
4. Summary

4.1. Development of the instrument, operation and analysis techniques

The AMS has represented a significant advance in the field of aerosol instrumentation. The instrument employs an aerodynamic lens, differential pumping, aerodynamic sizing, thermal vapourisation, electron impact ionisation and quadrupole mass spectrometry and is capable of the quantitative study of the submicron non-refractive fraction of aerosol particles with a high size and time resolution. In the years since the initial receipt, the UMIST AMS has undergone much development. These developments have included improvements to the vacuum system, the aerodynamic lens that focuses the particles and the quadrupole mass spectrometer.

Work has also been performed to refine the operational techniques. This includes the calibration protocols and making sure the correct supporting data is being measured. The issue of particle collection efficiency has also been investigated, as understanding this phenomenon is important when processing data. It has been found that in most cases, dry atmospheric particles tend to be captured by the vaporiser with only a 50 % efficiency due to a combination of beam divergence and bounce from the surface of the heater. It has been found that deliquescing these particles and making them liquid improves the collection efficiency.

Much of the work performed at UMIST and presented in this thesis has focused on the development of the analysis software needed to process the data produced. The software tools developed are capable of taking raw data acquired from ambient or laboratory sampling, automatically applying the relevant corrections and calibration values and producing quantitative and useful results. The inversion of mass spectra to mass concentrations for various chemical components entails the conversion of the continuous mass spectra to detected ion rates for discrete m/z and the use of matrix algebra to ensure that the entire mass spectrum is taken account of when calculating chemically-resolved ion rates, which allows for interferences between ions of the same m/z but different sources. To generate the chemical species-specific conversion matrices, a system of 'fragmentation tables' has been developed. These are user-definable, so can be tailored to specific applications, but it has also driven the collaborative effort by several groups worldwide to develop a set of general purpose tables for ambient sampling, work which is ongoing.

Finally, there has also been a programme that has been performed in tandem to validate the instrument, its operation and its analysis techniques. This has included the study of laboratory-generated particles of known compositions for comparison with established databases of mass spectral data and the comparison of AMS ambient data with those of other collocated instruments. These studies and comparisons have been very informative and have shown that the instrument can indeed produce reliable results, providing that the data is processed correctly.

4.2. Scientific Findings from Field Projects

Many of the problems faced in aerosol science stem from the fact that while there are many instruments available to study of the various properties of aerosol particles, no one instrument or combination of instruments can conclusively deliver the complete picture of the properties desired. For example, the standard method of probing the physiochemical properties of ambient particles normally involves the sizing and counting with one instrument (such as an SMPS) and the chemical analysis using a bulk sampling method (such as a cascade impactor). While this can provide a picture of the composition of an overall aerosol population, many assumptions have to be made when assigning a composition to the particle modes and events seen in counting and sizing instruments.

The technique of online aerosol mass spectrometry is uniquely suited to addressing this problem because it performs the sizing and chemical analysis on individual particles simultaneously and in real time. The Aerodyne AMS has the added advantage of being quantitative, so direct and meaningful comparisons with theory and other instruments can be made. The real strength of the instrument lies in being able to quantify changes in both the physical and chemical properties of the particles in a size-resolved manner during atmospheric events as they happen, which takes many of the assumptions and guesswork out of data analysis. During the course of the field-based work presented in this thesis, some new insights were made into atmospheric aerosol particles, some of which providing direct evidence to support existing theories while in other cases, some new behaviour was noted that could not have been seen with other instrumentation.

All the urban studies show a common mode at around $D_{va} < 200$ nm composed of organic carbon with a low degree of oxidation, which bear a strong correlation with gas phase traffic emissions. The AMS data were able to show that these particles bear a strong similarity to the non-refractory component of those produced by internal combustion engines studied in controlled laboratory conditions and show a mass spectral signature similar to that of lubricating oil. By comparing the ambient measurements with gas phase measurements and inventories, a primary organic emission budget applicable for central Manchester could be estimated.

All the sites studied in this thesis typically show a single accumulation mode made up of a mixture of sulphate, ammonium, nitrate and organics, but the modal

diameter, the shape of the mode and the proportions of the different species varies with time and from site to site. Typically, this mode made up the majority of the submicron non-refractory particulate mass. The largest particles were found in the summer at Manchester when the site was influenced by regional pollution and there was a high capacity for photochemistry and cloud processing. The sulphate present in the accumulation mode seemed to be dictated by regional as opposed to local sources. It was fairly ubiquitous at the sites mainly influenced by the MBL, which is known to be a major source of sulphate particles through the oxidation of DMS. The highest sulphate loadings reported were when MBL-processed sulphur emissions from mainland Asia were sampled.

The amounts of nitrate and ammonium present were linked for all sites. NAMBLEX and ITCT 2K2 were both ammonium deficient during most of their respective sampling periods, so the accumulation mode was generally acidic and there was very little nitrate present. Meanwhile, there was never more ammonium present than enough to achieve neutrality. This behaviour is expected, as both species will partition into the gas phase as nitric acid and ammonia until either the particles become neutralised or the gas phase species is exhausted.

The marine sites showed some episodic evidence of nitrate in the coarse mode, with an ion fragment ratio that was not consistent with ammonium nitrate. The elevated m/z 30 to 46 ratio seen can be associated with mineral nitrates such as sodium nitrate. The AMS data from ITCT 2K2 and supporting impactor data from ACE-Asia [Topping *et al.*, 2004a] showed that this was linked to the displacement of chloride from sea salt particles by nitric acid. While these data showed direct evidence for this phenomenon, the precise mechanism in the atmosphere is still a matter for debate. It is also possible that during ACE-Asia, calcium nitrate was also seen in the coarse mode, which would be due to nitric acid deposition on basic mineral dust particles from the gas phase.

It is an established fact that the organic fraction of particulate matter changes over the time it spends in the atmosphere. Generally, as the distance from the source increases, the ratio of organic carbon to elemental carbon increases, which is generally seen as a marker for secondary as opposed to primary organic carbon. It is also known that the organic chemicals present become increasingly polar in nature, showing a higher degree of oxidation, resulting in the particle populations generally becoming more hygroscopic. Specifically, HTDMA studies have shown that the 'less hygroscopic' mode seen in urban environments is not present in remote locations

[Swietlicki *et al.*, 2000], implying these particles become processed over time to become indistinguishable from the accumulation mode particles in terms of behaviour.

While many different initial sources for particulate organic matter have been identified, such as vehicle emissions, meat cooking, biomass burning and biogenic VOCs, the organic fraction of the accumulation mode bore a very similar signature between all of the sites studied during the work in this thesis (see section 3.3.1.). This signature is consistent with what would be expected if the majority of the mass of the organic matter were made up of macromolecular ‘humic-like’ substances. Organic matter may initially enter particle phase through a variety of different routes (primary emission or condensing as secondary organic matter) and in a variety of different forms, but the theory is that subsequent homogeneous, heterogeneous or multiphase processes further oxidise the molecules and cause them to bond within the particle, ultimately making them completely unlike their precursors.

The data from the AMS presented in this thesis certainly seem to support this theory because traffic emissions aside, all the organics seen at the multiple sites presented in this thesis all showed the same mass spectral signature. The signature in question has a high signal at m/z 44, which is indicative of di- and polycarboxylic acids, a highly oxidised hydrocarbon form. Other signals present include 43, which while potentially being an aliphatic fragment, is particularly pronounced when analysing carboxylic acids, aldehydes and ketones, and 55, which is a generic organic fragment. The signals at higher m/z were very small, meaning long, aliphatic chains were not present in abundance. This signature is almost identical to that of fulvic acid, a highly oxidised substance that can also be described as humic-like and has been used by other groups to simulate the analytical behaviour of ambient water-soluble particulate organics [Fuzzi *et al.*, 2001].

It is worth noting in that in almost all of the data presented, the major portion of the non-refractive, non-local particulate mass was contained within a single accumulation mode; there was rarely any significant contribution from a smaller mode, other than the primary vehicle emission. An exception is the in situ particle ageing episodes identified from the winter Manchester dataset. The absence of a significant Aitken mode during all other times may be partly because the sites presented either receive incoming air from a marine sector or are located in areas with a high capacity for cloud processing in the boundary layer, so the background aerosol will already be well processed. Other more intermediate patterns were seen during other studies at other

locations not presented in this thesis where emissions that have undergone less atmospheric processing were sampled [e.g. *Boudries et al.*, 2004; *Cubison et al.*, 2004].

4.3. Ongoing and future work

4.3.1. Technical developments

One of the most immediate challenges relating to AMS operation and analysis relates to the problem of collection efficiency. It is not desirable to simply continue to apply a factor of 2 to all datasets; it would be much better to be able to explore this factor explicitly. The humidity control described in section 2.2.2.2. is promising, although this does not seem to work very well for the smaller (<100 nm) particles. Also, its effectiveness is confined to purely to hygroscopic particles. The beam shape probe used in section 2.2.2.2. may provide part of the solution, as this could in theory be used to explicitly derive the amount of defocusing [Huffman *et al.*, 2004]. However, this will not quantify other aspects of the collection efficiency, such as lens transmission or particle bounce, which seem to be more important. More rigorous laboratory work is needed to characterise the former and the installation of a light scattering probe in the time-of-flight region of the instrument may help to directly probe the latter, as this would count all the particles prior to the detection region. Work is ongoing by various groups to address these [Cross *et al.*, 2004; Liu *et al.*, 2004]. A change in the design or construction of the vaporiser may help to mitigate the losses due to bounce.

While many valuable insights can be made from ground-based sampling operations such as those presented in this thesis, they provide very little information regarding the spatial or vertical distributions of the components of the aerosol and the study of specific pollution events is limited to those whose plumes pass directly over the measurement site. To address these questions, it is greatly desirable to be able to make measurements from an airborne platform and recent efforts have been concentrating on deploying a second AMS (the same instrument that was used during ITCT 2K2) aboard the new Facility for Airborne Atmospheric Research (FAAM). This is a NERC large research aircraft (BAe Systems model 146-301), featuring instrumentation from several UK academic research institutes and the Met Office. AMSs have been deployed successfully on airborne platforms by other groups previously, including the CIRPAS UV-18A ‘Twin Otter’ by Caltech [Bahreini *et al.*, 2003], the DOE Grumman G-1 by ARI [Onasch *et al.*, 2003] and the DLR Falcon 20-E by the Max Planck Institute for Chemistry [Schneider *et al.*, 2003].

Many challenges faced when deploying an AMS on board a mobile platform relate to the fact that a high time resolution is required, which in turn demands that the

instrument signal to noise ratio is high. Many of the vacuum system improvements that are described in section 2.2.1.2. were in part driven by the need of a high sensitivity when performing measurements in aircraft. The frequent changes in upstream inlet pressure experienced due to changes in altitude cause changes in the behaviour of the inlet system; the flow rate into the instrument, the velocity calibration of the lens and the characteristic cutoffs all vary as a function of upstream pressure, and these must be accounted for. Also, the fact that during flight, the ambient aerosols move very fast relative to the instrument places demands on the sampling system; the particle velocities must be changed rapidly, meaning the sampling point can be prone to turbulence, which must be avoided as it can cause significant and unpredictable losses through impaction. Additionally, larger particles (around 1 μm or larger) may not be able to follow the gas streamlines, so may be concentrated in the inlet or lost through impaction. Devices such as low turbulence inlets [Wilson *et al.*, 2004] and double diffusers (Brechtel Manufacturing Inc., Hayward, CA, USA) [Brechtel *et al.*, 2003] are specifically designed to reduce turbulent losses and deliver predictable particle transmission over a range of particles sizes, aircraft speeds and altitudes. The FAAM AMS is intended to use a low turbulence inlet during operation.

At the time of writing, the FAAM AMS has been used successfully in two measurement campaigns; Intercontinental Transport Of Pollutants (ITOP) and Aerosol Direct Radiative Impact Experiment (ADRIEX) [Crosier *et al.*, 2004], although the low turbulence inlet was not operational for either of these. The analysis of these datasets is ongoing. For more current information on the status of FAAM, the reader is directed to <http://www.faam.ac.uk/>.

One of the main frontiers of the ongoing instrument development has always been that of the detector sensitivity, as improvements to this have lead to and continue to lead to higher qualities of data being produced and have allowed the instrument to be used in increasingly wider ranges of applications. In addition to the hardware developments discussed previously, recent work has also focused on making changes to the operating procedure. A new mode of operation known as Jump Mass Spectrum (JMS) mode has been developed by ARI, the University of Colorado at Boulder and CEH Edinburgh. This was partly driven by the need for high enough time resolutions to perform eddy covariance flux measurements [Anderson *et al.*, 2003; Nemitz *et al.*, 2004], although this new mode of operation is also useful in other applications where high sensitivity is required, such as aircraft operation and when measuring very clean

environments. The mode works in a similar manner to MS mode, although instead of scanning all m/z 's between 0 and 300, only a small number of selected channels are monitored, thereby spending longer on these individual channels. This should increase the signal to noise ratio of key data products, for example sulphate, ammonium, nitrate and organics. This has been used recently when sampling free tropospheric aerosol during CLACE 3 (see section 4.3.2.) and ITOP (see above).

The continual push to enhance and expand the capabilities of the hardware and operations creates extra challenges for future analysis software developments. Currently, the analysis software holds all processed data in the computer's memory. While this was sufficient for many early experiments, analysing the data produced by instruments operating on two minute averaging times (such as the ARI instrument in ITCT 2K2) has been problematic. It has not been unusual for the analysis to use several hundreds of megabytes or more and sometimes multiple analysis files have been needed for individual campaigns. Within the near future, the software will have to be modified to store much of the data on a hard disc and access it randomly as required. Also, the ASCII format currently in use by the logging software (itx) tends to generate unnecessarily large volumes of data (tens of gigabytes have been generated during single campaigns), so instead, the binary hierarchical data format (HDF) may be used as standard instead, which is much more efficient. This has already been implemented in the logging software by ARI and Arizona State University but no provision has yet been implemented in the standard analysis code. Additionally, a method of analysing JMS data will have to be written and the capability to have time-dependent velocity calibrations (to take account of pressure variations) added to the analysis suite. The latter is not a trivial exercise; as the TOF data will no longer be able to be mapped onto a common D_{va} data space, they will have to be routinely rebinned during analysis, which must be performed carefully to avoid smoothing artefacts.

There is also more development required of the fragmentation tables presented. While the example tables presented in this thesis have shown to produce reliable data for species such as nitrate, ammonium and sulphate, there is much work to be done to refine these measurements and investigate the fragmentation properties of other chemicals. For instance, the precise fragmentation mechanism of sulphate, bisulphate and sulphuric acid still requires further resolution and there is much work to be done in quantitatively separating different classes of organic chemicals. The work to further develop the tables will entail the continuation of the extensive laboratory measurements

and sharing of data and experience by several groups worldwide, which has so far proved very fruitful to date.

The most significant recent development to the AMS detection region has been to replace the quadrupole mass spectrometer with a recently developed model of time of flight detector (Tofwerk model C-TOF, Thun, Switzerland). Conventional time of flight mass spectrometers are generally not very well suited to EI ionisation, because they require a pulsed ion source. However, this new design employs orthogonal extraction [Chen *et al.*, 1999], whereby ions are focused into a tightly confined beam and extracted at right angles in pulses for the time of flight spectrometry. As well as being compatible with continuous ion sources such as EI, both the location and velocities of the ions are also very well constrained within the axis of extraction, which means the instrument has a very high resolving power (m/z relative resolutions of 10^{-3} FWHM or less). This in turn means the drift region can be shortened, which in addition to reducing the overall bulk, means that it can be cycled at a very rapid rate (hundreds of Hz), providing a high enough time resolution to still allow particle TOF sizing.

The immediate benefits of this implementation are fourfold. Firstly, because all ions are being counted, rather than those of a single m/z , the overall instrument sensitivity is also increased accordingly. Secondly, an instrument using this form of mass spectrometry should be able to monitor all m/z channels simultaneously in TOF mode, negating the need to selectively monitor a few and enabling the sort of inversions that can be used for MS data to be applied to the TOF data. Thirdly, time of flight mass spectrometers do not have an upper m/z limit to their spectra, which should allow larger molecules to be studied. Finally, the mass spectrometer, in having a higher m/z resolution than a quadrupole, especially for the small m/z , may allow more detailed investigation of the precise masses of ions.

Further to these, it should be possible in the future to inspect the entire mass spectra of the single particle events from TOF mode, allowing the quantitative probing of mixing states. This analysis will be very powerful when comparing with HTDMA data, enabling closure between theory and observations to be reached more conclusively. Also, being able to study and quantify distinct populations downwind of a source will be a useful tool when looking at pollutant dispersal and evolution, which in turn can feed directly into air quality and climate models. The first versions of this new instrument (known as the ToF-AMS) are already in use by ARI, the University of

Colorado at Boulder and the Max Planck Institute for Chemistry at Mainz. Initial results have been promising [*Drewnick et al.*, 2004].

4.3.2. Further scientific work

One of the main motivations in atmospheric science as an overall discipline is being able to apply what is known on a basic scientific level to provide accurate information that is useful to policymakers and the general public. The sorts of important information produced include weather forecasts, air quality statistics, chemical cycling information and climate predictions. However, the quality of these end products is dictated by the accuracy of the science upon which they are founded, and there are still many uncertainties, especially where aerosols are concerned. The work presented in this thesis gives some important insights into the general phenomenology, but there are still many aspects that require further investigation. Much of this work will entail the further combination of AMS with other data sources.

While it is important to make detailed measurements of the aerosol compositions close to the sources of emission (as presented in this thesis), it is just as important to know how these pollutants disperse and evolve through the atmosphere when trying to make predictions of their effects on air quality and climate on both regional and global levels. The work shown here has contrasted the two cases of urban and remote sites, but more work needs to be done in investigating how exactly the aerosol makes the transition between these two states in the atmosphere. For instance, it is known that the particles in a more aged polluted plume are generally more hygroscopic, but the many processes that may contribute to this phenomenon are not completely understood.

Aircraft provide very useful measurement platforms for the study of the evolution of emissions, as they can study a single plume or air mass at multiple stages of its lifetime, potentially in a Lagrangian manner. The FAAM AMS will provide excellent opportunities for further studies of this nature. Regional pollution from individual sources such as cities can be tracked as it evolves in the troposphere. Also, on a wider scale, the export or import of pollutants to a particular land mass or continent can be studied by making detailed measurements at multiple points over open sea or ocean. These types of studies must be accompanied with accurate meteorological forecasts to predict the route of the plumes. However, a real strength of the AMS is that it can produce data in near real time, so this, along with other online data sources,

should be able to provide useful information for the mission scientists when attempting to determine the status of a an air mass during a mission.

The organic fraction of particulate matter continues to present large areas of uncertainty in the science, due to the complexities of the chemical processes and the difficulties in conclusively analysing all the various components. The AMS has proved useful in studying these, as it measures both the entire polar and non-polar fractions and has also show how significant and ubiquitous the nature of the processed organic fraction is at various sites around the world. This component will need much more investigation, employing many analytical techniques, to fully characterise its chemical nature and how it will affect issues such as cloud formation, atmospheric chemistry and aerosol radiative properties. Further to this, the two patterns identified in section 3.3.1. merely scratch the surface of the types of chemicals that are present in the atmosphere. More work will also be required to make observations in environments where different types of sources dominate the organic particulates (such as biogenic emissions or biomass burning). The analysis of these observations, along with current and historic measurements, will need to be carefully linked to laboratory measurements of particles of known compositions and those generated under controlled conditions. For example, the unknown component in section 3.2.2.2. hypothesised to be an organic nitrogen species needs to be positively identified. The intermediate stages of the atmospheric chemical ageing will also require further investigation.

The hygroscopic behaviour of ambient particles is crucially important when considering their optical properties and the aforementioned interactions with clouds, which in turn makes it a key parameter in climate prediction models. Quantitatively predicting their behaviour is notoriously difficult, especially when considering the organic fraction, which as this work shows, is both an important component of the atmosphere but also tends to be mixed with the inorganic fraction. Work is ongoing to develop the modelling tools needed to make these predictions accurately [*Topping et al.*, 2003; *Topping et al.*, 2004b]. As part of the development of these models, various chemical and physical parameters must be constrained, which requires data from both the laboratory and the ambient atmosphere. The model also needs to be continuously validated, by comparing the behaviours predicted based on observed particle compositions and size with the appropriate measurements. The AMS data routinely gathered during intensive field studies is ideally suited to these exercises, as it possesses the size, time and chemical resolving power needed to study the particle dynamics and

actively compare with the data produced from instruments such as the HTDMA [Cubison *et al.*, 2003; Cubison *et al.*, 2004]. The work to develop the model and perform these comparisons is ongoing [McFiggans *et al.*, 2004b] and as part of this, an extensive collection of detailed and accurate collocated AMS and HTDMA measurements from multiple environments will be built up, in addition to the data already collected. Supporting laboratory work is also required, which again the AMS will be well suited for. In particular, high time resolution composition measurements will be needed when performing the reaction chamber studies designed to simulate specific atmospheric processes. When these modelling tools are fully developed, they will be parameterised and feed into larger scale models, meaning more accurate predictions of the effect of aerosols on clouds and climate can be made.

In addition to pursuing the scientific questions raised in this thesis further, the AMS will also be able to address many other areas of uncertainty in the atmosphere. An example of one such aspect of is new particle formation. While the overall level of understanding of these phenomena has improved considerably over recent years, particle repopulation still represents a very large source of uncertainty when considering particle number budgets regionally and globally, which is a major factor in predicting cloud behaviour. As mentioned previously, nucleation mode particles are known to form in discrete bursts in the atmosphere but are very difficult to study and the precise mechanisms of the nucleation and growth processes in the different environments are the subject of much debate. While the 30 nm lower cutoff of the AMS prevents the study of the nucleation process itself, it has successfully been used to study the growth and evolution of the new particles. The AMS has been able to give direct evidence for the production of iodine-based particles from macroalgae emissions [McFiggans *et al.*, 2004a] and investigate the new particles formed in a forested environment, likely formed from the oxidation products of biogenic VOCs [Allan *et al.*, 2003c; Allan *et al.*, 2004a]. The latter observation, made during the QUEST 2 experiment during the spring of 2003 in southern Finland, gave an organic mass spectral signature unlike anything seen previously in ambient air. Further work will be needed and is ongoing to positively identify the chemical species present, which involves a series of experiments in controlled conditions in reaction chambers. Other similar field experiments in environments where nucleation events are known to occur will also prove useful in investigating these phenomena.

Another field that the AMS can contribute to and is currently involved in is the study of aerosol-cloud interactions. The indirect radiative effect has been identified as one of the major sources of uncertainty in global climate predictions [Penner *et al.*, 2001]. It is important to know how particles created directly or indirectly from human activity will affect clouds, but the factors controlling the availability of CCN are very complex and are highly dependent on the number, size and composition of the aerosol, which are what the AMS is particularly useful in evaluating. By sampling from a counter-flow virtual impactor onboard FAAM, it should be possible for the AMS to selectively study the interstitial particles or droplet residuals from a cloud, as well as studying particles before and after cloud processing. In providing high-resolution size and compositions data, the AMS could also be highly useful when performing ground-based hill cloud experiments of a format such as that described by Bower *et al.* [2000].

The ice clouds that form at higher altitudes and are likewise important in global radiation budgets, but the formation processes of ice particles are again complex and the exact nature of the cloud is highly dependent on the particles that form the potential ice nuclei. It is probable that anthropogenic particle emissions can significantly change the properties of these clouds, but in what manner is uncertain. To study this, the UMIST AMS was deployed at the Cloud and Aerosol Characterisation Experiments (CLACE) 2 (summer 2002) [Bower *et al.*, 2003; Coe *et al.*, 2002] and 3 (spring 2004), which took place at the Sphinx observatory in the Jungfraujoch, a high altitude site in the Swiss Alps. The instrument alternated between a heated inlet that evaporated all the water from cloud particles and a 2.5 μm cyclone that only captured the interstitial particles. By comparing these two data, the physical and chemical nature of the ice nuclei can be investigated, which can in turn be linked to the physical properties of the ice crystals themselves, as measured by a variety of cloud microphysics instrumentation. During cloud-free periods, the AMS was also able to study free tropospheric aerosols. This work to analyse the data from these projects is ongoing and further experimentation work of this nature is planned.

4.4. Acknowledgements

The work in this thesis was supported by Natural Environmental Research Council (NERC) studentship ref. NER/S/A/2000/03653. The UMIST AMS was purchased and maintained through NERC research grant GR3/12499. The Edinburgh site infrastructure was funded by the Sources And Sinks of Urban Aerosol (SASUA) project of the NERC Urban Regeneration and the Environment (URGENT) thematic program, grant no. GST 022244. Many thanks to Mrs. Dorothy Marsh of the City of Edinburgh Council for access to the measurement site. Funding for the Pacific 2001 deployment was provided by Environment Canada, the Georgia Basin Ecosystem Initiative and the Panel on Energy Research and Development (PERD). Funding for the ITCT deployment and data analysis was provided by the National Oceanographic and Atmospheric Administration (NOAA). Site infrastructure and support was provided by the Humboldt State University Marine Laboratory. Additional thanks to Robert Prescott of ARI for logistical support during the Pacific 2001 and ITCT experiments. UK and Irish back trajectories were calculated using the British Atmospheric Data Centre (BADC) trajectory service (<http://cirrus.badc.rl.ac.uk/trajectory/>). USA and South Korean back trajectories were calculated using the HYSPLIT transport and dispersion model website, provided by the NOAA Air Resources Laboratory (<http://www.arl.noaa.gov/ready/hysplit4.html>). Coastline data used in the trajectory plots and maps were taken from the coastline generator service by Rich Signell, hosted by the National Geophysical Data Center (<http://rimmer.ngdc.noaa.gov/mgg/coast/getcoast.html>). Maps were taken from Multimap.com (<http://www.multimap.com/>) and MapQuest.com (<http://www.mapquest.com/>). UK gas and Air Quality Statistics Database data were taken from of the National Air Quality Information Archive (<http://www.airquality.co.uk/archive/index.php>). UK inventory data were taken from the National Atmospheric Emissions Inventory (<http://www.naei.org.uk/>). Library mass spectra, thermodynamic data and some general nomenclature were taken from the National Institute of Standards and Technology (NIST) Chemistry WebBook (<http://webbook.nist.gov/chemistry/>) [*Linstrom and Mallard, 2003*], in particular the sections “Mass Spectra” by NIST Mass Spec Data Center (director S.E. Stein) and “Thermodynamics Source Database” by Thermodynamics Research Center, NIST Boulder Laboratories (director M. Frenkel).

On a personal level, I'd also like to extend thanks the rest of the worldwide AMS community for all the ideas, support, guidance and enthusiasm, without all of which the work in this thesis would probably not have amounted to as much and would definitely not have been half as much fun. There are way too many people to list here but John Jayne, Jose Jimenez and Doug Worsnop definitely deserve a specific mention.

Also, many thanks to the others here at UMIST, in particular the other AMS people (Keith Bower, Rami Alfarra and Paul Williams), for all the mutual support and for generally being great people to work with. And to my supervisor, Hugh Coe, for keeping me on the right track and getting me involved from day one.

Thanks as well to all the people from field projects that I've been involved with both socially as well as professionally. You made it all that more bearable when either nothing was working and I was going spare or everything was working and I was getting bored. You know who you are.

And last but definitely not least, I'm eternally grateful to my girlfriend Eimear, not just for all the emotional support but also for putting up with my frequent and often protracted disappearances to different countries.