, being carried by the prevailing winds. This is important to consider when budgeting for pollutants, as it will carry material from eastern Asia. While this is a major pollution source, the emissions will have had time to disperse and chemically age before reaching North America. Several platforms were used, including ship, aircraft and ground-based sites [Tang *et al.*, 2004].

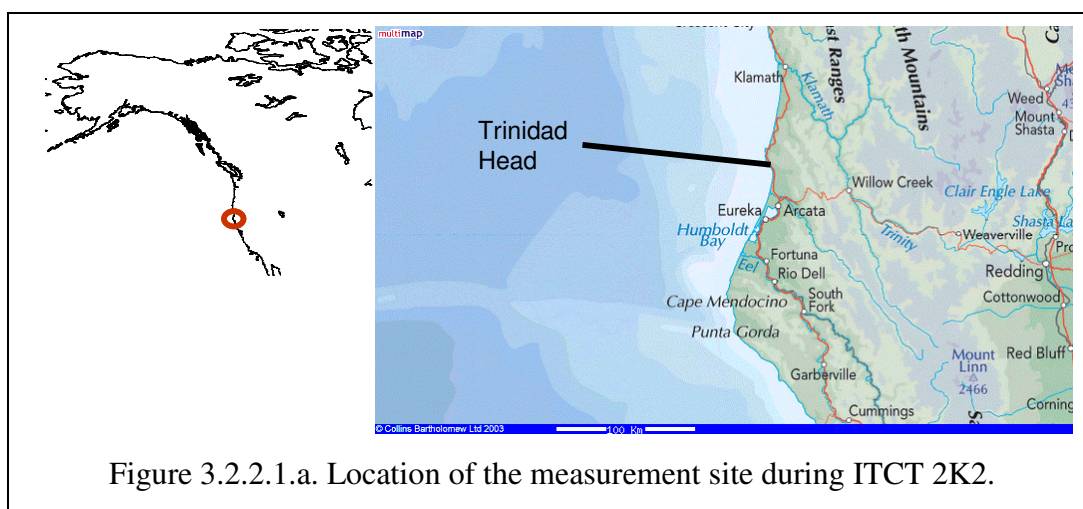


Figure 3.2.2.1.a. Location of the measurement site during ITCT 2K2.

The site at Trinidad Head (41.054 °N, 124.151 °W, 107 m elevation) was on a coastal cliff top in northern California (figure 3.2.2.1.a). The two AMSs were deployed at this site in a joint experiment by UMIST and ARI, sampling ambient air through a 2.5  $\mu\text{m}$  cutoff cyclone (URG-200-30EN, URG, Chapel Hill, NC, USA), positioned 15 m above ground level on a scaffold tower. The first instrument, referred to in this section as the ARI instrument, was operated under the standard configuration and protocol for ambient aerosol sampling, except for using a temperature control system on its inlet, described previously in section 2.2.2.1. The second instrument, in this section referred to as the UMIST AMS, was modified to be able to detect sea salt particles, as described in section 2.2.1.3. This deployment and the arising results were first presented in Allan *et al.* [2004c].

An automated in-situ gas chromatograph - mass spectrometer - flame ionization detector (GC-MS-FID) system was deployed and operated by the University of California at Berkeley to measure the gas phase mixing ratios of a wide suite of volatile organic compounds (VOCs). The GC-MS-FID was configured to draw ambient samples

from the measurement tower and measure C<sub>3</sub>-C<sub>6</sub> alkanes, alkenes and alkynes, along with other VOCs, including aromatic, oxygenated and halogenated compounds at hourly intervals. This instrument, its deployment and results during the campaign are described by *Millet et al.* [2004]. The sampling was performed on the same tower using PTFE tubing.

Also located at the Trinidad Head site was a PILS-IC (see section 1.2.2.), which was operated by the Georgia Institute of Technology and the NOAA Pacific Marine Environmental Laboratory. The PILS also sampled from the same height as the other instruments, although its inlet had a 1  $\mu\text{m}$  cutoff cyclone, maintained at  $56 \pm 6$  % RH. Sodium carbonate and citric acid denuders were placed upstream of the instrument to remove gas phase acids and bases prior to sampling. This yielded quantitative data on the total mass concentrations of water-soluble ions present in the ambient aerosol particles with a time resolution of thirty minutes.

### 3.2.2.2. Results

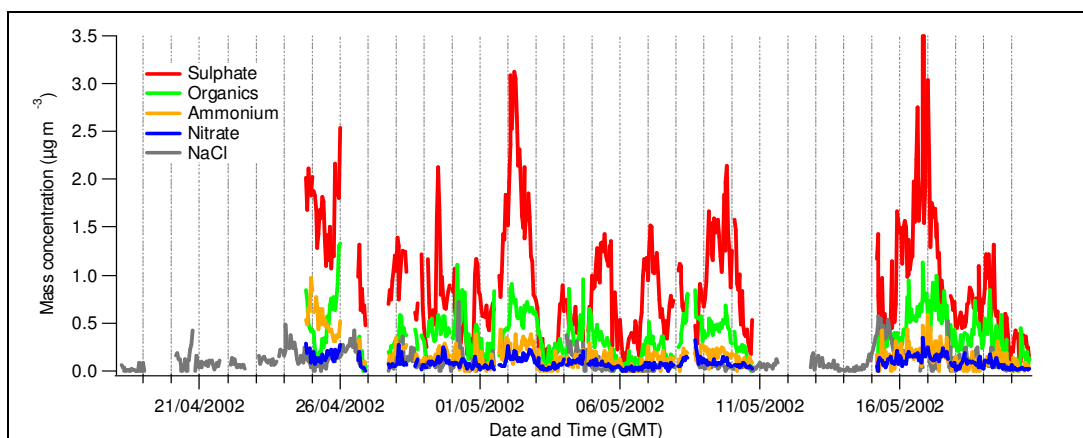


Figure 3.2.2.2.a. Mass concentrations observed during ITCT 2K2. The nitrate, sulphate, organic and ammonium data are taken from the ARI instrument during high ( $>10$  °C)  $t-t_d$  sampling. The NaCl data were taken from the UMIST (hot vaporiser) instrument.

The data from the ARI instrument were binned according to the difference between inlet temperature and the ambient dew point, as discussed in section 2.2.2.1. The sulphate, ammonium, organics and nitrate data shown in figure 3.2.2.2.a are hourly averages, using only the data from when the inlet temperature was at least 10 °C greater than the dew point. Under these conditions, the particles were sampled relatively dry and therefore the standard analysis techniques could be applied. The ammonium, sulphate and organic data reported from the UMIST instrument are not used for the

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general scientific discussion, due to the fact that its vaporizer and ionizer configuration affected the relative sensitivities of the different species in a manner not accounted for by the standard calibrations; the temporal variations reported for these species qualitatively agree with those of the ARI instrument, but the absolute loadings disagree by factors of around 1.5. However, this is partly expected because the UMIST instrument was optimized primarily for sea salt and it was anticipated that the other species would be compromised, so the ARI instrument is deemed more reliable for these.

The overall composition of the particles is dominated by sulphate and organics, with mean average loadings of 0.93 and 0.38  $\mu\text{g m}^{-3}$  respectively. There was very little nitrate, which had an average concentration of 0.09  $\mu\text{g m}^{-3}$  and was rarely above 0.3  $\mu\text{g m}^{-3}$ . Ammonium loadings, which averaged at 0.16  $\mu\text{g m}^{-3}$ , were relatively low and did not always reach the amounts necessary to fully neutralize the sulphate present; the ratio of the averaged ammonium and sulphate loadings was 17.2 % by mass, as opposed to the 37.5 % required to achieve a 2:1 molar ratio.

The sodium chloride loading was derived from the UMIST AMS and calculated by summing the signals at  $m/z$  23 ( $\text{Na}^+$ ), 35 ( $\text{Cl}^+$ ), 36 ( $\text{HCl}^+$ ) and 58 ( $\text{NaCl}^+$ ), after subtracting any signals due to gas-phase components (e.g.  $^{36}\text{Ar}^+$ ) using the method described in section 2.4.2.2. The contributions of fragments containing the  $^{37}\text{Cl}$  isotope were predicted from the intensity of the other peaks, assuming an isotopic ratio of 3.13:1 [Coplen *et al.*, 2002]. Tests with atomizer-generated particles using both pure sodium chloride and sea salt solutions showed that there were no significant peaks from NaCl at higher  $m/z$ 's to be expected. The measured mass loadings at Trinidad Head were fairly low, averaging at 0.1  $\mu\text{g m}^{-3}$ . Note that the reported concentrations are likely to be only a fraction of the total suspended sodium chloride present in the atmosphere, as most of it will exist in coarse particles, which are not measured with 100 % efficiency due to the low transmission efficiency by the aerodynamic lens in that regime and the 2.5  $\mu\text{m}$  cutoff of the cyclone. Also note that this particular chemical species is measured with a very low signal to noise ratio, due to the high background levels in the instrument and the relatively long vaporization times. The data must be averaged over large time periods to obtain meaningful results at the analysis stage, especially when dealing with the time of flight data.

The particle time of flight data in figure 3.2.2.2.b show that there was an accumulation mode at vacuum aerodynamic diameters of around 300 to 400 nm,

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consisting mainly of sulphate, ammonium and organics. The modal diameter of the accumulation mode varied little during the experiment and was consistent between the four species, implying internal mixing, although nitrate has some presence in the supermicron regime and the organics show a small amount of signal below 100 nm. Conversely, the sea salt distribution was broad and stretched into the coarse mode (figure 3.2.2.2.c), implying an external mixture with the other chemical components.

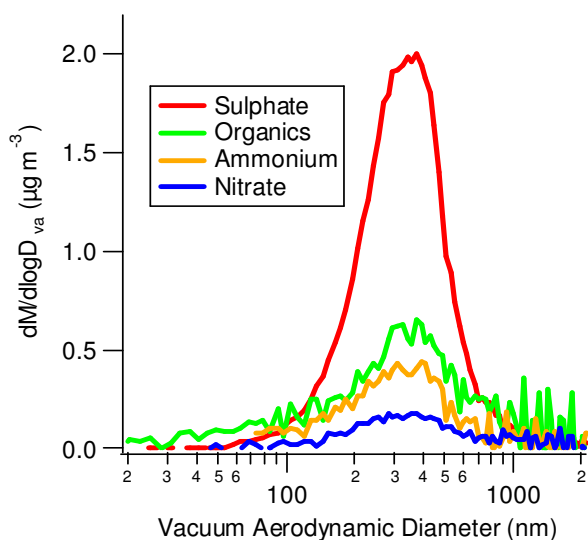


Figure 3.2.2.2.b. Averaged size distributed mass concentrations from ITCT 2K2.

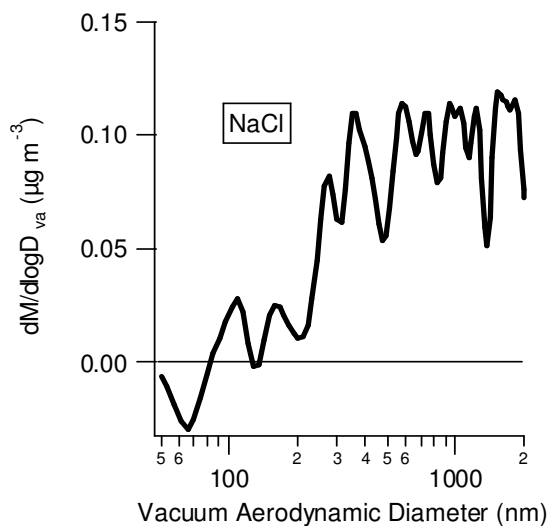


Figure 3.2.2.2.c. The average size-resolved mass distribution of sodium chloride measured during ITCT 2K2.

By comparing the standard deviations of the time series of the aerosol mass concentrations derived from this experiment with those of various gas phase components, *Millet et al.* [2004] were able to estimate their atmospheric lifetimes in this environment. The values derived from the AMS data for nitrate, sulphate, ammonium

and organics were 5.6, 5.7, 4.1 and 6.3 days respectively. The PILS-IC derived estimates were 3.9, 7.1 and 2.9 days for nitrate, sulphate and ammonium respectively, which compares well, given that the calculated equivalent lifetimes of the different VOC species had values that spanned over 4 orders of magnitude. Statistics of this nature are useful when attempting to model and predict global atmospheric chemistry. Back trajectory analysis showed that, local influences aside, the air masses sampled during the experiment had all spent at least the previous 10 days over the open ocean. As the chemical lifetime estimates were much less than this and were filtered for local influences at the analysis stage, it can be assumed that MBL processes were the dominant factor governing the marine sector particle populations at this site, rather than long-range transport within the boundary layer. The main loss mechanism for accumulation-mode particulate mass in the MBL is thought to be wet deposition.

### 3.2.3. NAMBLEX, Mace Head, Republic of Ireland, August 2002

#### 3.2.3.1. Deployment

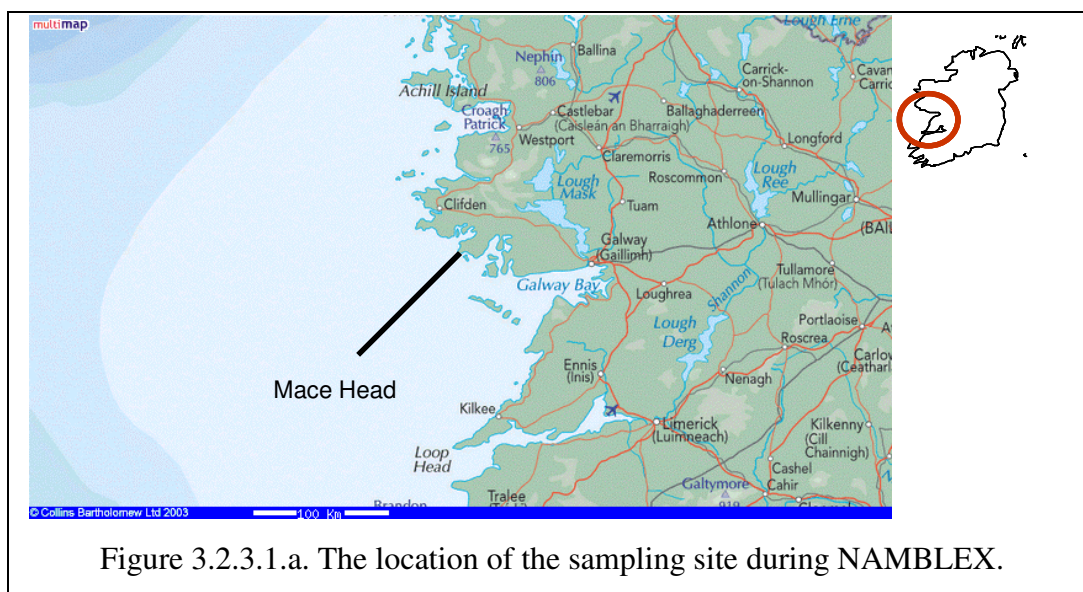


Figure 3.2.3.1.a. The location of the sampling site during NAMBLEX.

The North Atlantic Marine Boundary Layer Experiment (NAMBLEX) took place at a permanent background measurement site at Mace Head, County Galway in the Republic of Ireland during August 2002. This site is situated at the shore of a headland in a remote part of the west Irish coastline at 53.33 °N, 9.90 °W (figure 3.2.3.1.a). It is 88 km west of Galway city, the nearest major conurbation, over 150 km from the main Atlantic shipping routes and 80 km from the transatlantic air corridors, making it a good site for background measurements. The meteorological records show that on average, over 60% of the air masses arrive at the station via a clean sector to the

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west, largely unperturbed by human activity [NUI Galway, 2004]. The overall aim of the experiment was to characterise the chemical properties of the air within the Atlantic MBL, which included the study of gas phase chemicals, radicals and aerosol particles. This is important, because in the same manner as the Pacific MBL, this provides the background for the atmosphere of Western Europe.

The AMS was deployed in its standard configuration, averaging on a ten-minute basis. It took a sub-sample from the main UMIST sampling stack, which was attached to the site scaffold tower, located near the shoreline. The stack consisted of a 150 mm ID polypropylene tube, down which a continuous laminar flow of  $180 \text{ l min}^{-1}$  was drawn. It had two inlets, one located at 7 m above ground level and another at 22 m. Part of the purpose of this arrangement was that it has been suggested that macroalgae exposed at low tide are a significant source of new particle formation [O'Dowd *et al.*, 2002a]. The precise mechanism for this has not yet been proven, but iodine compounds are thought to be key [Jimenez *et al.*, 2003b; McFiggans *et al.*, 2004a]. New particle formation events have been observed at the Mace Head site before [O'Dowd *et al.*, 2002b]. It was hoped that by comparing the data of both inlets would facilitate being able to distinguish between background particles in the MBL and those created or influenced in the locality of the site. The two inlet heights were alternated between on an hourly basis using a shutter in the inlet stack.

### 3.2.3.2. Results

Unfortunately, due to some technical problems, the instrument did not perform as well as on previous field projects. One problem was a loose connection to one of the quadrupole rods, which caused the mass spectrometer to periodically malfunction. Another was the multiplier, which while giving good amplification of the ions detected (the standard gauge of multiplier performance), the ion collection efficiency unexpectedly degraded during the course of the experiment. These combined to give data with generally lower signal to noise ratios. There was significant downtime on the 12<sup>th</sup> to the 14<sup>th</sup> of August and the 17<sup>th</sup> and 18<sup>th</sup>, during which the quadrupole problem was so severe the data became unusable. These have been removed from the data presented.

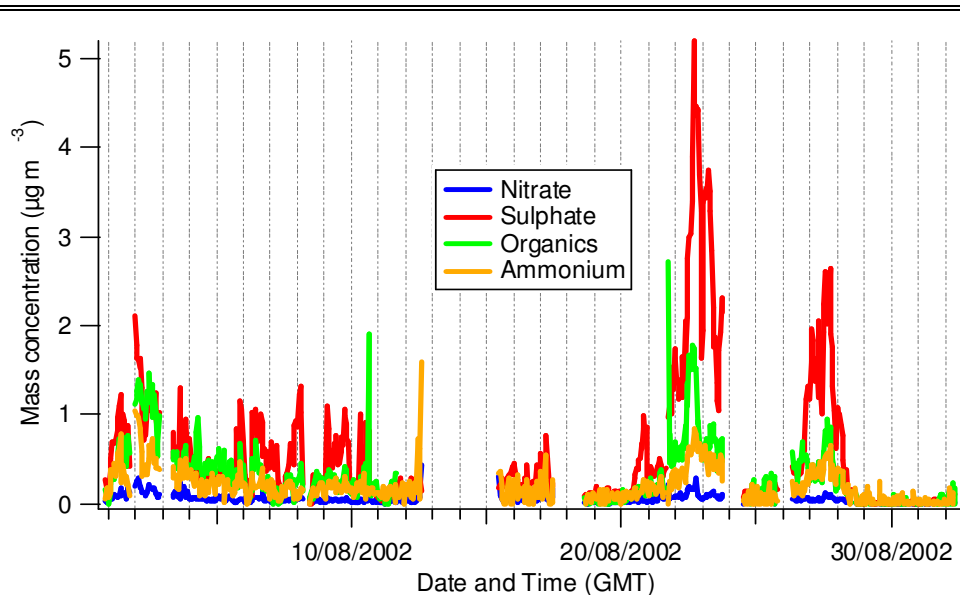


Figure 3.2.3.2.a. The mass concentrations measured during NAMBLEX.

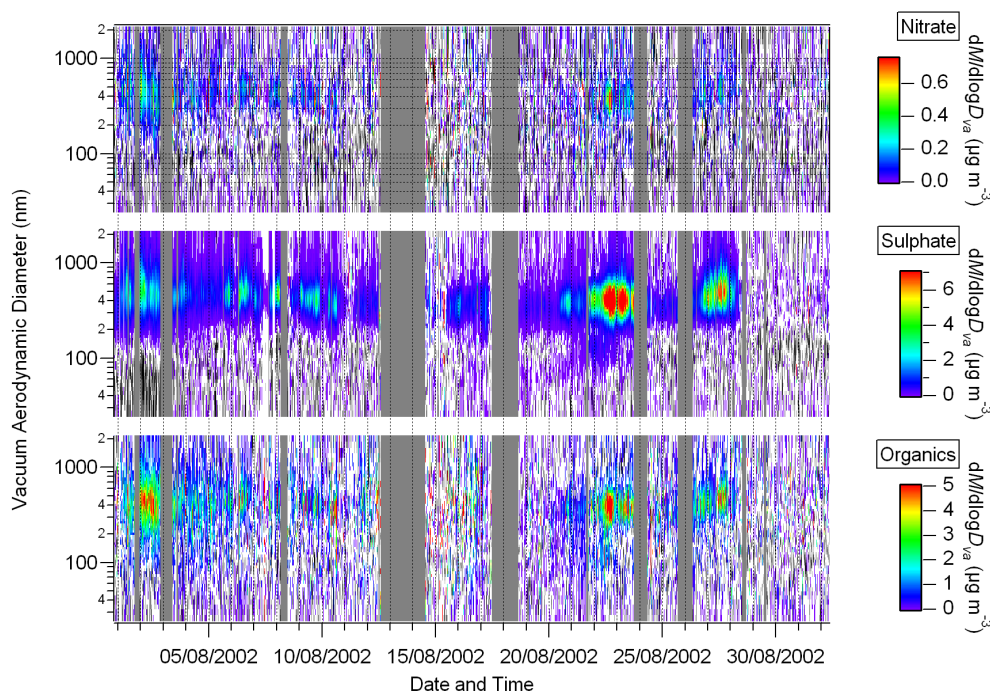
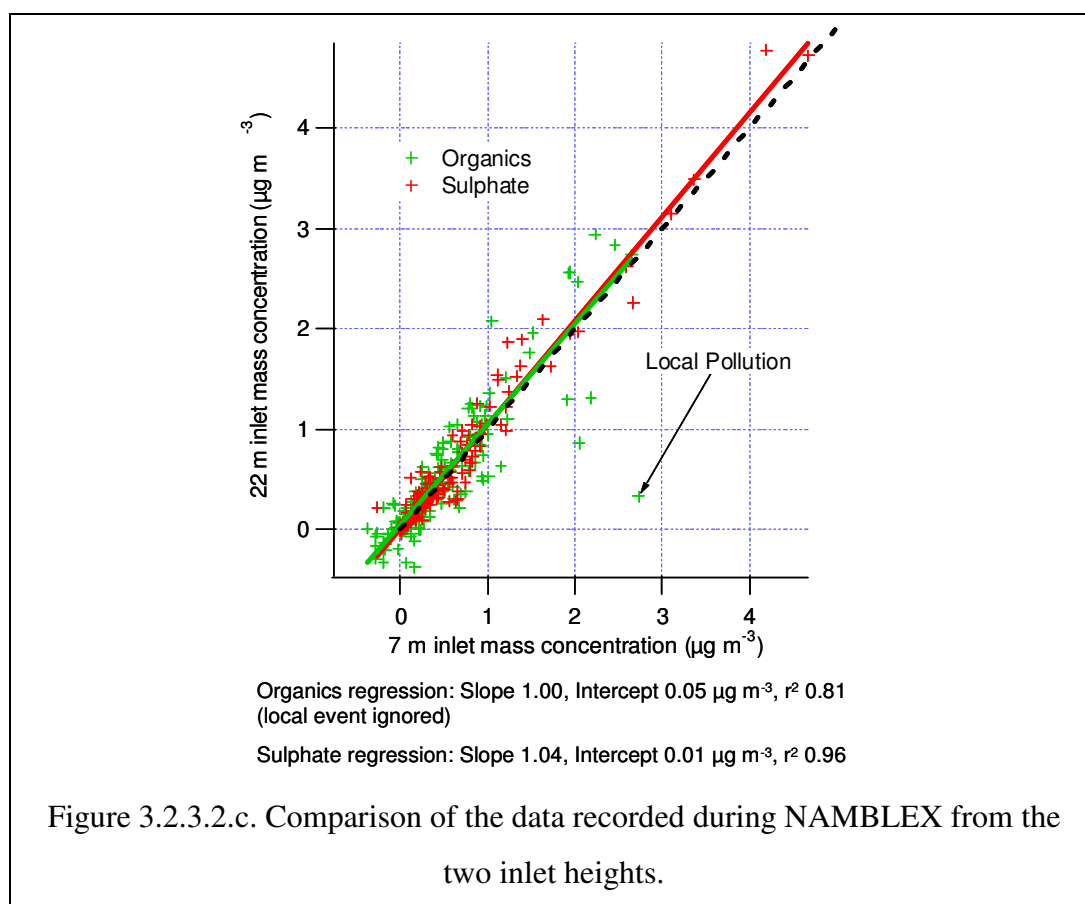


Figure 3.2.3.2.b. The size-resolved mass distributions recorded during NAMBLEX.

The overall behaviour of the particles shown in figure 3.2.3.2.a was largely very similar to the other MBL experiments, in that sulphate and organics dominated the loadings roughly equally overall with mean loadings of  $0.56$  and  $0.65 \mu\text{g m}^{-3}$  respectively, and there was only a very small contribution from nitrate, at an average of  $0.05 \mu\text{g m}^{-3}$ . Ammonium is present at an average of  $0.18 \mu\text{g m}^{-3}$ , but does not always completely neutralise the sulphate. However, the overall loadings were smaller compared to the other studies. There is a period at the start where organics tend to

dominate, whereas later on, from the 21<sup>st</sup> of August, it is sulphate that represents the majority of the mass. There is a clean period from around the 28<sup>th</sup> of August onwards, where virtually nothing was detectable. This was a period of heavy rain, so most of the particulate material had been presumably washed out.

In the size-resolved mass concentration (figure 3.2.3.2.b), there is again a single dominant peak in the accumulation mode around 400-500 nm, which is common to all the chemical types. There was no significant coarse mode detected in this experiment, which is expected because in this experiment, the vaporiser was not hot enough to vaporise sea salt particles.



The AMS-reported data showed very little dependence on the inlet used on the sampling stack. Most of the time, the measured aerosol composition was the same for the 22 m inlet as the 7 m inlet, as can be seen in figure 3.2.3.2.c, which shows 3-hour averaged data in order to remove artefacts caused by slow increases or decreases of mass concentrations. The first 10 minutes after each inlet switch have also been ignored to prevent artefacts caused by the time needed to purge stagnant air from the stack. A notable exception to the correlation was on the 8<sup>th</sup> of August between 18:00 and 19:00. At this time, the inlet was set to sample at 7 m and the organic mass concentration leapt

from less than  $1 \mu\text{g m}^{-3}$  to around  $4 \mu\text{g m}^{-3}$  and displayed a lower diameter mode (figure 3.2.3.2.d), with a mass spectral signature identical to that seen in urban environments. At this time, a casual observation was made that some motorboats were operating a short distance off the coast, which would explain the exhaust emission signature. The fact that this was not seen at 22 m showed that this sampling height was indeed not influenced by emissions closer than the shoreline. Also, the lack of a detectable difference between the two sampling heights at all other times shows that the majority of the mass detected had not been influenced by any local influences or the increased length of the stack itself.

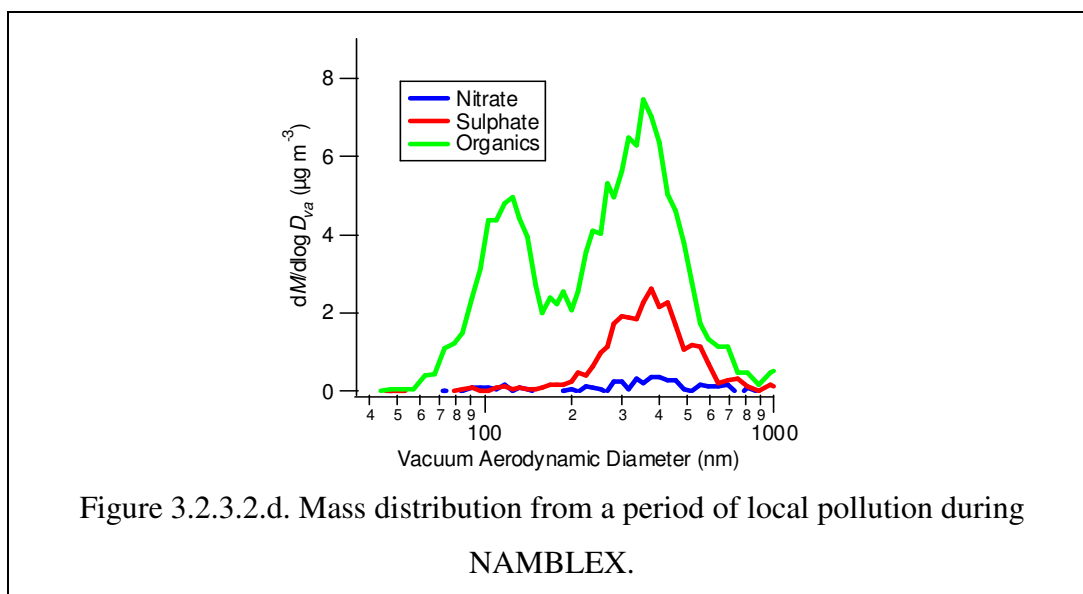


Figure 3.2.3.2.d. Mass distribution from a period of local pollution during NAMBLEX.

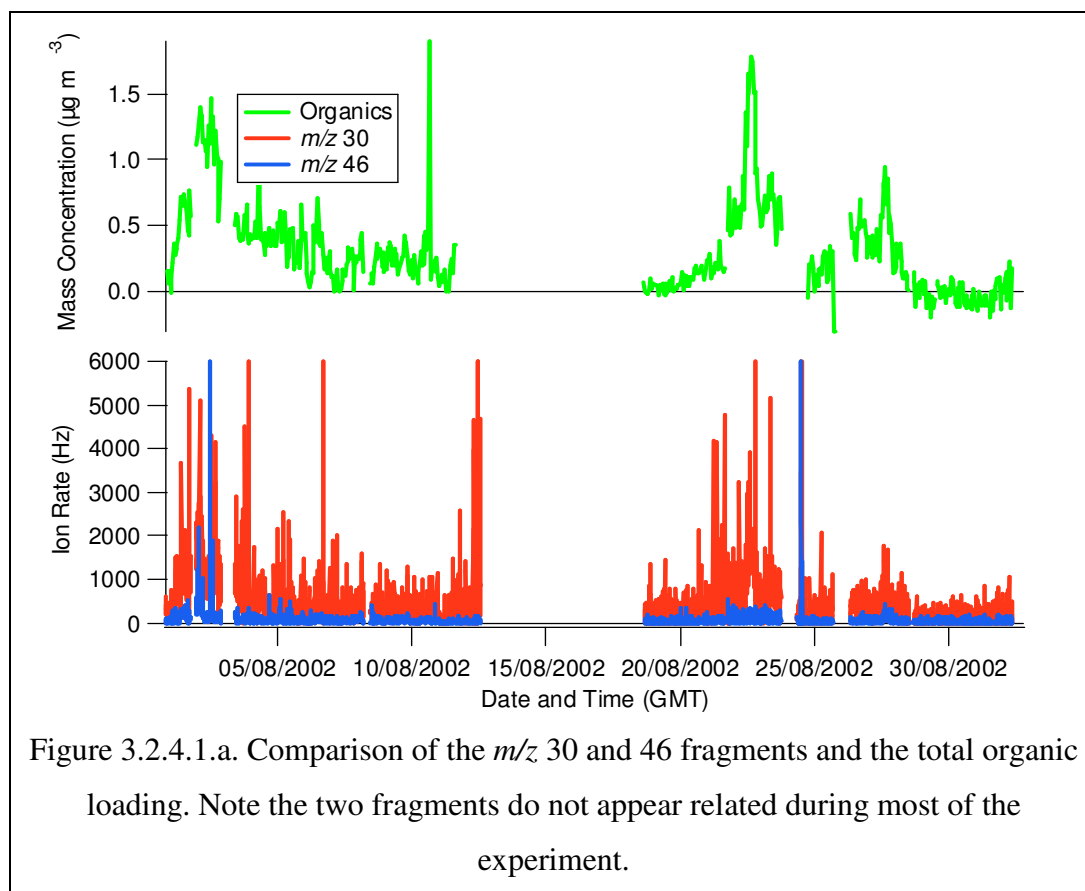
The AMS unfortunately did not see any direct evidence for new particle formation and growth events. While co-located DMPS and SMPS instruments recorded numerous new particle bursts at low tides during the campaign, the new particles never grew large enough in diameter or total mass to be detectable by the AMS.

### 3.2.4. MBL discussion

#### 3.2.4.1. Accumulation mode behaviour

All three marine environments presented in this thesis exhibited similar climatologies, in that the majority of the fine particulate mass is made up of sulphate and organics, apparently internally mixed in a single mode most of the time. This is in total agreement with the conclusions of other MBL aerosol chemistry studies [e.g. *Raes et al.*, 2000 and references therein]. There was ammonium present, but not always in amounts sufficient to neutralise the sulphate. Unlike urban environments, the organics were almost always unimodal at all three sites, although the  $m/z$  channels that exhibited

this mode were principally the ones indicative of more oxidised organic species (44, 43, 55, etc.) which is similar to the higher diameter mode seen previously at other sites.



The nitrate concentrations were generally extremely low compared to urban environments, particularly when there was insufficient ammonium to balance out the sulphate. When the NAMBLEX nitrate data are separated into the 30 and 46 contributions (figure 3.2.4.1.a), it can be seen that the only time when  $m/z$  46 follows the same temporal trend as 30 is during a polluted period on the 1<sup>st</sup> and the 2<sup>nd</sup>, discussed below. On this occasion, there was more than enough ammonium present to neutralise the sulphate present, so it is most likely that the nitrate seen was ammonium nitrate. At other times, there is very little activity at  $m/z$  46, so what is being referred to as ‘nitrate’ is likely to be something else. In this case, the activity in  $m/z$  30 seems to closely resemble that of the organics, so it would seem reasonable to assume that the chemical species responsible is somehow linked to the overall organic loading.

ITCT 2K2 also showed similar nitrate behaviour, with low mass concentrations and a generally high 30 to 46 ratio. As shown in section 2.5.2.2., the one major source of disagreement between the PILS-IC and the AMS is the reported nitrate, in which the AMS generally measured more. The source for this excess may be in the form of

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organic nitrogen (amines or organic nitrates). A similar discrepancy was found by *Middlebrook et al.* [2003b] off the east coast of the USA during the New England Air Quality Study (NEAQS), aboard the research vessel Ronald H. Brown. As previously shown, the excess nitrate reported by the AMS over the PILS-IC can be linked to the particulate organics and was also compared with the corresponding  $\text{NO}_y$  concentrations (*E. Williams*, NOAA AL, personal communication, 2003), but only a very weak correlation was found with the latter (slope =  $0.0225 \mu\text{g m}^{-3} \text{ppb}^{-1}$ , intercept =  $0.023 \mu\text{g m}^{-3}$ ,  $r^2 = 0.078$ ). Using the ideal gas law and assuming standard temperature and pressure and a parent molecular mass of 30 amu, the particulate mass concentration can be converted to a molar mixing ratio, which corresponds to a slope of 0.018 when compared to the  $\text{NO}_y$  data. As the parent molecules are almost certainly more massive than the 30 amu used, the above provides an upper estimate of the total mixing ratio of nitrogen-containing particulate organics, which is small (<1.8 %) compared to the total  $\text{NO}_y$  budget.

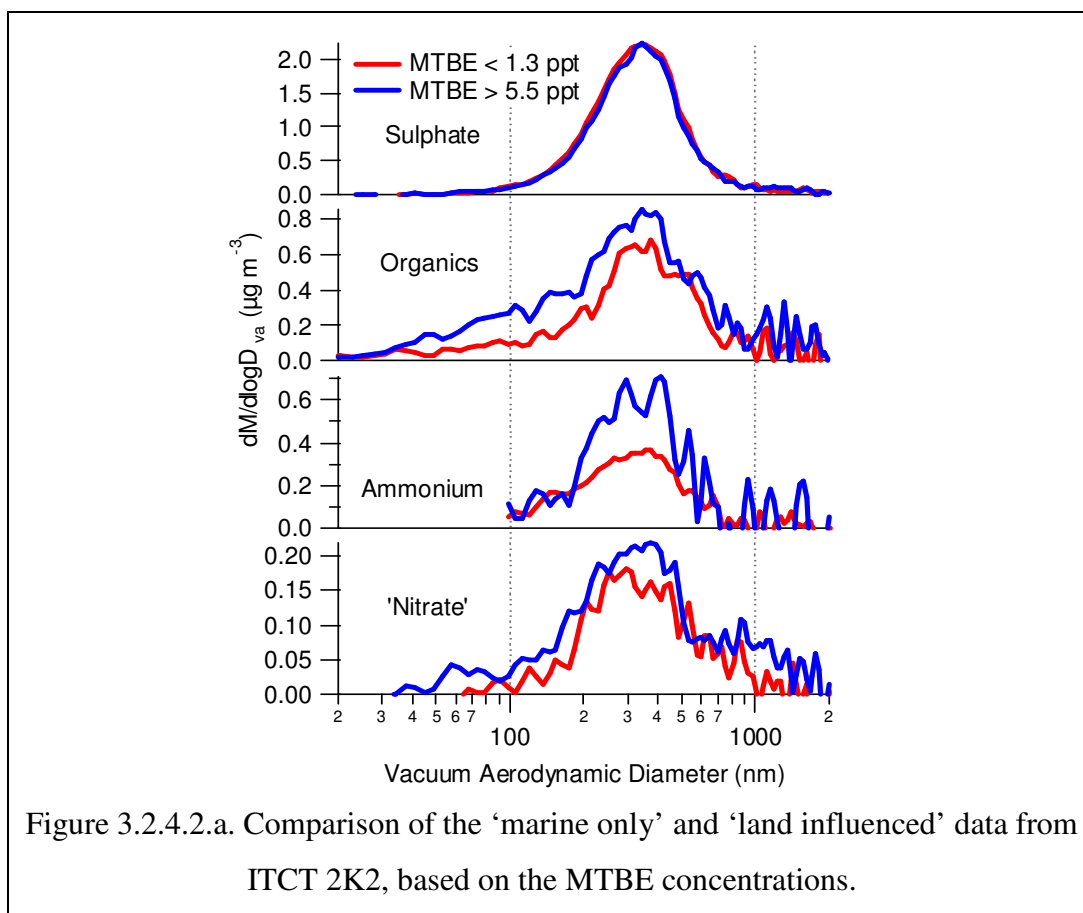
While the precise source of these signals cannot be identified in this analysis, it would seem that the term ‘nitrate’ should be treated as a very general term in these experiments, as there appears to be multiple contributions to the reported chemical loadings.

#### 3.2.4.2. Clean and polluted environments

One of the biggest differences between ACE Asia and the other two experiments is that it was sited much closer to the sources of pollution and this is reflected in the aerosol climatology. In particular, during the two major pollution episodes identified above, the absolute mass concentrations were much higher than what was seen during the other experiments. Additionally, the ammonium concentrations, for the majority of the time, are sufficient to neutralise the sulphate present. The main exception is during the event from the 18<sup>th</sup> to the 20<sup>th</sup> of April, where there was an excess of sulphate due to the MBL processing of sulphur emissions from China. In contrast, the sites used for ITCT 2K2 and NAMBLEX have nothing but open ocean to the west. For the majority of the time in both cases, the air had not been affected by any terrestrial sources for several days prior to sampling. As the ocean is much less significant a source of ammonia compared to land, the air histories are reflected in the relatively low ammonium concentrations. The excess of sulphate (or, more correctly, bisulphate or

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sulphuric acid) in turn causes the nitrate concentrations to be much lower in comparison, because nitrate partitions into the gas phase from acidic particles as  $\text{HNO}_3$ .



While the majority of the long-term history of the air sampled at Trinidad Head was dominated by time spent over the Pacific Ocean at high latitudes, the 48 hours immediately prior to sampling were more variable and often the air sampled had spend short periods over the coastal areas of the north-western United States. This was evident in the methyl tertiary butyl ether (MTBE) concentrations measured by the GC-MS-FID. This is a fuel additive used in petrol and having a relatively short atmospheric lifetime (see section 3.3.2.) and is a commonly used tracer for recent vehicle activity within an air mass. In this case, it is useful indicator for periods where that the air sampled at any one time has been subject to terrestrial emissions. To systematically compare the locally influenced air with the 'clean' Pacific air, separate, averaged size-resolved mass distributions were generated for periods when the MTBE concentrations were below their lower quartile (1.3 ppt) and above their upper quartile (5.5 ppt) levels and are shown in figure 3.2.4.2.a.

This analysis shows that on average, the sulphate was unaffected in the shape of its distribution and the average magnitude was actually reduced by 5.3 % during periods

of elevated MTBE. The overall reduction could be due to deposition of the MBL sulphate after reaching the coast, but a difference this small is probably a chance finding. Nitrate and ammonium saw increases of 44 and 59 % in their magnitudes, but their shapes and mode diameters remained similar. The increase in ammonium will be due to the fact that there are more significant sources of ammonia over land than sea (both biogenic and anthropogenic) that will quickly be taken up onto the acidic sulphate-containing particles from the MBL. The increase in nitrate may be due to nitric acid depositing from the gas phase on the particles once the ammonia has sufficiently neutralized the particles but an increase in the ammonium nitrate fraction would be reflected in a relative decrease in the ratio of the average signals at  $m/z$  30 and 46 towards around 2.5. When calculated, this ratio actually increases from 5.4 to 7.3, implying that the additional perceived nitrate is mostly in the form of mineral nitrates or nitrogen-bearing organics instead. The organics, on average, increased by 56 % during periods of high MTBE concentrations, partly due to an increase in activity at around 100 nm, which is a small manifestation of the primary traffic emissions seen in urban studies. However, there also appears to be additional material in the larger sizes as well, which is probably organic chemicals depositing onto the accumulation mode particles from the gas phase. These could be processed VOCs of either biogenic or anthropogenic origin, as sources of both exist on land.

Similarly in NAMBLEX, There was sometimes a mode detected around 100 nm in the organics. This is strongest around the 1<sup>st</sup>-2<sup>nd</sup> August, when the calculated back trajectory arrived from the east, across Ireland, England and mainland Europe (figure 3.2.4.2.b). The source of the small particles may be Galway city or other settlements further upwind.

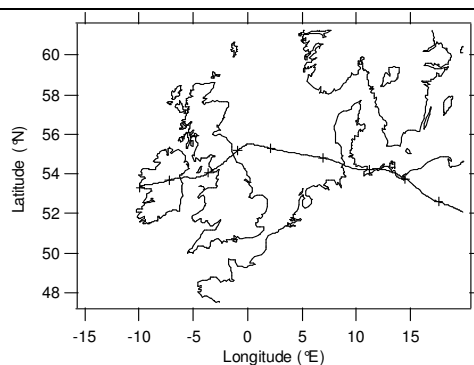


Figure 3.2.4.2.b. Back trajectory of a polluted period from NAMBLEX. Tick marks are shown one per day.

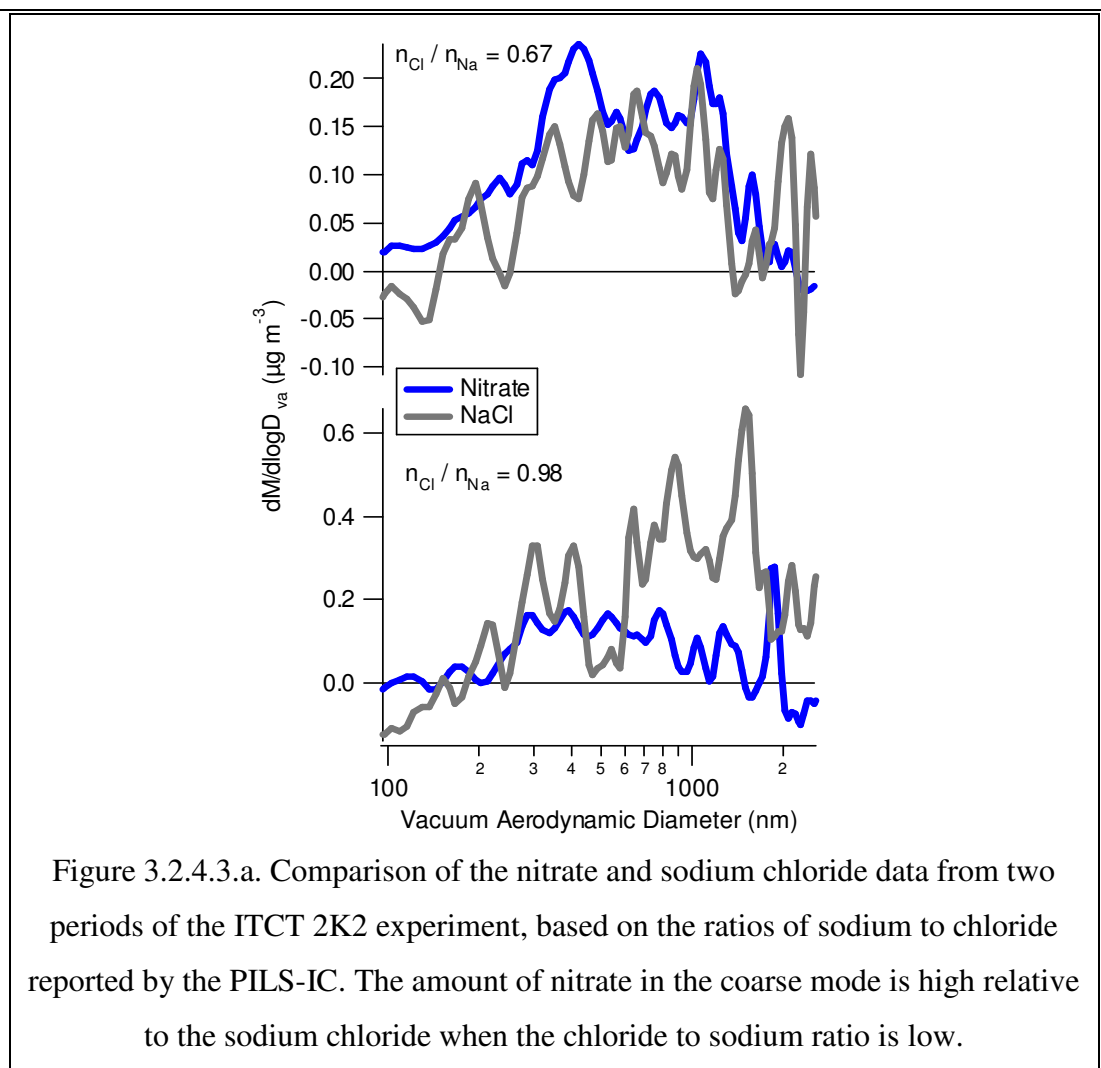
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### 3.2.4.3. Coarse mode behaviour

During the MBL experiments presented, particulate matter was observed in the coarse regime. The aerodynamic lens design used in the AMS means that these are not studied with 100 % efficiency but it is unfortunately not possible to correct for this. The numerical modelling that predicts this reduction in efficiency is believed to underestimate the true transmission, as it does not take into account particle bounce events. This is very difficult to predict as it could conceptually depend on the particle phases, compositions and morphologies, meaning that it is not possible to be absolutely quantitative in this regime.

However, it is possible to make statements regarding some of the relative contributions of the chemical components. In all three experiments, to a greater or lesser degree, an additional mode was noted in the supermicron regime whose tail stretched into lower sizes. This was mainly present in the nitrate data and the UMIST instrument confirmed that it was also present in the sea salt data during ITCT 2K2. Sea salt particles are ubiquitous in the marine environment and are produced mechanically by wave action and bubbles bursting on the surface. Once suspended, nitric acid may adsorb into them from the gas phase, causing the more volatile hydrochloric acid to be released from the particles as the pH decreases. In effect, some of the  $\text{Cl}^-$  ions are displaced directly by  $\text{NO}_3^-$ .

Direct evidence for this displacement can be obtained by selectively comparing two periods from ITCT 2K2, chosen based on the Na to Cl ratio, as seen by the PILS-IC. The mass distributions for these periods can be seen in figure 3.2.4.3.a. Note that for the purpose of these graphs, the collection efficiency correction has not been applied to either nitrate or the sea salt, as the true collection efficiency for these large sea salt particles is not known. The top graph shows an averaged trace from 17:00 on the 24<sup>th</sup> of April 2002 until 01:30 on the 26<sup>th</sup> of April, where the molar ratio of chloride to sodium ions averaged 0.67. During this period, significant amounts of nitrate can be observed and the ratio of the integrated supermicron nitrate mass to sea salt is roughly 1.2. Conversely, during the period of 06:00 until 21:00 on the 26<sup>th</sup> of April 2002, when the molar ratio was 0.98, the supermicron mass ratio was only 0.13.



Evidence to support the presence of  $\text{NaNO}_3$  can also be obtained by inspecting the ratio of the  $m/z$  30 and 46 channels. When sampling ammonium nitrate, the ratio of the two signals tends to be around 2.5:1, but when sampling aerosols generated using nitrate solutions with different cations (such as sodium, calcium and magnesium), the  $m/z$  46 signal ranges from relatively small to non-existent. This is because when ammonium nitrate vaporises in the instrument, it is in the form of molecular ammonia ( $\text{NH}_3$ ) and nitric acid ( $\text{HNO}_3$ ). However, when mineral nitrates vaporise, there is no spare proton, so the vapour will be in a different form (such as the nitrate radical,  $\text{NO}_3$ ), which will fragment differently when ionised. These higher ratios of 30 to 46 were observed in the coarse mode in all three experiments.

However, sodium nitrate may not be the only mineral nitrate compound observed in the case of ACE-Asia. The IC analysis from the impactors showed that the majority of the nitrate mass was in the coarse mode stages and was indeed accompanied by sodium. However, another cation observed in large quantities in these stages was

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calcium, which will be due to the large amount of dust particles observed at this location. It is also entirely likely that these particles will contain amounts of nitrate, again through nitric acid adsorption from the gas phase, to form  $\text{Ca}(\text{NO}_3)_2$  [Goodman *et al.*, 2001; Hanisch and Crowley, 2001]. While the AMS would not have been able to vaporise the entire dust particles, it may have been able to desorb the nitrate in the outer layers.

Also noted during ACE-Asia was the occasional presence of sulphate or organics in the coarse mode. Both of these species are known to exist in primary sea salt particles [Middlebrook *et al.*, 1998], but they may also be adsorbing onto coarse particles from the gas phase. Additionally,  $\text{SO}_2$  from the gas phase may be converting to sulphuric acid in aqueous phase sea salt particles, in a manner similar to the cloud processing mentioned previously.